CANDIDATE’S NAME: ________________________________ CTG: ____________

YISHUN JUNIOR COLLEGE

2018 JC2 PRELIMINARY EXAMINATION

CHEMISTRY 9729/01
HIGHER 2

Paper 1 Multiple Choice

THURSDAY 13 SEPTEMBER 2018
1400hrs − 1500hrs
(1 hour)

Additional Materials: Optical Mark Sheet (OMS)
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, CTG, and NRIC / FIN number on the Optical Mark Sheet (OMS), and shade the corresponding boxes for your NRIC / FIN number.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This question paper consists of **16** printed pages.

1 10 cm^3 of a pure hydrocarbon was completely burned in 80 cm^3 of excess oxygen at 425 K. After cooling to room temperature, the volume of the gaseous mixture was found to be 55 cm^3. A reduction of 40 cm^3 was observed when the residual gases were passed through calcium hydroxide. All gas volumes were measured at the same temperature and pressure.

What is the formula of the hydrocarbon?

A C_4H_{10} **B** C_4H_8 **C** C_2H_6 **D** C_2H_4

2 Sodium hydrogen carbonate, $NaHCO_3$, can be prepared from sodium sulfate by a three-step process as shown.

$$Na_2SO_4(s) + 4C(s) \rightarrow Na_2S(s) + 4CO(g)$$
$$Na_2S(s) + CaCO_3(s) \rightarrow CaS(s) + Na_2CO_3(s)$$
$$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$$

Assuming a yield of 90% in each step, determine the mass of sodium hydrogen carbonate, to the nearest kg, that could be obtained from 100 kg of sodium sulfate.

A 146 kg **B** 122 kg **C** 86 kg **D** 43 kg

3 Ions of the two common isotopes of nickel are shown below.

$^{58}Ni^{2+}$ & $^{60}Ni^{2+}$

Which statements about these ions are correct?

1 $^{58}Ni^{2+}$ ion has a greater number of nucleons in its nucleus than the $^{60}Ni^{2+}$ ion.

2 Both ions have the same number of protons.

3 Both ions have more neutrons than electrons.

4 A beam of $^{58}Ni^{2+}$ ion is deflected to a larger extent than that of $^{60}Ni^{2+}$ ion in an electric field.

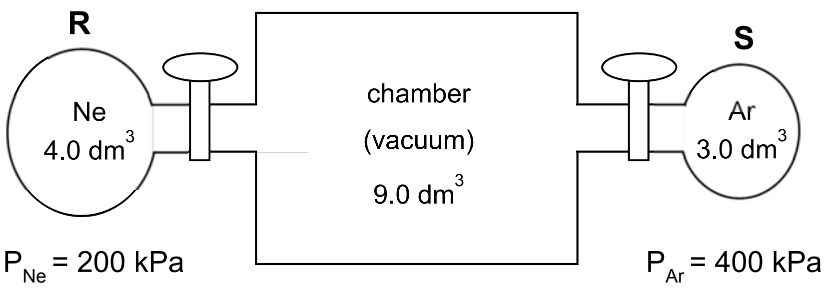
A 1, 2, 3 and 4

B 1, 2 and 3

C 2 and 3

D 2, 3 and 4

4 Two bulbs **R** and **S** are connected to a 9 dm^3 vacuum chamber as shown.



What will be the total pressure in the vessel when the valves are opened at constant temperature?

A 600 kPa

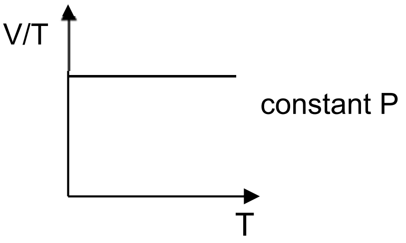
B 286 kPa

C 222 kPa

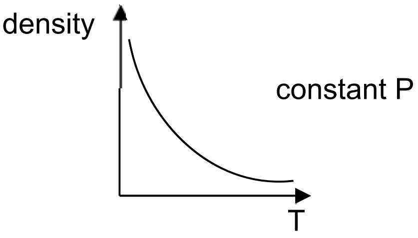
D 125 kPa

5 Which graph incorrectly describes the behaviour of a fixed mass of an ideal gas?

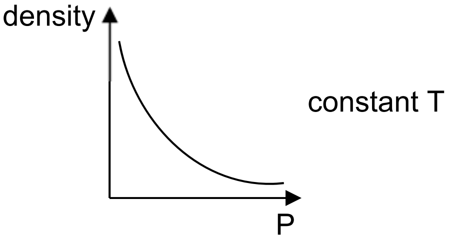
A



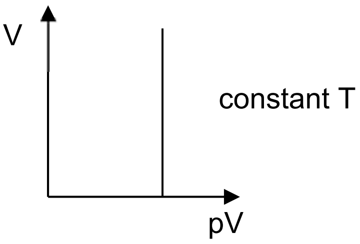
B



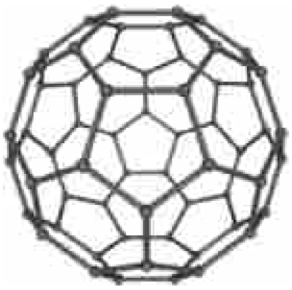
C



D



6 Allotropes of carbon include diamond, graphite and fullerene. A spherical fullerene, known as buckminsterfullerene, has the formula C_{60} with the following structure.



Which statement is correct?

A All the bond angles in buckminsterfullerene are 120°.

B There are delocalised electrons within buckminsterfullerene.

C Buckminsterfullerene sublimes at a higher temperature than graphite.

D On complete combustion, buckminsterfullerene forms carbon dioxide and water.

7 The enthalpy change of solution of magnesium fluoride is found to be negative while that of barium fluoride is positive.

Which statement best explains this observation?

A Magnesium fluoride is soluble in water, but barium fluoride is insoluble.

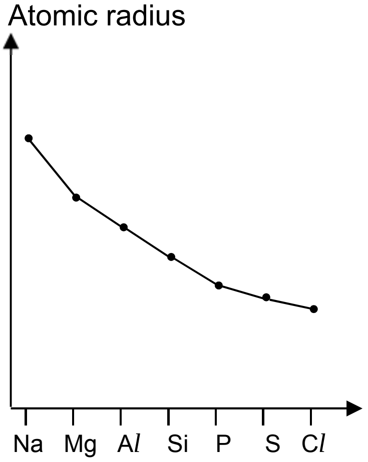
B The hydration energy of the barium ion is bigger in magnitude than that of the magnesium ion.

C The lattice energy of barium fluoride is bigger in magnitude than that of magnesium fluoride.

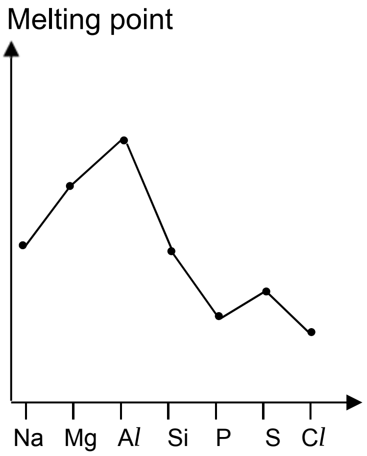
D The lattice energy of barium fluoride is bigger in magnitude than the sum of the hydration energies of the barium and fluoride ions.

8 Which sketch shows the incorrect trend for the stated property for elements in the third period of the Periodic Table?

A



B



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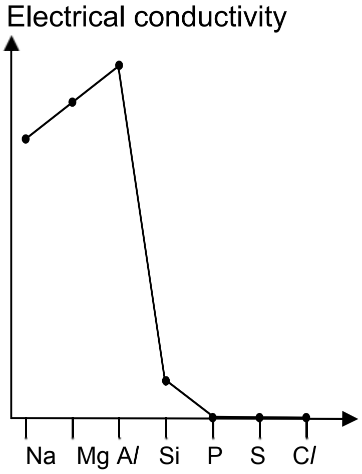
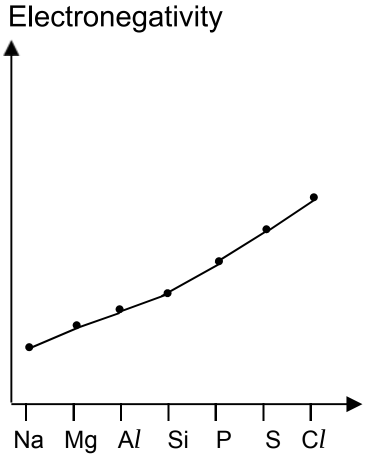


D



9 The table shows the results of experiments in which the halogens $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$ are added to aqueous solutions containing $\mathbf{X}^-$, $\mathbf{Y}^-$, and $\mathbf{Z}^-$ ions.

	X^-(aq)	**Y^-(aq)**	**Z^-(aq)**
X_2	no reaction	no reaction	no reaction
Y_2	**X_2** formed	no reaction	**Z_2** formed
Z_2	**X_2** formed	no reaction	no reaction

Which row shows the correct order of the reducing strength of the halide ions?

	strongest		weakest
A	**X^-**	**Z^-**	**Y^-**
B	**Y^-**	**Z^-**	**X^-**
C	**Z^-**	**Y^-**	**X^-**
D	**X^-**	**Y^-**	**Z^-**

10 The diagram below shows the positions of four elements **W**, **X**, **Y** and **Z** in periods 2 and 3.

	W		
X		**Y**	**Z**

Element **Y** has the following successive ionisation energies(IE).

IE /kJ mol^{-1}	1011	1907	2914	4963	6273	21268	29872

Which statement about elements **W**, **X**, **Y** and **Z** and their compounds is incorrect?

A The oxide of **X** is insoluble in water.

B The first ionisation energy of **Z** is lower than that of **Y**.

C When HC*l*(aq) is added to a sample containing oxide of **X**, the solid dissolves.

D **W**, **Y** and **Z** form chlorides which will react with water to produce acidic solutions.

11 *Use of Data Booklet is relevant to this question.*
The lattice energy of beryllium nitride can be determined via the following energy cycle.

$$\begin{tikzcd}
Be_3N_2(s) \arrow[r, "\Delta H_1"] \arrow[ddr, "\Delta H_6"'] & 3Be(s) + N_2(g) \arrow[d, shift right=2, "\Delta H_2"'] \arrow[d, shift left=2, "\Delta H_3"] \\
 & 3Be(g) + 2N(g) \arrow[d, shift right=2, "\Delta H_4"'] \arrow[d, shift left=2, "\Delta H_5"] \\
 & 3Be^{2+}(g) + 2N^{3-}(g)
\end{tikzcd}$$

Enthalpy Change	ΔH / kJ mol^{-1}
ΔH_2	+324
ΔH_5	+1404
ΔH_6	+11300

Which statements are correct?

1 The enthalpy change of formation, ΔH_f, of Be_3N_2 is +648 kJ mol^{-1}.

2 ΔH_3 is always endothermic.

3 The average energy of the electrostatic forces of attraction present in Be_3N_2 is 11300 kJ mol^{-1}.

A 1 only

B 2 and 3 only

C 1 and 2 only

D 1, 2 and 3

12 In which processes will ΔS be negative?

1 The burning of sulfur in oxygen to produce sulfur dioxide gas.

2 The dissolution of solute in solvent.

3 The synthesis of an ionic compound from its constituent gaseous ions.

A 3 only

B 1 and 3 only

C 1 and 2 only

D 1, 2 and 3

13 A bomb calorimeter contains 225 dm^3 of hydrazine, N_2H_4 as fuel. After combustion, the temperature change in the calorimeter was found to be $\boldsymbol{w}$ °C.

The heat capacity of the calorimeter is $\boldsymbol{z}$ kJ K^{-1}. The density of liquid hydrazine is 1.02 g cm^{-3} and its enthalpy change of combustion, $\Delta H_{c,}$ is −622.2 kJ mol^{-1}

Which of the following represents the percentage efficiency of the bomb calorimeter?

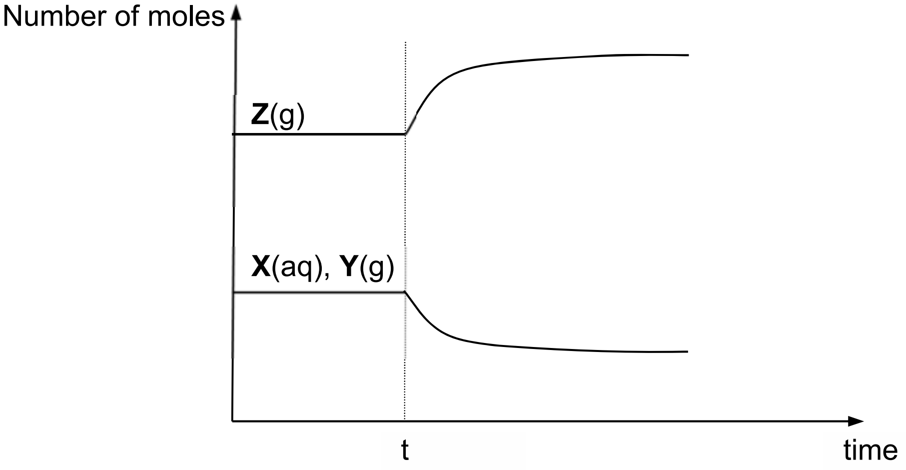
A Percentage efficiency = $\dfrac{225 \times 1000 \times 1.02 \times \boldsymbol{z} \times \boldsymbol{w}}{622.2} \times 100\%$

B Percentage efficiency = $\dfrac{225 \times 1000 \times 1.02 \times \boldsymbol{z} \times (\boldsymbol{w} + 273)}{622.2} \times 100\%$

C Percentage efficiency = $\dfrac{(\boldsymbol{w} + 273) \times \boldsymbol{z}}{\dfrac{225 \times 1000 \times 1.02}{\text{Molar mass } (N_2H_4)} \times 622.2} \times 100\%$

D Percentage efficiency = $\dfrac{\boldsymbol{w} \times \boldsymbol{z}}{\dfrac{225 \times 1000 \times 1.02}{\text{Molar mass } (N_2H_4)} \times 622.2} \times 100\%$

14 Consider the following reaction: $\mathbf{X}(aq) + \mathbf{Y}(g) \rightleftharpoons \mathbf{Z}(g)$ $\Delta H < 0$
The graph shows the number of moles of gases in a reaction mixture as it changes with time.



The reaction mixture is initially at equilibrium until time, *t*, when a disturbance is introduced to the system. Which of the disturbances at time, *t*, can account for the observed change in the graph above?

1 An increase in pressure

2 Addition of water into the aqueous solution

3 Increase in temperature

A 1 only

B 2 only

C 1, 2 and 3

D None of the above

15 Given that the K_p for the following equilibrium is 64,

$$\mathbf{P}(s) + 2\mathbf{Q}(g) \rightleftharpoons 2\mathbf{R}(g)$$

What is the mole ratio of **Q** : **R** at equilibrium?

A 1 : 1

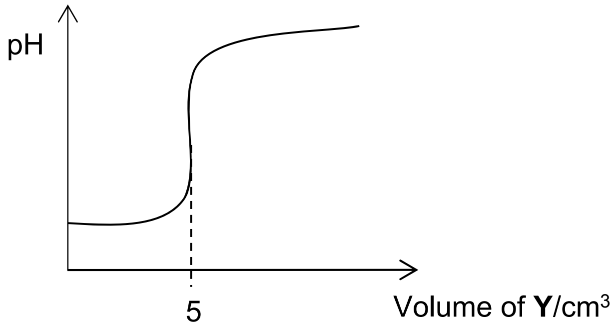
B 1 : 8

C 8 : 1

D 64 : 1

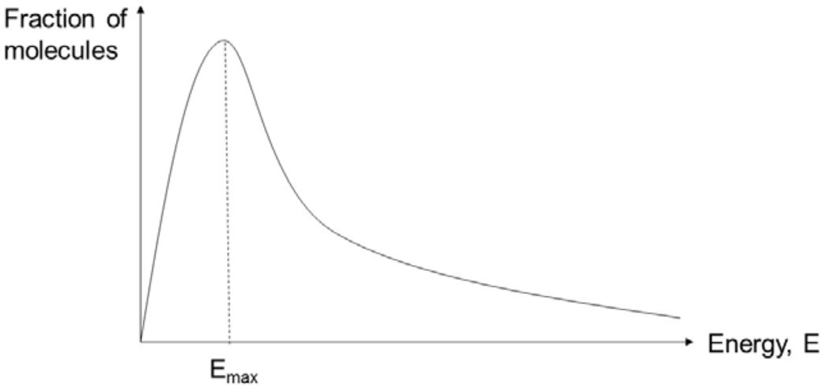
16 The graph below shows how the pH changes when 0.1 mol dm^{-3} solution of **Y**(aq) was gradually added to 10 cm^3 of 0.1 mol dm^{-3} solution of **X**(aq).

What could **X** and **Y** be?



	X	**Y**
A	NaOH	HC*l*
B	HC*l*	NaOH + KOH
C	HC*l*	Na_2CO_3
D	HC*l*	$NaHCO_3$

17 The diagram below represents the Boltzmann distribution of molecular energies at a given temperature.



With an increase in temperature, which statements are correct?

1 At all energies, the proportion of molecules increases.

2 The peak of the graph decreases.

3 The value of the rate constant, k, increases.

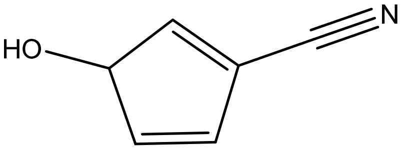
A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

18 *Use of Data Booklet is relevant to this question.*
Solid compound **J** has the following structure. It undergoes complete combustion in air to produce carbon dioxide, water and nitrogen dioxide only.



Compound **J**

Which statement about compound **J** is correct?

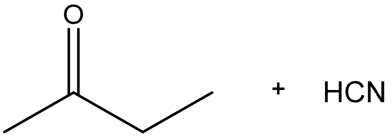
A On complete combustion, 0.10 g of compound **J** produces 0.230 g of CO_2.

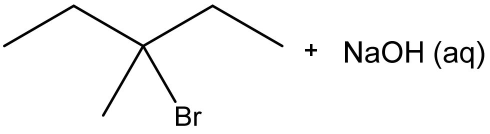
B On complete combustion, 0.10 g of compound **J** produces 22.4 cm^3 of NO_2 measured under room conditions.

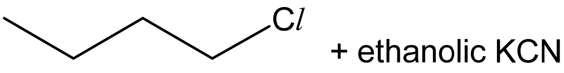
C 0.10 g of compound **J** reacts with excess bromine in organic solvent to produce 0.380 g of product.

D 0.10 g of compound **J** reacts with hydrogen gas and platinum catalyst to produce 0.100 g of product.

19 Which reaction will produce a mixture which is optically inactive?

1 

2 

3 

A 1, 2 and 3

B 1 and 2 only

C 1 only

D 2 and 3 only

20 How many constitutional isomers are possible for a substituted benzene, C_8H_{10}?

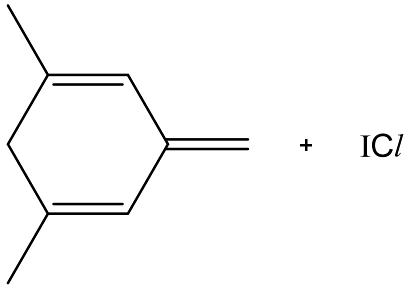
A 3

B 4

C 5

D 6

21 How many chiral carbons are formed in the major product of the following reaction?



A 2

B 3

C 4

D 5

22 Which statement best explains why benzene undergoes substitution reaction while ethene undergoes addition reaction?

A Benzene provides steric hindrance to repel reactive species.

B The C=C bonds in benzene are shorter and stronger than the C=C bonds in ethene.

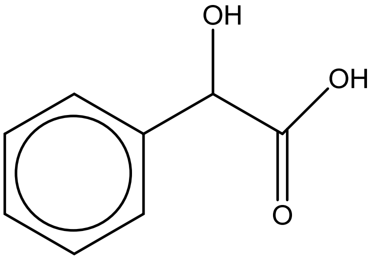
C There is delocalisation of π electrons in benzene which is absent in ethene.

D Benzene contains more C=C bonds than ethene, hence it is more electron rich.

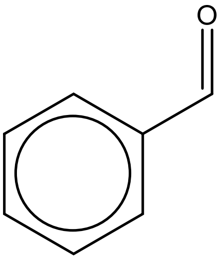
23 Benzoic acid can be obtained using either a one-step or two-step synthesis.

Which of the following cannot be used as the starting material?

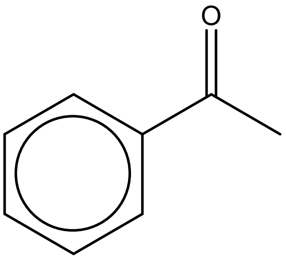
A



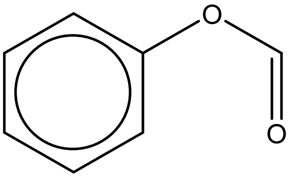
B



C



D



24 A catalytic converter is a device used to reduce the toxicity of emissions from an internal combustion engine. It works by using a catalyst (platinum, palladium or rhodium) to stimulate a chemical reaction in which toxic by-products of combustion are converted to less toxic substances.

Identify the chemical reactions occurring.

1 $2CO + O_2 \rightarrow 2CO_2$

2 $2NO \rightarrow O_2 + N_2$

3 $NO + \frac{1}{2}O_2 \rightarrow NO_2$

4 $SO_2 + NO_2 \rightarrow SO_3 + NO$

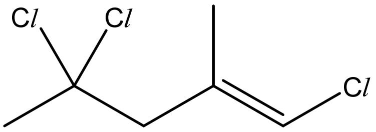
A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3 only

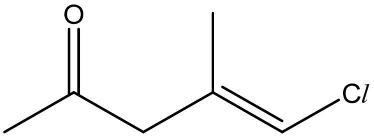
D 3 and 4 only

25 The following compound is heated with dilute sodium hydroxide.

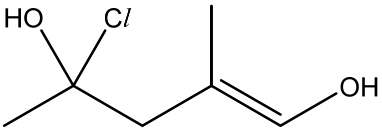


Which of the following product is obtained?

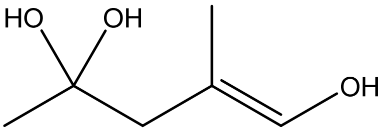
A



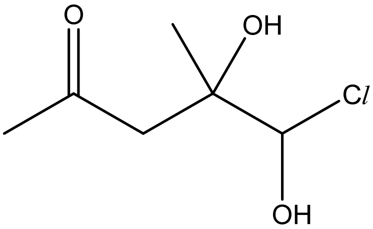
B



C



D



26 Consider the following four compounds.

1 propanol

2 phenol

3 propanoic acid

4 water

What is the relative order of **decreasing** acidity of these compounds?

A 1 2 4 3

B 3 2 1 4

C 3 2 4 1

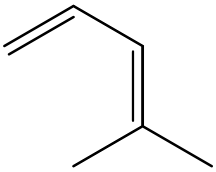
D 1 4 2 3

27 Compound **X** decolourises aqueous bromine. Compound **X** reacts with hot acidified potassium manganate(VII) to form compound **Y**. The following table shows some tests and observations carried out on compound **Y**.

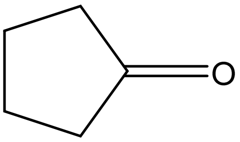
compound	Tests	Observations
Y	Na_2CO_3	Effervescence observed. Gas evolved forms white precipitate with limewater
	2,4-dinitrophenylhydrazine	Orange precipitate

What could compound **X** be?

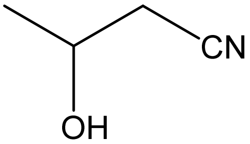
A



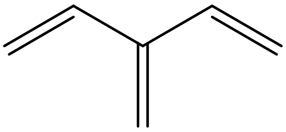
B



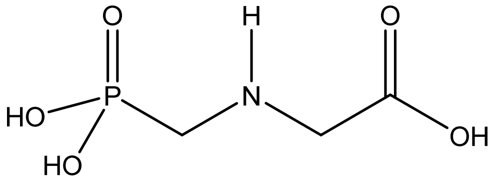
C



D



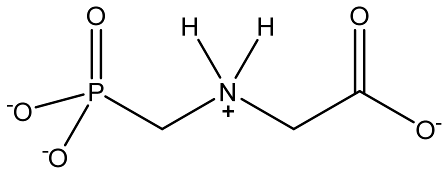
28 Glyphosate is a herbicide used to kill weeds.



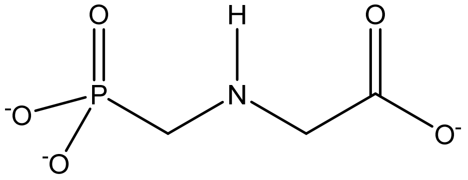
glyphosate

Glyphosate has pK_a values of 0.8, 2.3, 6.0 and 11.0.
What is the structure of the major species in a solution of glyphosate at pH 7?

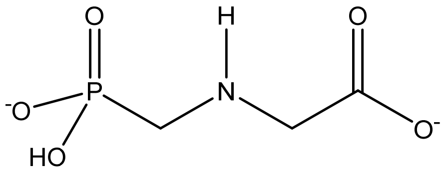
A



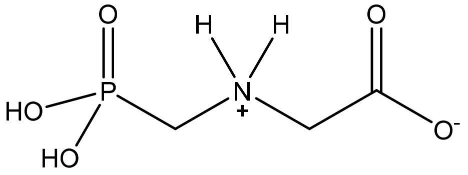
B



C



D



29 *Use of Data Booklet is relevant to this question.*
Which of the following reactions of transition metals is incorrect?

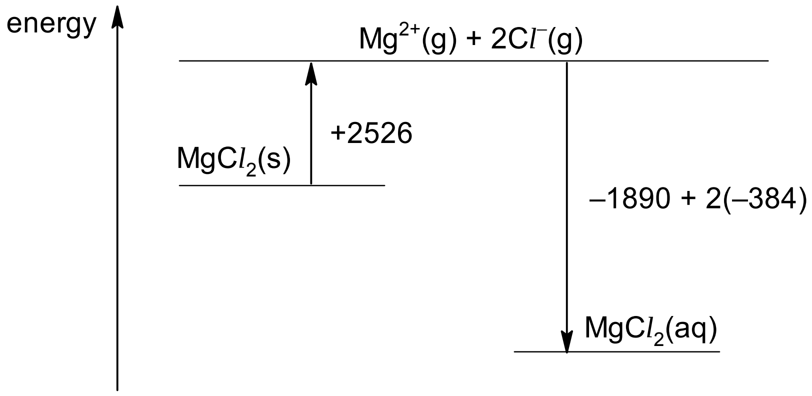
A Addition of H_2O_2(aq) to acidified $K_2Cr_2O_7$(aq) produces a green solution.

B V^{3+} is a suitable catalyst for the reaction: $2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$.

C Addition of concentrated HCl to $CuSO_4$(aq) produces a yellow solution.

D Addition of Na_2CO_3(aq) to Cr^{3+}(aq) produces a gas that gives a white precipitate when bubbled through limewater.

30 The following energy level diagram represents the dissolving of anhydrous magnesium chloride in a large volume of water.



Which statements about the process are correct?

1 The lattice energy of magnesium chloride is –2526 kJ mol^{-1}.

2 The enthalpy change of hydration of the chloride ion is –384 kJ mol^{-1}.

3 The enthalpy change of solution of anhydrous magnesium chloride is –132 kJ mol^{-1}.

4 $Mg^{2+}(g)$ and $Cl^{-}(g)$ are less thermally stable than $MgCl_2(aq)$.

A 1, 2, 3 and 4

B 1, 2 and 3 only

C 2 and 3 only

D 2 and 4 only

Paper 1 Worked Solutions

1	A	**2**	C	**3**	D	**4**	D	**5**	C
6	B	**7**	D	**8**	B	**9**	A	**10**	D
11	B	**12**	A	**13**	D	**14**	D	**15**	B
16	C	**17**	C	**18**	B	**19**	A	**20**	B
21	C	**22**	C	**23**	D	**24**	A	**25**	A
26	C	**27**	D	**28**	A	**29**	B	**30**	A

1

$C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2H_2O$

$V_{O_2(excess)} + V_{CO_2} = 55$
Since V_{CO_2} = 40 cm^3, $V_{O_2(excess)}$ = 55 – 40 = 15 cm^3
$V_{O_2(reacted)}$= 80 – 15 = 65 cm^3

Mole ratio of C_xH_y : CO_2 = 1:x = 10:40 ⇒ x = 4
Mole ratio of C_xH_y : O_2 = 1:(x+y/4) = 10:65 ⇒ y = 10
Formula of the hydrocarbon is C_4H_{10}.
Ans: A

2 Given 90% in each of the three steps,
1 mol of Na_2SO_4(s) yields 0.9 mol of Na_2S(s).
In turn, 0.9 mol of Na_2S(s) yields 0.81 mol of Na_2CO_3(s).
In turn, 0.81 mol of Na_2CO_3(s) yields 1.458 mol of $NaHCO_3$(s).

⇒ Mole ratio of Na_2SO_4(s) : $NaHCO_3$(s) = 1:1.458
Mass of $NaHCO_3$(s) = $\left(\frac{100000}{142} \times 1.458\right) \times 84.0 = 86248\ g = 86.2\ \text{kg}$
Ans: C

3 Option 1 is incorrect. $^{58}Ni^{2+}$ ion has 58 nucleons while $^{60}Ni^{2+}$ ion has 60 nucleons.
Option 2 is correct. Both Ni isotopes have 28 protons.
Option 3 is correct. $^{58}Ni^{2+}$ ion has 30 neutrons and 26 electrons while $^{60}Ni^{2+}$ ion has 32 neutrons and 26 electrons.
Option 4 is correct. Angle of deflection is directly proportional to $\frac{charge}{mass}$ ratio. Since $^{58}Ni^{2+}$ ion has a smaller mass than that of $^{60}Ni^{2+}$ ion, it has a bigger angle of deflection.

Ans: D

4

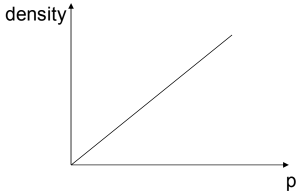
$V_1P_1 + V_2P_2 = V_TP_T$
$(4)(200) + (3)(400) = P_T(16)$
P_T = 125 kPa

Ans: D

5

Option C is incorrect.
$pV = nRT$
$p = \rho.\frac{RT}{Mr}$
$\rho = p.\frac{Mr}{RT}$

A plot of density against pressure, at constant temperature, would give a linear graph of a positive gradient.



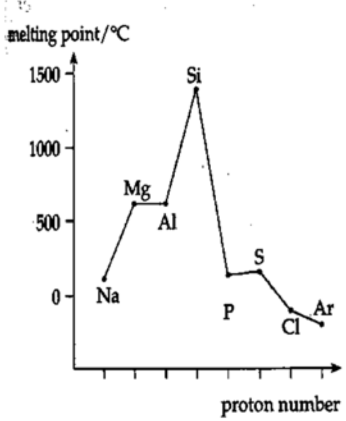
Ans: C

6 Option A is incorrect. From the given diagram, the presence of hexagons and pentagons imply different bond angles within buckminsterfullerene.
Option B is correct. From the given diagram, all the carbon in buckminsterfullerene is sp^2 hybridised hence the 4th electron of each carbon is delocalised within the sphere.
Option C is incorrect. The sublimation point of buckminsterfullerene should be lower than that of graphite, as it has a simple molecular structure with instantaneous dipole-induced dipole interactions between molecules whereas graphite has a giant molecular structure with strong covalent bonds between atoms.

Option D is incorrect. The absence of hydrogen in buckminsterfullerene implies the absence of water during combustion.
Ans: B

7 Option A is incorrect. Compounds can dissolve endothermically hence it is possible that barium fluoride can dissolve in water.
Option B is incorrect. Ba^{2+} is bigger in size than Mg^{2+} hence Ba^{2+} has a lower charge density and therefore less polarising. The hydration energy of Ba^{2+} will be smaller in magnitude than that of Mg^{2+}.
Option C is incorrect. LE depends on the charge and size of the ions. Since Ba^{2+} is bigger in size than Mg^{2+}, LE of BaF_2 will be smaller in magnitude than MgF_2.
Option D is correct. Both ΔH_{LE} and $\Delta H_{hydration}$ are negative and $\Delta H_{solution} = \Sigma\Delta H_{hydration} - \Delta H_{LE}$. For $\Delta H_{solution}(BaF_2)$ to be negative, ΔH_{LE} must be bigger in magnitude than $\Sigma\Delta H_{hydration}$.
Ans: D

8 Option A is correct: Atomic radius decreases across the period. Nuclear charge increases as number of protons increases across the period. Electrons are added to the same valence shell hence shielding effect remains almost constant. Effective nuclear charge increases and thus, the valence electrons are more strongly attracted to the nucleus.
Option B is incorrect: Melting point trend should be as shown instead, where the melting point of Si is the highest.



Option C is correct: The ability to conduct electricity depends on the presence of mobile charge carriers. Electrical conductivity increases from Na to Al due to the increase in number of valence electrons available in "sea" of delocalised electrons. Si is a semiconductor, while P, S and Cl are non-conductors.
Option D is correct: Electronegativity increases across the period. Nuclear charge increases. Shielding effect remains relatively constant as the number of inner shell electrons remains the same. There is a larger effective nuclear charge, and thus a stronger net attraction for a bond pair of electrons in a covalent bond.
Ans: B

9 A halogen that is a stronger oxidising agent can oxidise a halide below it in the group. From the results of the table, it can be deduced that the oxidising power of the halogens: $\mathbf{Y}_2 > \mathbf{Z}_2 > \mathbf{X}_2$
Thus the reducing power of the halide ions is: $\mathbf{X}^- > \mathbf{Z}^- > \mathbf{Y}^-$

Ans: A

10 From the successive IE, there is a big jump between the 5th IE and 6th IE. Hence, the 6th electron must have been removed from an inner principal quantum shell. Hence there are 5 electrons in the outermost shell and element **Y** is from Group 15.
It can be inferred therefore that **X**: Group 13; **W**: Group 14; **Z**: Group 16

Option A is correct: The oxide of **X** (i.e. Al_2O_3) is insoluble in water. The small and highly charged Al^{3+} ion results in highly exothermic lattice energy. Hence, the energy that is released during hydration cannot compensate for the larger amount of energy that is required to overcome the strong ionic bonds in the giant lattice.
Option B is correct. The first IE of **Z** (i.e. sulfur) is lower than that of **Y** (i.e. phosphorous). This is one of the two exceptions in the 1st IE trends - for Z, electron is removed from a paired electron occupying the same 3p orbital. Thus, the electron experiences inter-electronic repulsion and lesser energy is required to remove it.
Option C is correct. Oxide of **X** (i.e. Al_2O_3) is amphoteric, and will react with both acids and bases. $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$
Option D is incorrect. The chloride of W (i.e. CCl_4) does not undergo hydrolysis in water as it does not have energetically accessible vacant 3d orbitals (unlike the chlorides of **Y** and **Z**) which can accommodate lone pair of electrons from oxygen atoms of water during hydrolysis.
Ans: D

11 Option 1 is incorrect.
$-\Delta H_1$ = The enthalpy change of formation ,ΔH_f , of Be_3N_2
Since 3 Be(s) + 3 N_2 (g) → Be_3N_2
$-\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - \Delta H_6$
= +324 + 944 (BE of N≡N) + 3(900+1760) + 1404 - 11300
= −648 kJ mol^{-1}
Option 2 is correct. Enthalpy change of atomisation is always endothermic. In this question, energy is absorbed to break N≡N to produce 2 N atoms.
Option 3 is correct. ΔH_6 represents −|Lattice Energy of Be_3N_2|. Lattice energy is a measure of the ionic bond strength.
Ans: B

12 Option 1 is incorrect. S(s) + O_2(g) → SO_2(g)
There is no change in the number of moles of gaseous reactants and products.
Option 2 is incorrect. When a solute dissolves in solvent, there is an increase in the disorderliness of the system.
Option 3 is correct. Formation of a solid ionic compound from its constituent gaseous ions results in a decrease in disorderliness of the system as the ions are now held in fixed positions.
Ans: A

13 Percentage efficiency

$$= \frac{\text{heat transferred to calorimeter}}{\text{heat released due to the combustion of hydrazine}} \times 100\%$$

$$= \frac{\Delta T \times C}{\text{amount of hydrazine used} \times \text{enthalpy change of combustion}} \times 100\%$$

$$= \frac{\boldsymbol{W \times Z}}{\frac{225 \times 1000 \times 1.02}{\text{Molar mass } (N_2H_4)} \times 622.2} \times 100\%$$

Ans: D

14. Option 1 is incorrect. An increase in pressure will not result in a shift in position of equilibrium since the number of moles of gaseous reactants = number of moles of gaseous products.

Option 2 is incorrect. Addition of water results in a decrease in concentration of **X**. Hence, position of equilibrium will shift to the left in order to increase the concentration of **X**. Hence, concentration of **Z** should decrease.

Option 3 is incorrect. An increase in temperature will result in the position of equilibrium shifting left in order to absorb heat energy since the backward reaction is endothermic. Hence, concentration of **Z** should decrease.
Answer: **D**

15 Since $P_{\boldsymbol{Q}} = \frac{n_{\boldsymbol{Q}}}{n_T} \times P_T$ and $P_{\boldsymbol{R}} = \frac{n_{\boldsymbol{R}}}{n_T} \times P_T$

$K_p = \frac{(P_R)^2}{(P_Q)^2} = \frac{(n_R)^2}{(n_Q)^2} = 64$
$\frac{n_R}{n_Q} = 8$
$n_Q : n_R = 1 : 8$

Ans: **B**

16 Option A is incorrect.
From the graph (increasing pH as volume of Y added increases), it can be inferred that a base (**Y**) was added to an acid (**X**). **Y** cannot be HC*l*.
Option B is incorrect. Even though **Y** contains 2 strong bases, the total $[OH^-]$ is still 0.1 mol dm^{-3}, hence 10 cm^3 of **Y** is needed to neutralise **X**.
Option C is correct. Na_2CO_3 is dibasic. A simple balanced chemical equation (carbonates react with acids to give salt, water and carbon dioxide) will prove that Na_2CO_3 : HC*l* is 2 : 1 and thus only 5 cm^3 of Na_2CO_3 is needed to react with HC*l*.
Option D is incorrect. $NaHCO_3$ is monobasic and 10 cm^3 of $NaHCO_3$ is required to neutralise HC*l*.
Ans: C

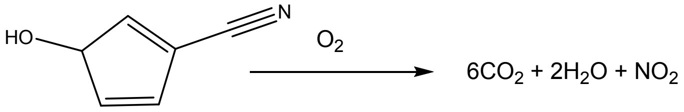
17 Option 1 is incorrect. When temperature increases, the curve is displaced right and the peak is lowered as the total number of molecules remains constant. Proportion of molecules does not increase at all energies.
Option 2 is correct. When temperature increases, the curve is displaced right and peak of graph is lowered as the total number of molecules

remains constant.
Option 3 is correct. When temperature is increased, the value of rate constant k increases.

Ans: C

18 C_6H_5NO

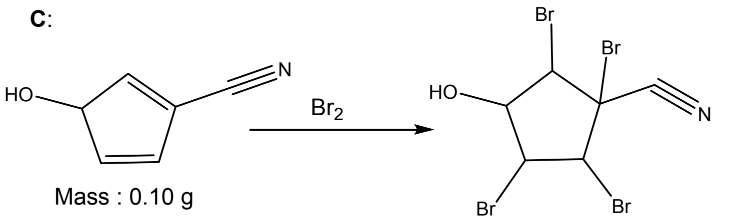
M_r : 107



A: Mass of CO_2 formed : 6 x 9.3458 x 10^{-4} x 44 = 0.247 g

B: Volume of NO_2 formed : 9.3458 x 10^{-4} x 24000 = 22.4 cm^3

C:



Mass : 0.10 g

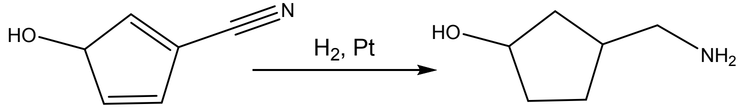
M_r : 107

n = 9.3458 x 10^{-4} mol

M_r : 426.6 *(an easy way to get this M_r is to add 4 x A_r (Br) to 107)*

Mass : n x M_r = 0.399 g

D:



Mass : 0.10 g

M_r : 107

n = 9.3458 x 10^{-4} mol

M_r : 115 *(an easy way to get this M_r is to add 8 x A_r (H) to 107)*

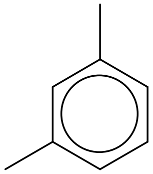
Mass : n x M_r = 0.107 g

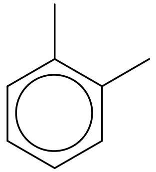
Ans: B

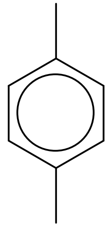
19 Option 1: CN^- can approach the planar carbonyl carbon from top and bottom with equal probability to give enantiomers (with chiral carbon).
Option 2: Even though a tertiary carbocation is formed as intermediate via the S_N1 mechanism, the final product does not have a chiral carbon, hence no enantiomers are formed.
Option 3: S_N2 mechanism has occurred as the reactant is a primary halogenoalkane. The product formed does not have a chiral centre, thus it is optically inactive.

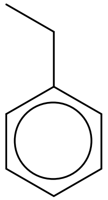
Ans: A

20



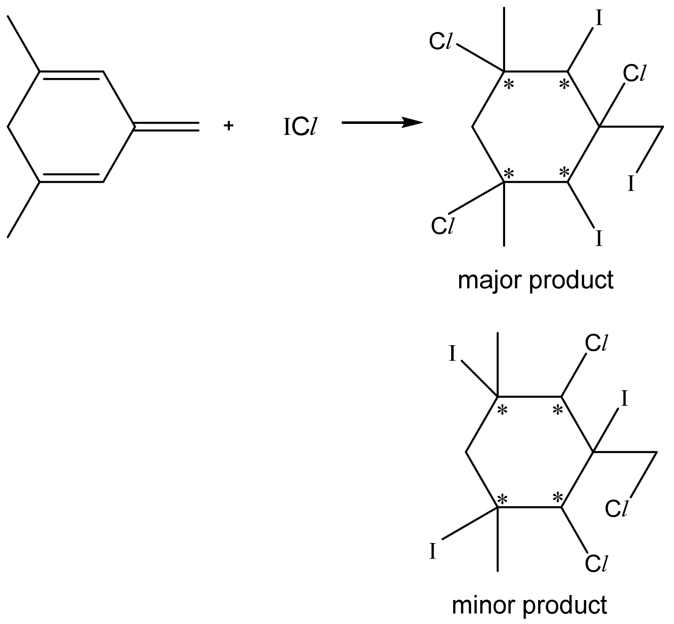






Ans: B

21



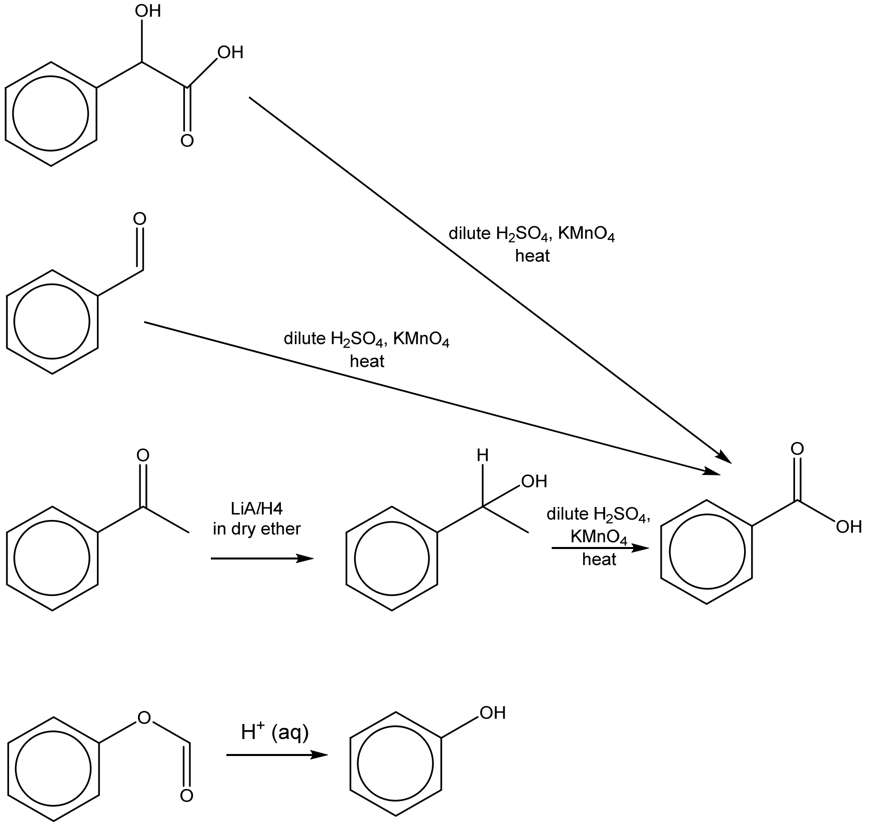
Applying Markovnikov's rule, there are 4 chiral carbons in the major product.

Ans: C

22 Benzene prefers to undergo substitution reactions rather than addition reactions due to delocalisation of π–electrons, which leads to resonance stability. Addition reaction destroys this stability. Options A, B and D are true but does not explain why benzene undergoes substitution instead of addition.

Ans: C

23



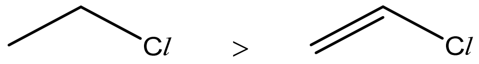
Ans: D

24 The following reactions occur:

- Reduction of nitrogen oxides to nitrogen and oxygen with rhodium catalyst: $2NO_x \rightarrow xO_2 + N_2$
- Oxidation of carbon monoxide to carbon dioxide with platinum and palladium catalyst: $2CO + O_2 \rightarrow 2CO_2$
- Oxidation of unburnt hydrocarbons to carbon dioxide and water with platinum and palladium catalyst.

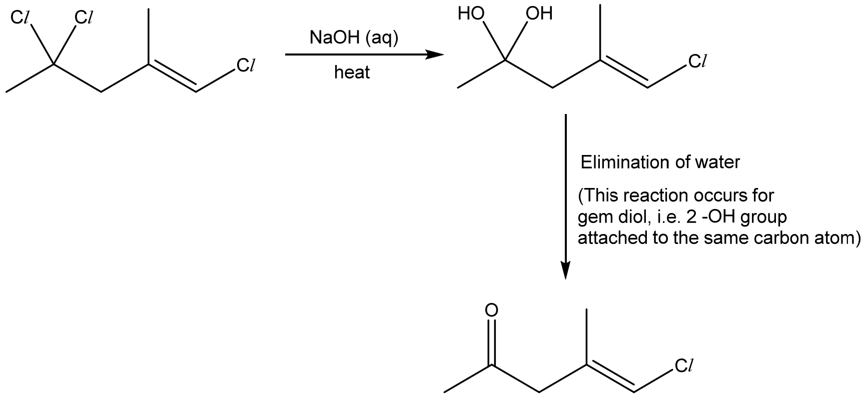
Ans: A

25 Ease of nucleophilic substitution with water:



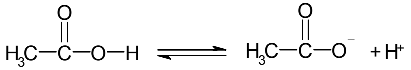
reacts after heating with NaOH

little to no reaction after prolonged heating with NaOH



Ans: A

26 To discuss the strength of the acids, **compare** the **stability** of the **conjugate base** of the acids.
e.g.



$$H_3C\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O\!-\!H \rightleftharpoons H_3C\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O^- + H^+$$

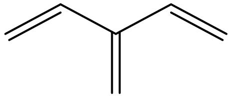
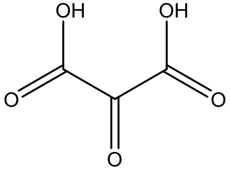
When the conjugate base is more stable, the acid has a greater tendency to dissociate to form the conjugate base and H^+ ions

- The forward reaction occurs to a greater extent
- The equilibrium position lies more to the right.

propanol	phenol	propanoic acid
$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$	$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$	$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$
Alkyl groups are electron donating. Hence negative charge on the oxygen atom in RO^- is intensified compared to OH^-. RO^- is destabilised and hence alcohols are weaker acids than water.	Lone pair of electrons on the oxygen atom delocalised into the benzene ring. The negative charge on the oxygen atom in $C_6H_5O^-$ is delocalised into the ring. This dispersion of charge stabilises $C_6H_5O^-$, hence phenol is more acidic than water.	The negative charge on the oxygen atom in $RCOO^-$ is delocalised between the 2 electronegative oxygen atoms and it is resonance stabilised. Hence carboxylic acids are more acidic than phenol.

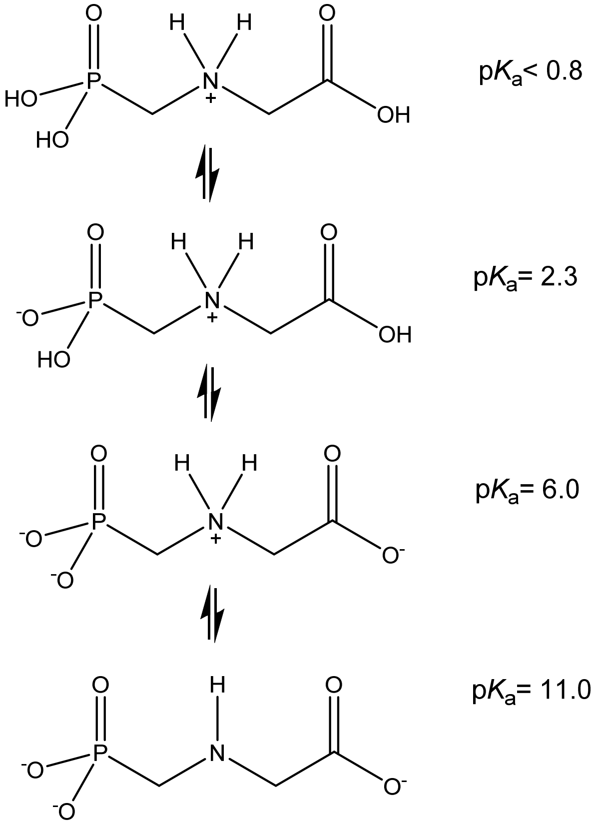
Ans: C

27

Information	Deduction
X, is found to decolourise aqueous bromine.	electrophilic addition ⇒ Presence of alkene
X reacts with hot acidified potassium manganate(VII) to form compound **Y**.	Oxidative cleavage of alkene
Y reacts with Na_2CO_3.	Neutralisation ⇒ presence of carboxylic acid
Y reacts with 2,4-dinitrophenylhyrazine.	Condensation ⇒ Presence of ketone (oxidative cleavage of alkene gives either carbon dioxide gas, carboxylic acid or ketone only)
Compound **X**	
Compound **Y**	

Ans: D

28 Both phosphonic acid and carboxylic acid moieties can be ionised and the amine group can be protonated and the substance exists as a series of zwitterions.



Ans: A

29 Option A is correct: addition of H_2O_2(aq) to acidified $K_2Cr_2O_7$(aq) produces a green solution of Cr^{3+}.

From Data Booklet: $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ +0.68V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ +1.33V

E_{cell} = 1.33 – (+0.68) = +0.65V >0, thus reaction is spontaneous.

Option B is incorrect:

From Data Booklet: $I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54V

$S_2O_8^{2-} + 2e^- \rightleftharpoons SO_4^{2-}$ +2.01V

A suitable catalyst will have an E^θ value in between +0.54V and +2.01V.

Since $V^{3+} + e^- \rightleftharpoons V^{2+}$ −0.26V

It is not a suitable catalyst.

Option C is correct: Ligand exchange reaction occurred. Water molecules in $[Cu(H_2O)_6]^{2+}$ are replaced by Cl^- ions to form $[CuCl_4]^{2,}$ accounting for the yellow solution.

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$

Option D is correct: Hydrolysis reaction occurs for ions with acidic properties such as highly polarising Cr^{3+}(aq) due to its high charge density.

$[Cr(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Cr(H_2O)_5OH]^{2+} + H_3O^+$

When Na_2CO_3 is added: $CO_3^{2-} + 2H_3O^+ \rightarrow CO_2 + 3H_2O$

The CO_2 evolved gives a white ppt with limewater.

Ans: B

30 Option 1 is correct. Lattice energy is the heat released when 1 mole of $MgCl_2$ is formed from its constituent gaseous ions i.e –2526 kJ mol^{-1}.

Option 2 is correct. As seen from the diagram, $\Delta H_{hydration}$ of Cl^- is –384 kJ mol^{-1}.

Option 3 is correct.
$\Delta H_{solution}$ = 2526 + [–1890 + 2(–384)] = –132 kJ mol^{-1}.

Option 4 is correct. The higher energy level, the less thermally stable a species is.

Ans: A

Section A: Structured Questions

Answer **all** the questions in the spaces provided.

1 **(a)** Fig. 1.1 shows the second ionisation energies of eight elements with consecutive proton numbers and one of the elements is aluminium.

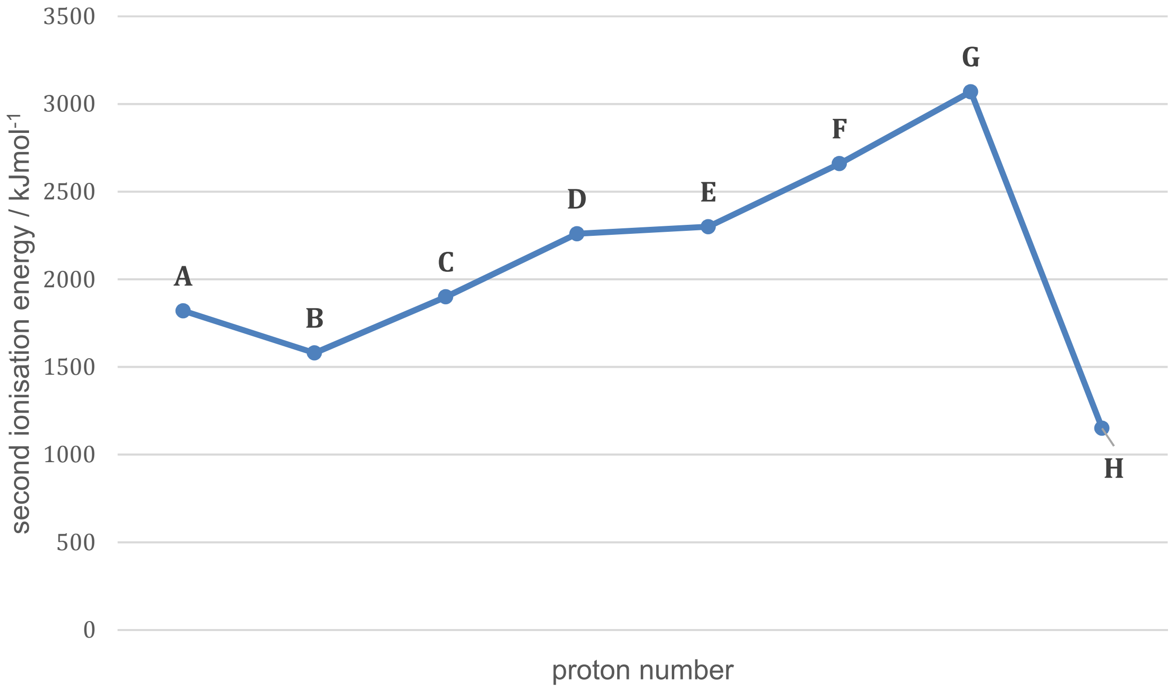


Fig.1.1

(i) Define, with the aid of an equation, what is meant by the second ionisation energy of aluminium.

....

....

....

[2]

(ii) Explain why the second ionisation energy of aluminium is usually more endothermic than the first ionisation energy.

....

....

....

....

[2]

(iii) Identify the element which represents aluminium. Explain the reasoning.

....

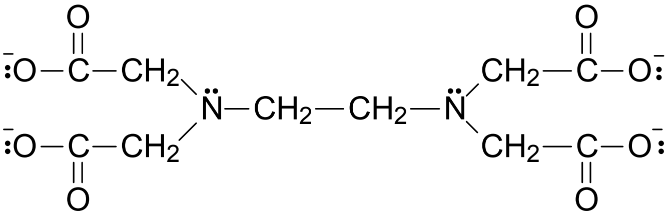
....

....

.... [2]

(b) Hard water is high in dissolved minerals, specifically calcium ions. Although hard water does not pose a health risk, it causes poor soap performance. The soap used in hard water combines with the dissolved minerals to form a sticky soap curd which consists of insoluble salts.

(i) Ethylenediaminetetraacetate or EDTA is a component in laundry detergent.



EDTA

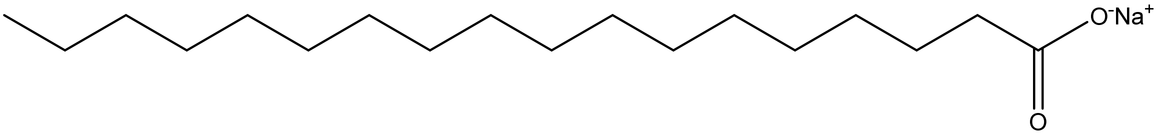
Suggest how EDTA could improve the soap performance in hard water.

....

.... [1]

(ii) Soap has effective cleaning properties because it contains one or more surfactants.

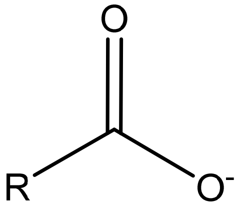
A surfactant is a molecule with a *non-polar* tail and a *polar* head. An example is sodium stearate, as shown below.



A simplified representation of stearate ion is $RCOO^-$.

Complete the diagram by drawing the relevant dipoles and indicate the type of intermolecular forces of attraction between stearate ion, an oil molecule and a water molecule. Hence explain how stearate ion helps to remove oil from surface during washing.

You may use R' to represent an oil molecule.



stearate ion

....

....

....

[3]

[Total: 10]

2 The table below shows the melting points of some of the chlorides of the elements in period 3 of the periodic table.

Chlorides	Melting points/ ºC
Magnesium chloride, , $MgCl_2$	714
Aluminium chloride, $AlCl_3$	192
Phosphorus pentachloride, PCl_5	161
Sulfur dichloride, SCl_2	–121

(a) Account, in terms of structure and bonding, the difference in the melting points between

(i) magnesium chloride and aluminium chloride

....

....

....

.... [2]

(ii) phosphorus pentachloride and sulfur dichloride

....

....

....

.... [2]

(b) When PCl_5 is added to water, liquid phosphorus oxychloride, $POCl_3$ is formed as an intermediate compound.

(i) Reactions of covalent chlorides with water can be rationalised as step–wise replacement of $–Cl$ with –OH. Deduce a three–step reaction sequence for the formation of $POCl_3$ from PCl_5.

Step 1: ....

Step 2: ....

Step 3: .... [3]

$POCl_3$ can also acts as a *Lewis base* to remove the $AlCl_3$ at the end of a Friedel–Crafts reaction, resulting in the formation of a covalent product.

(ii) Define the term '*Lewis base*'.

....

[1]

(iii) Draw a diagram to illustrate the shape of the product which results in the removal of $AlCl_3$, stating the type of bonding present and the bond angles around the central atoms.

Type of bonding: ....

[2]

[Total: 10]

3 **(a)** When steam is passed over hot coke (a form of carbon obtained from coal), water gas is produced. Water gas, consists of a mixture of carbon monoxide and hydrogen, is an important industrial fuel.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

When 0.100 mol of steam was reacted with coke in a vessel of 1.00 dm^3 and allowed to reach equilibrium at 800 °C, the partial pressure of steam was found to be 2.67 atm.

(i) Calculate the initial pressure of steam, in atm, introduced into the vessel.

[2]

(ii) Using your answer in **a(i)**, calculate a value for K_p, in atm, at 800 °C.

[2]

(iii) Calculate the minimum mass of carbon required in the vessel.

[2]

(iv) State and explain whether high or low pressure would favour a higher yield of water gas.

[2]

(v) The reaction was repeated at a lower temperature and the numerical value of K_p was found to have decreased.

State and explain whether the forward reaction is endothermic or exothermic.

[2]

(b) **(i)** The relationship between $\Delta G^{\ominus}$ and K_p for the reaction between carbon and steam is

$$\Delta G^{\ominus} = -\mathrm{RT} \ln K_p$$

where $\Delta G^{\ominus}$ is the standard Gibbs free energy change in J mol^{-1}, R is the gas constant, T is the temperature in Kelvin at which the equilibrium is established and K_p is the equilibrium constant.

Given that the K_p of the reaction at 298 K is 2.97×10^{-18} atm, calculate the $\Delta G^{\ominus}$ of the reaction.

[1]

(ii) Comment on the sign of $\Delta G^{\ominus}$ with reference to the position of equilibrium of the reaction.

[2]

[Total: 13]

4. **(a)** Ethers have the general formula, R-O-R' (where R and R' are alkyl or aryl groups).

The most useful method of preparing ethers is by the Williamson ether synthesis, in which an alkoxide ion (RO^-) reacts with an alkyl halide (R'X) in an S_N2 mechanism.

A reaction scheme is shown below:

$$\mathrm{ROH} \xrightarrow[\text{step } \mathbf{1}]{\text{NaH}} \mathrm{RO^{-}Na^{+}} \xrightarrow[\text{step } \mathbf{2}]{\text{R'X (alkyl halide)}} \mathrm{ROR'}$$

(i) Suggest why step **1** is necessary in the Williamson ether synthesis.

[1]

(ii) Using 1-chloropropane as the alkyl halide and $CH_3CH_2O^-$ as the alkoxide ion, outline the mechanism for step **2** of the Williamson ether synthesis. Show all charges and relevant lone pairs of electrons and show the movement of electron pairs by using curly arrows.

[3]

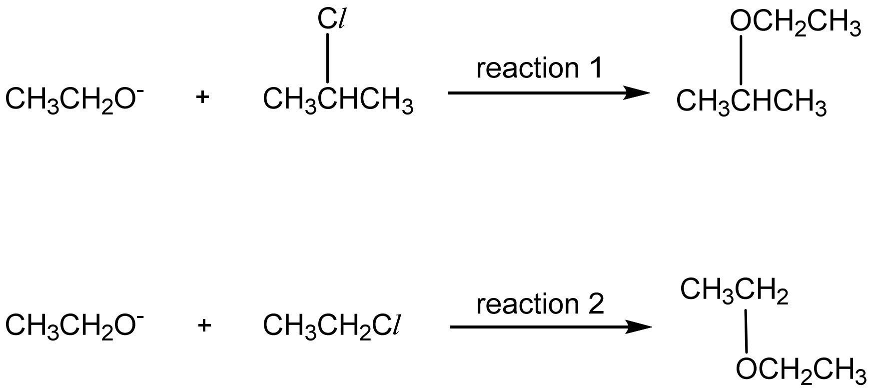
(iii) The same reaction in **a(ii)** was repeated using iodopropane instead of chloropropane. Using relevant data from the *Data Booklet*, state and explain the effect on the rate of reaction.

[2]

(iv) Suggest why the product obtained in **a(ii)** shows no optical activity.

[1]

Fig. 4.1 shows two separate reactions to synthesise ethers using the Williamson ether synthesis method.



$$CH_3CH_2O^- + CH_3\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow{\text{reaction 1}} CH_3\overset{\overset{OCH_2CH_3}{|}}{C}HCH_3$$

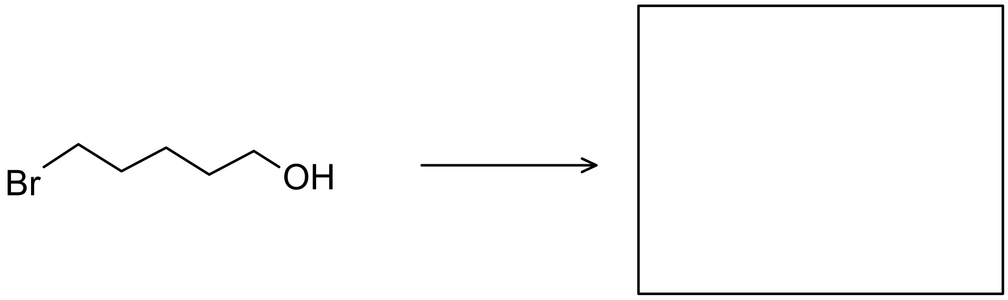
$$CH_3CH_2O^- + CH_3CH_2Cl \xrightarrow{\text{reaction 2}} \begin{array}{l} CH_3CH_2 \\ \quad | \\ \quad OCH_2CH_3 \end{array}$$

Fig 4.1

(v) State and explain which reaction will give a higher yield.

[2]

(vi) Suggest the structure of the product when 5-bromopentan-1-ol undergoes the Williamson ether reaction.



5-bromopentan-1-ol

[1]

(b) Halogenated organic compounds can be synthesised from various functional groups.

Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerants, but are now known to destroy ozone in the upper atmosphere through a free radical chain reaction.

(i) A student wrongly proposed that a propagation step for the formation of 1–chlorobutane from butane to be:

$$CH_3CH_2CH_2CH_3 + Cl\bullet \rightarrow CH_3CH_2CH_2CH_2Cl + H\bullet$$

Write the correct propagation step. Hence use relevant data from the *Data Booklet*, calculate the enthalpy change of reaction to explain why the propagation step proposed by the student is incorrect.

....

....

....

....

....

[3]

(ii) 2,5-dimethylhexane is reacted with chlorine in the presence of UV light to form 3 monochlorinated alkanes.

It has been found experimentally that in free radical substitution of alkanes, the primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

type of hydrogen atom	**reaction**	**relative rate**
primary	$RCH_3 \rightarrow RCH_2Cl$	1
secondary	$R_2CH_2 \rightarrow R_2CHCl$	7
tertiary	$R_3CH \rightarrow R_3CCl$	21

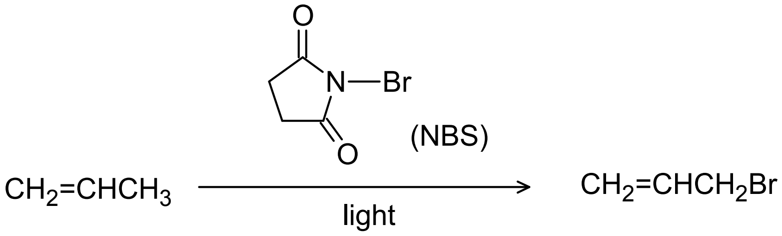
Draw the structural formula of the 3 possible monochlorinated products of 2,5-dimethylhexane and using the information in the table, suggest the relative ratios in which they are formed.

Ratio: .... : .... : ....

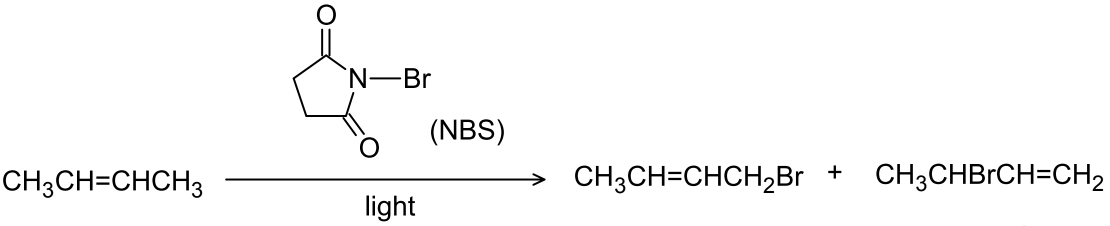
[3]

(c) Another method of preparing alkyl halides from alkenes is by the reaction with N-bromosuccinimide (NBS) in the presence of light to give products which are substituted at the allylic position i.e. the position *next* to the double bond. NBS is used as a source of bromine.

The process is similar to the free radical substitution mechanism of alkanes.



(i) However, a mixture of 2 products (**W** and **X**) is formed when but-2-ene undergoes this reaction.



compound **W** compound **X**

Suggest a reason for the formation of compound **X**.

....

.... [2]

(ii) State the type of isomerism shown by compound **W** and compound **X.**

.... [1]

[Total: 19]

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5 Infra–red(IR) absorptions can be used to identify functional groups in organic compounds. For example, ethyl ethanoate shows absorption at 100 − 1300 cm^{-1} and 1680 − 1750 cm^{-1}.

A student used infra–red spectrometer to obtain an infra-red(IR) spectrum of benzyl alcohol $C_6H_5CH_2OH$ as shown in Fig. 5.1.

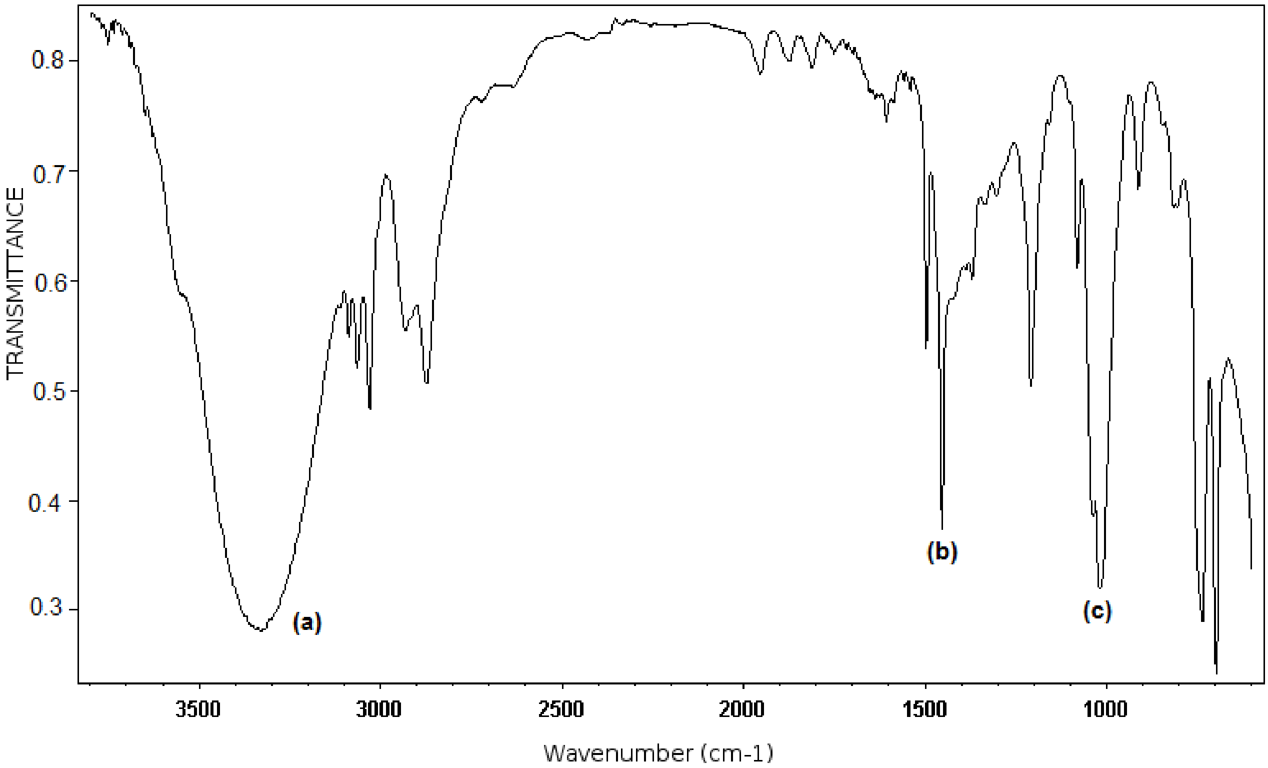


Fig. 5.1

(a) **Use the table of characteristic infra-red absorption frequencies in the *Data Booklet* to** identify the infra–red absorption range shown by benzyl alcohol.

IR region	Wavenumbers/ cm^{-1}	Functional groups present
(a)		
(b)		
(c)		

[3]

(b) The student carried out reflux of benzyl alcohol with acidified potassium dichromate and the product **A** obtained was analysed using IR spectrometer. Fig. 5.2 shows the IR spectrum obtained.

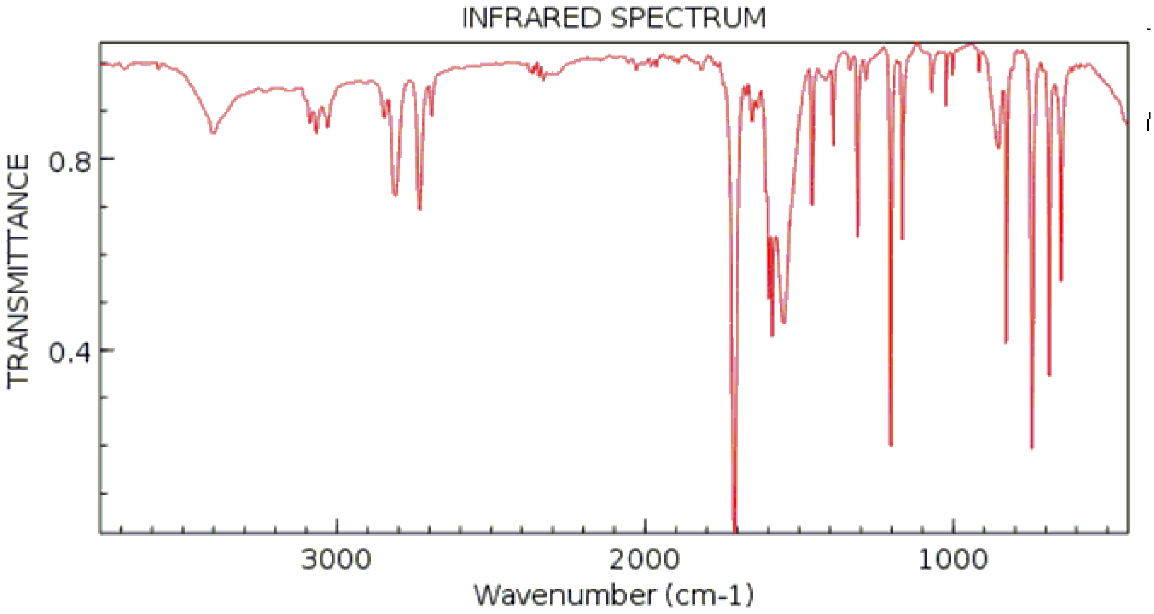


Fig. 5.2

By comparing the two infra-red spectra, suggest two differences from the infra–red spectra and draw the structure of the product **A** obtained.

Product **A:**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[3]

(c) Suggest a simple chemical test that could be used to confirm benzyl alcohol $C_6H_5CH_2OH$ has been completely converted into product **A** in **(b)**.

Test : ……………………………………………………………………………

Observations: ……………………………………………………………………

……………………………………………………………………………………

[2]

(d) A student wishes to determine the concentration of product **A** obtained. The student prepares 5 solutions of known concentrations, 0.0100, 0.0200, 0.0400, 0.0800 and 0.100 mol dm^{-3} of product **A**. 10 μL of each solution with the sample was used and a high performance liquid chromatogram was obtained. The peak areas of the chromatographs are given in the table below and a graph of concentration against peak area was obtained in Fig.5.3.

Solution concentration / mol dm^{-3}	0.0100	0.0200	0.0400	0.0800	0.100	sample
Peak area / cm^2	0.50	0.83	1.39	2.63	3.18	2.53

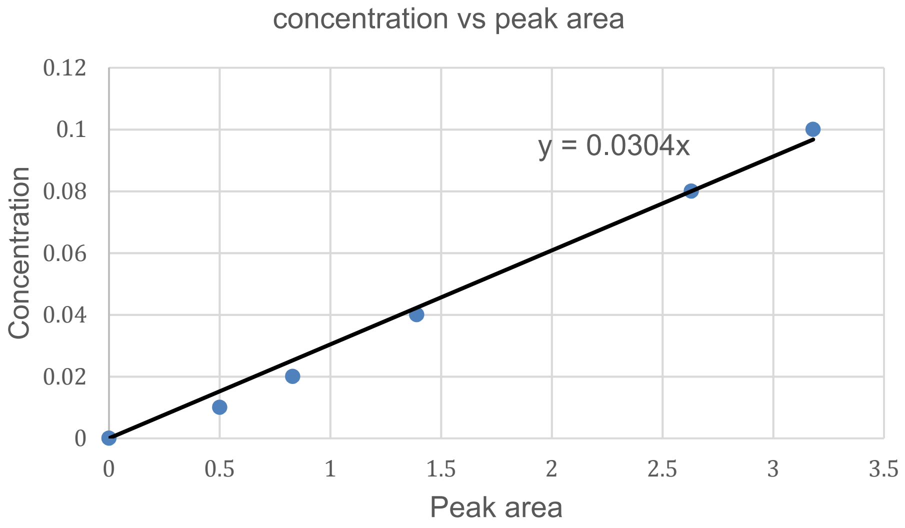


Fig. 5.3

(i) Using the peak area of the sample from the table and information from the graph, determine the concentration of product **A** in the sample.

[1]

(ii) Suggest what the student can do to ensure high yield of product **A** from the reaction of benzyl alcohol with acidified potassium dichromate in **(b)**. Use Le Chatelier's Principle to explain your suggestion.

[2]

(e) Fig. 5.4 shows a Ritter reaction.

The Ritter reaction transforms a nitrile to amide using a strong acid and water as follows.

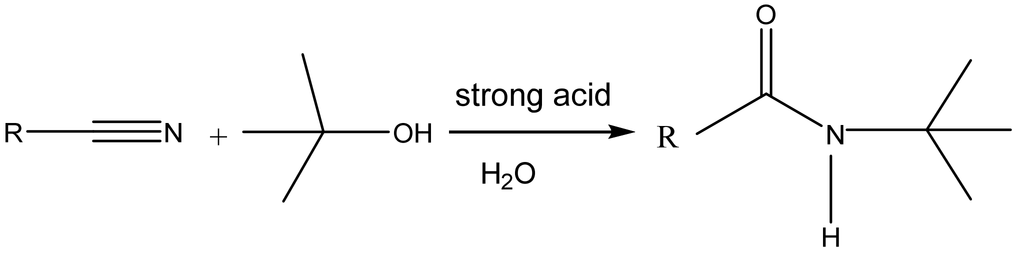


Fig. 5.4

(i) Side products will be formed from the Ritter reaction if heating was carried out.

Suggest the type of reaction which occurs and draw the structures of two side products formed.

Type of reaction: ....

[3]

(ii) Benzyl alcohol, $C_6H_5CH_2OH$ undergoes Ritter reaction with CH_2CHCN as shown in Fig. 5.4. Draw the structure of the amide formed.

[1]

(f) Fig. 5.5 shows a possible process in the human body where benzyl alcohol is oxidised to benzoic acid, conjugated with amino acid, glycine in the liver, and excreted as benzoylaminoethanoic acid, as shown.

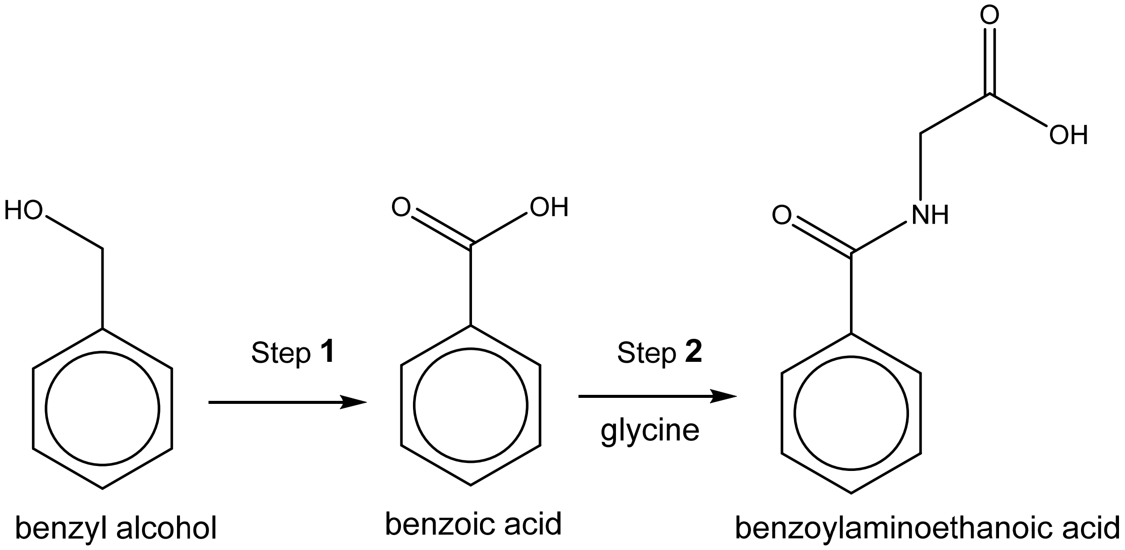


Fig 5.5

(i) Write an equation for the oxidation of benzyl alcohol to form benzoic acid. Use [O] to represent the formula of the oxidising agent.

....

[1]

(ii) What type of reaction takes place in step **2**?

....

[1]

(iii) Draw the displayed formula of a tripeptide consisting of glycine only.

[1]

(iv) Benzoylaminoethanoic acid can be reduced by $LiAlH_4$ in dry ether at room temperature and hydrogen gas with nickel catalyst under high heat and pressure. The organic products formed in the two reactions are different. Compound **B** has a molecular mass of 151 and compound **C** has a molecular mass of 185.

Deduce the structures of **B** and **C**.

compound **B**

compound **C**

[2]

The synthesis of glycine in the liver is catalysed specifically by glycine synthase enzyme.

(v) Describe, with the aid of a sketch how the rate of synthesis of glycine is affected by the concentration of the substrate.

[3]

[Total: 23]

Section A: Structured Questions

Answer **all** the questions in the spaces provided.

1 **(a)** Fig. 1.1 shows the second ionisation energies of eight elements with consecutive proton numbers and one of the elements is aluminium.

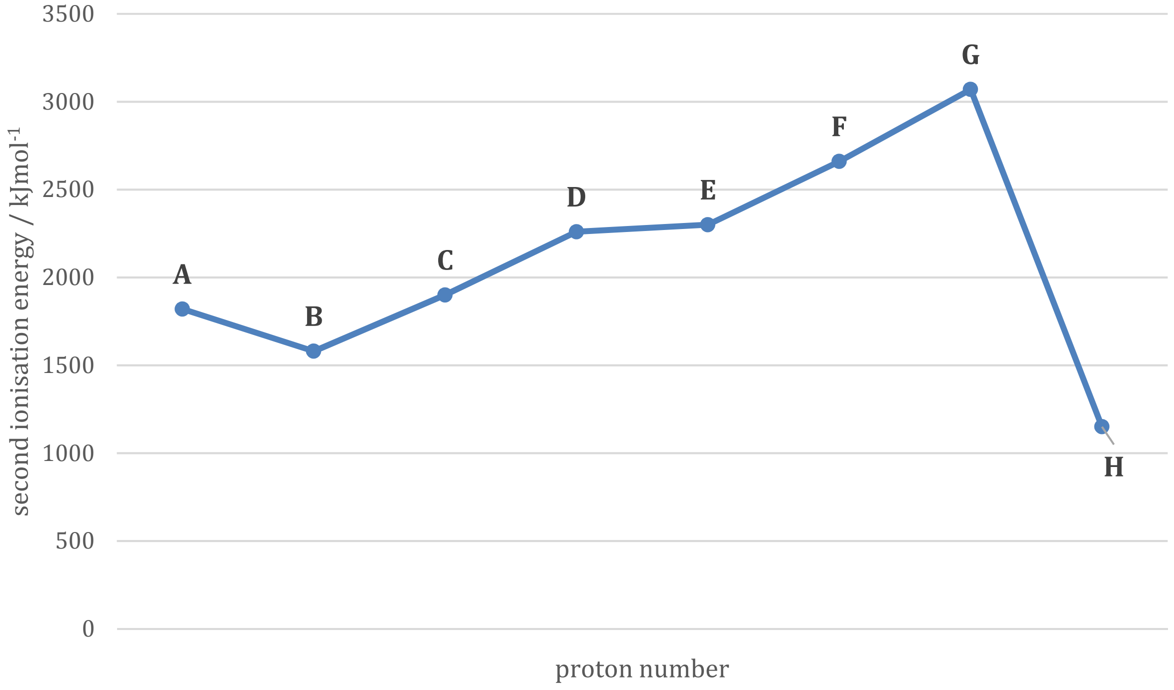


Fig.1.1

(i) Define, with the aid of an equation, what is meant by the second ionisation energy of aluminium.

$Al^+(g) \rightarrow Al^{2+}(g) + e$

Second ionisation energy is the energy required to remove one mole of outermost electrons from one mole of $Al^+(g)$ cations to form one mole of $Al^{2+}(g)$ cations.

[2]

(ii) Explain why the second ionisation energy of aluminium is usually more endothermic than the first ionisation energy.

1st IE: $Al(g) \rightarrow Al^+(g) + e$

2nd IE: $Al^+(g) \rightarrow Al^{2+}(g) + e$

The general increase is due the increasing positive charge on the cation.
As successive electrons are being removed, the same number of protons is attracting fewer electrons.

Consequently, there is an increase in the effective nuclear charge of the cation and requires more energy to remove the next electron.

[2]

(iii) Identify the element which represents aluminium. Explain the reasoning.

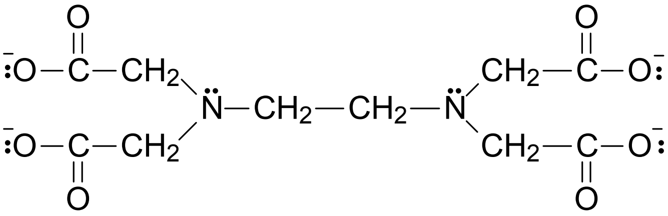
The sharp drop in 2nd IE value from **G** to **H** indicates the removal of the second electron from the inner shell, thus **G** is an element in Group 1. **[any other logical deduction]**

Element **A** is in Group 13 and is aluminium.

[2]

(b) Hard water is high in dissolved minerals, specifically calcium ions. Although hard water does not pose a health risk, it causes poor soap performance. The soap used in hard water combines with the dissolved minerals to form a sticky soap curd which consists of insoluble salts.

(i) Ethylenediaminetetraacetate or EDTA is a component in laundry detergent.



EDTA

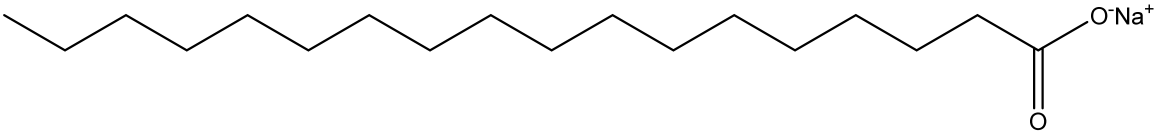
Suggest how EDTA could improve the soap performance in hard water.

EDTA forms a complex with metal ion Ca^{2+}, thus removing Ca^{2+}.

[1]

(ii) Soap has effective cleaning properties because it contains one or more surfactants.

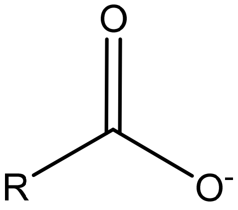
A surfactant is a molecule with a *non-polar* tail and a *polar* head. An example is sodium stearate, as shown below.



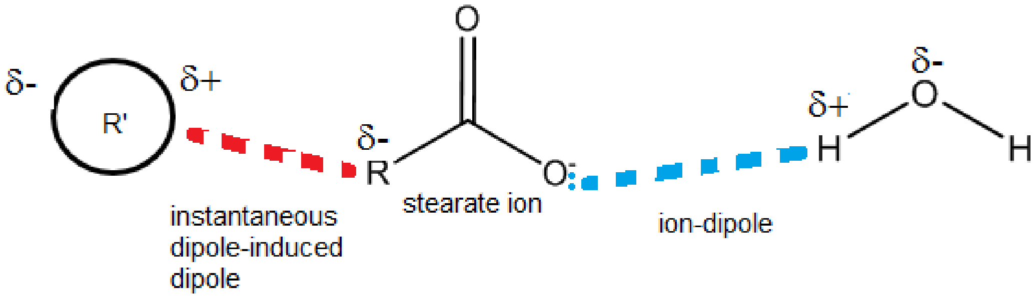
A simplified representation of stearate ion is $RCOO^-$.

Complete the diagram by drawing the relevant dipoles and indicate the type of intermolecular forces of attraction between stearate ion, an oil molecule and a water molecule. Hence explain how stearate ion helps to remove oil from surface during washing.

You may use R' to represent an oil molecule.



stearate ion



The surfactant/ stearate ion is able to interact with both water and oil - the negatively charged COO^- of the surfactant forms ion-dipole interactions with water, and the non-polar tail forms instantaneous dipole-induced dipole (id-id) interactions with oil (non-polar). Thus it can help to remove oil.

[3]

[Total: 10]

2 The table below shows the melting points of some of the chlorides of the elements in period 3 of the periodic table.

Chlorides	Melting points/ °C
Magnesium chloride, , $MgCl_2$	714
Aluminium chloride, $AlCl_3$	192
Phosphorus pentachloride, PCl_5	161
Sulfur dichloride, SCl_2	–121

(a) Account, in terms of structure and bonding, the difference in the melting points between

(i) magnesium chloride and aluminium chloride

$MgCl_2$ has a giant ionic structure while $AlCl_3$ has a simple molecular structure.

More energy is required to overcome the electrostatic forces of attraction between Mg^{2+} and Cl^- compared to instantaneous dipole-induced dipole attraction between $AlCl_3$ molecules. Hence $MgCl_2$ should have a higher melting point.

[2]

(ii) phosphorus pentachloride and sulfur dichloride

Both PCl_5 and SCl_2 have simple molecular structure.

PCl_5 has larger and more polarisable electron cloud than SCl_2. More energy is required to overcome the stronger instantaneous dipole-induced dipole attraction between molecules of PCl_5 compared to molecules of SCl_2. Hence PCl_5 should have a higher melting point.

[2]

(b) When PCl_5 is added to water, liquid phosphorus oxychloride, $POCl_3$ is formed as an intermediate compound.

(i) Reactions of covalent chlorides with water can be rationalised as step–wise replacement of –C*l* with –OH. Deduce a three–step reaction sequence for the formation of $POCl_3$ from PCl_5.

Step 1: $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$

Step 2: $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$

Step 3: $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$

[3]

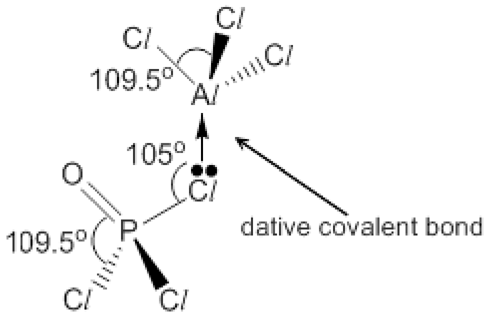
$POCl_3$ can also acts as a *Lewis base* to remove the $AlCl_3$ at the end of a Friedel–Crafts reaction, resulting in the formation of a covalent product.

(ii) Define the term '*Lewis base*'.

A Lewis base is an electron–pair donor.

[1]

(iii) Draw a diagram to illustrate the shape of the product which results in the removal of $AlCl_3$, stating the type of bonding present and the bond angles around the central atoms.



Type of bonding: **Dative covalent bond , (accept if student draw O to A*l*.)**

[2]

[Total: 10]

3 **(a)** When steam is passed over hot coke (a form of carbon obtained from coal), water gas is produced. Water gas, consists of a mixture of carbon monoxide and hydrogen, is an important industrial fuel.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

When 0.100 mol of steam was reacted with coke in a vessel of 1.00 dm^3 and allowed to reach equilibrium at 800 °C, the partial pressure of steam was found to be 2.67 atm.

(i) Calculate the initial pressure of steam, in atm, introduced into the vessel.

Using pV = nRT

$p = \frac{(0.1 \times 8.31 \times (800 + 273)}{(1 \times 10^{-3})} = 8.9166 \times 10^5$ Pa = 8.80 atm (1 atm = 101325 Pa)

[2]

(ii) Using your answer in **a(i)**, calculate a value for K_p, in atm, at 800 °C.

	C(s)	$H_2O(g)$	CO(g)	$H_2(g)$
Initial P/atm	-	8.80	0	0
Change/atm	-	- 6.13	+6.13	+6.13
Equilibrium P/atm	-	2.67	6.13	6.13

$$K_p = \frac{p_{CO}p_{H_2}}{p_{H_2O}} = \frac{(6.13)^2}{2.67} = 14.1\ atm$$

[2]

(iii) Calculate the minimum mass of carbon required in the vessel.

Since 6.13 atm of steam was reacted,

number of moles of steam = $\frac{pV}{RT} = \frac{(6.13 \times 101325 \times 10^{-3})}{8.31 \times (800+273)} = 0.06966 mol$

Mass of C = 0.06966 × 12.0 = 0.836 g

[2]

(iv) State and explain whether high or low pressure would favour a higher yield of water gas.

To obtain higher yield, the position of equilibrium must shift to the right.
Since the forward reaction produces greater number of moles of gaseous molecules, low pressure favours higher yield.

[2]

(v) The reaction was repeated at a lower temperature and the numerical value of K_p was found to have decreased.

State and explain whether the forward reaction is endothermic or exothermic.

At low temperature, K_p value decreased. This shows that the equilibrium position shifts to the left which produces heat (exothermic).
Hence forward reaction is endothermic.

[2]

(b) **(i)** The relationship between $\Delta G^{\ominus}$ and K_p for the reaction between carbon and steam is

$$\Delta G^{\ominus} = -RT \ln K_p$$

where $\Delta G^{\ominus}$ is the standard Gibbs free energy change in J mol^{-1}, R is the gas constant, T is the temperature in Kelvin at which the equilibrium is established and K_p is the equilibrium constant.

Given that the K_p of the reaction at 298K is 2.97×10^{-18} atm, calculate the $\Delta G^{\ominus}$ of the reaction under standard conditions.

$$\Delta G^{\ominus} = -8.31\ (298) \ln (2.97 \times 10^{-18} \times 101325)$$
$$= +7.14 \times 10^{4}\ \text{J mol}^{-1}$$

[1]

(ii) Comment on the sign of $\Delta G^{\ominus}$ with reference to the position of equilibrium of the reaction under standard condition.

The sign of $\Delta G^{\ominus}$ is positive, the reaction is not spontaneous under standard conditions and position of equilibrium lies to the left.

[2]

[Total: 13]

4. **(a)** Ethers have the general formula, R-O-R' (where R and R' are alkyl or aryl groups).

The most useful method of preparing ethers is by the Williamson ether synthesis, in which an alkoxide ion (RO^{-}) reacts with an alkyl halide (R'X) in an S_N2 mechanism.

A reaction scheme is shown below:

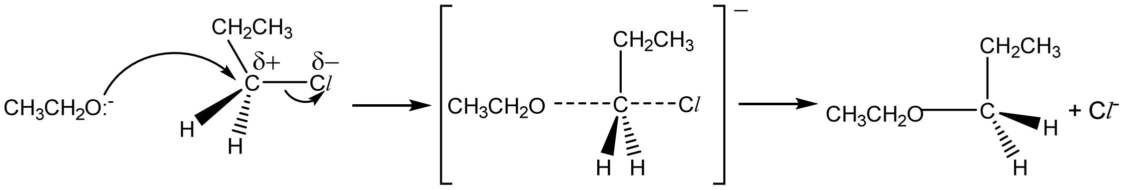
$$ROH \xrightarrow[\text{step } \mathbf{1}]{NaH} RO^{-}Na^{+} \xrightarrow[\text{step } \mathbf{2}]{\text{R'X (alkyl halide)}} ROR'$$

(i) Suggest why step **1** is necessary in the Williamson ether synthesis.

To generate a stronger nucleophile

[1]

(ii) Using 1-chloropropane as the alkyl halide and $CH_3CH_2O^{-}$ as the alkoxide ion, outline the mechanism for **step 2** of the Williamson ether synthesis. Show all charges and relevant lone pairs of electrons and show the movement of electron pairs by using curly arrows.



[3]

(iii) The same reaction in **a(ii)** was repeated using iodopropane instead of chloropropane. Using relevant data from the *Data Booklet*, state and explain the effect on the rate of reaction.

The rate of reaction using iodopropane will be faster.
From the Data Booklet,
Bond Energy (C-C*l*) = 340 kJmol^{-1};
Bond energy (C-I) = 240 kJmol^{-1}.
The C-I bond is weaker, thus less energy is needed to break the bond.

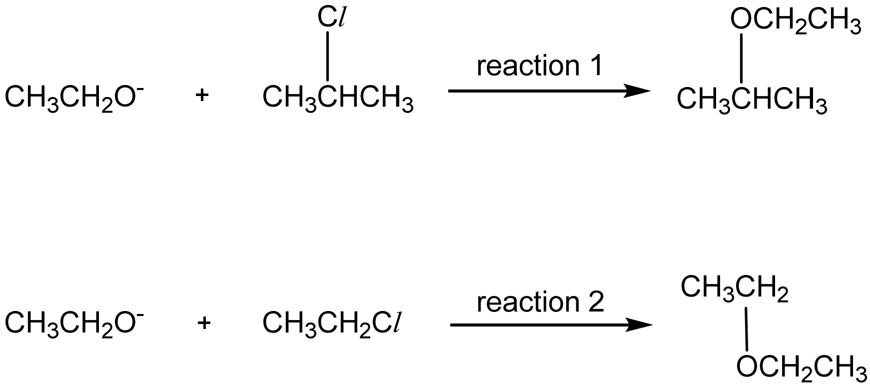
[2]

(iv) Suggest why the product obtained in **a(ii)** shows no optical activity.

There is absence of chiral carbon, thus it is unable to form enantiomers.

[1]

Fig. 4.1 shows two possible reaction sequence to synthesise compound **P**.



$$CH_3CH_2O^- + CH_3CH(Cl)CH_3 \xrightarrow{\text{reaction 1}} CH_3CH(OCH_2CH_3)CH_3$$

$$CH_3CH_2O^- + CH_3CH_2Cl \xrightarrow{\text{reaction 2}} CH_3CH_2OCH_2CH_3$$

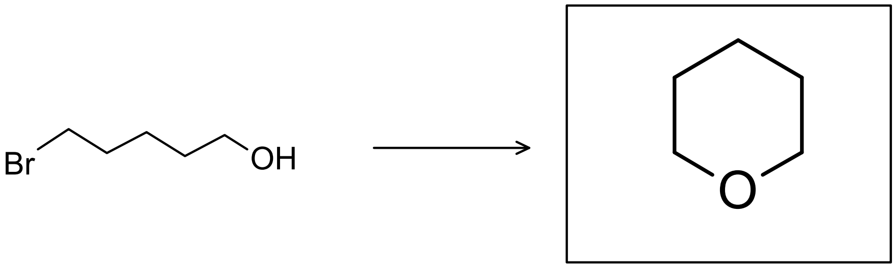
Fig 4.1

(v) State and explain which reaction will give a higher yield.
Reaction 2 will give higher yield.

The Williamson ether synthesis method proceeds via S_N2 mechanism which is favoured by primary halogenoalkane as there is less steric hindrance posed to the attacking nucleophile.

[2]

(vi) Suggest the structure of the product when 5-bromo-pentan-1-ol undergoes the Williamson ether reaction.



5-bromopentan-1-ol

[1]

(b) Halogenated organic compounds can be synthesised from various functional groups.

Chlorofluorocarbons (CFCs) have been widely used in aerosol sprays, refrigerants, but are now known to destroy ozone in the upper atmosphere through a free radical chain reaction.

(i) A student wrongly proposed that a propagation step for the formation of 1–chlorobutane from butane to be:

$$CH_3CH_2CH_2CH_3 + Cl\bullet \rightarrow CH_3CH_2CH_2CH_2Cl + H\bullet$$

Write the correct propagation step. Hence use relevant data from the *Data Booklet*, calculate the enthalpy change of reaction to explain why the propagation step proposed by the student is incorrect.

The correct propagation step is:
$CH_3CH_2CH_2CH_3 + Cl\bullet \rightarrow CH_3CH_2CH_2\overset{\bullet}{C}H_2 + HCl$

BE (C – H) = 410 kJ mol^{-1} BE (H – C*l*) = 431 kJ mol^{-1} ; BE (C –C*l*) = 340 kJ mol^{-1}

ΔH_r for the incorrect propagation step is 410 – 340 = = +70 kJ mol^{-1}
ΔH_r for the correct propagation step is 410 – 431 = –21 kJ mol^{-1}

Since the ΔH_r for the correct propagation step is more exothermic, the reaction is more spontaneous.

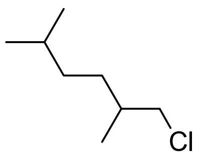
[3]

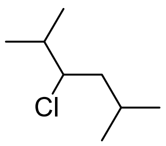
(ii) 2,5-dimethylhexane is reacted with chlorine in the presence of UV light to form 3 monochlorinated alkanes.

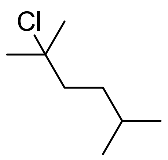
It has been found experimentally that in free radical substitution of alkanes, the primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

type of hydrogen atom	reaction	relative rate
primary	$RCH_3 \rightarrow RCH_2Cl$	1
secondary	$R_2CH_2 \rightarrow R_2CHCl$	7
tertiary	$R_3CH \rightarrow R_3CCl$	21

Draw the structural formula of the 3 possible monochlorinated products of 2,5-dimethylhexane and using the information in the table, suggest the relative ratios in which they are formed.





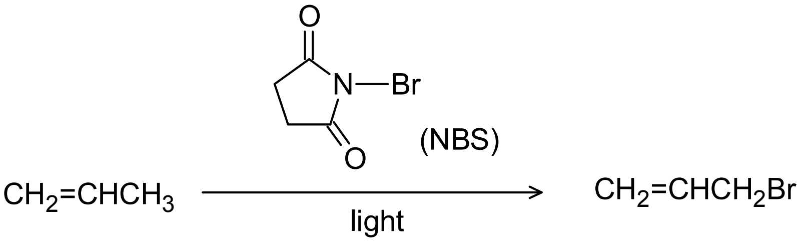


Ratio (12 × 1) = 12 (4×7) = 28 (2×21) = 42
6 14 21

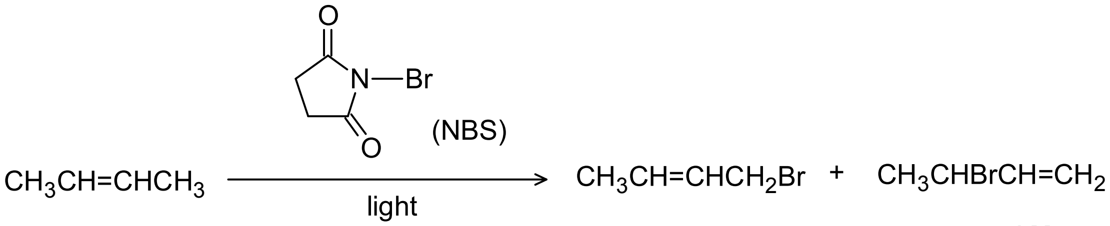
[3]

(c) Another method of preparing alkyl halides from alkenes is by the reaction with N-bromosuccinimide (NBS) in the presence of light to give products which are substituted at the allylic position i.e. the position *next* to the double bond. NBS is used as a source of bromine.

The process is similar to the free radical substitution mechanism of alkanes.



(i) However, a mixture of 2 products (**W** and **X**) is formed when but-2-ene undergoes this reaction.



compound **W** compound **X**

Suggest a reason for the formation of compound **X**.

Another resonance structure can be obtained due to the delocalisation of the electron.

secondary radical is more stable than primary radical as it has more electron-donating group or

$CH_3CH=CH\dot{C}H_2 \leftrightarrow CH_3\dot{C}H\text{-}CH=CH_2$

[2]

(ii) State the type of isomerism shown by compound **W** and compound **X.**

They are constitutional / positional isomers.

[1]

[Total: 19]

5 Infra-red(IR) absorptions can be used to identify functional groups in organic compounds. For example, ethyl ethanoate shows absorption at 100 – 1300 cm^{-1} and 1680 – 1750 cm^{-1}.

A student used infra-red spectrometer to obtain an infra-red(IR) spectrum of benzyl alcohol $C_6H_5CH_2OH$ as shown in Fig. 5.1.

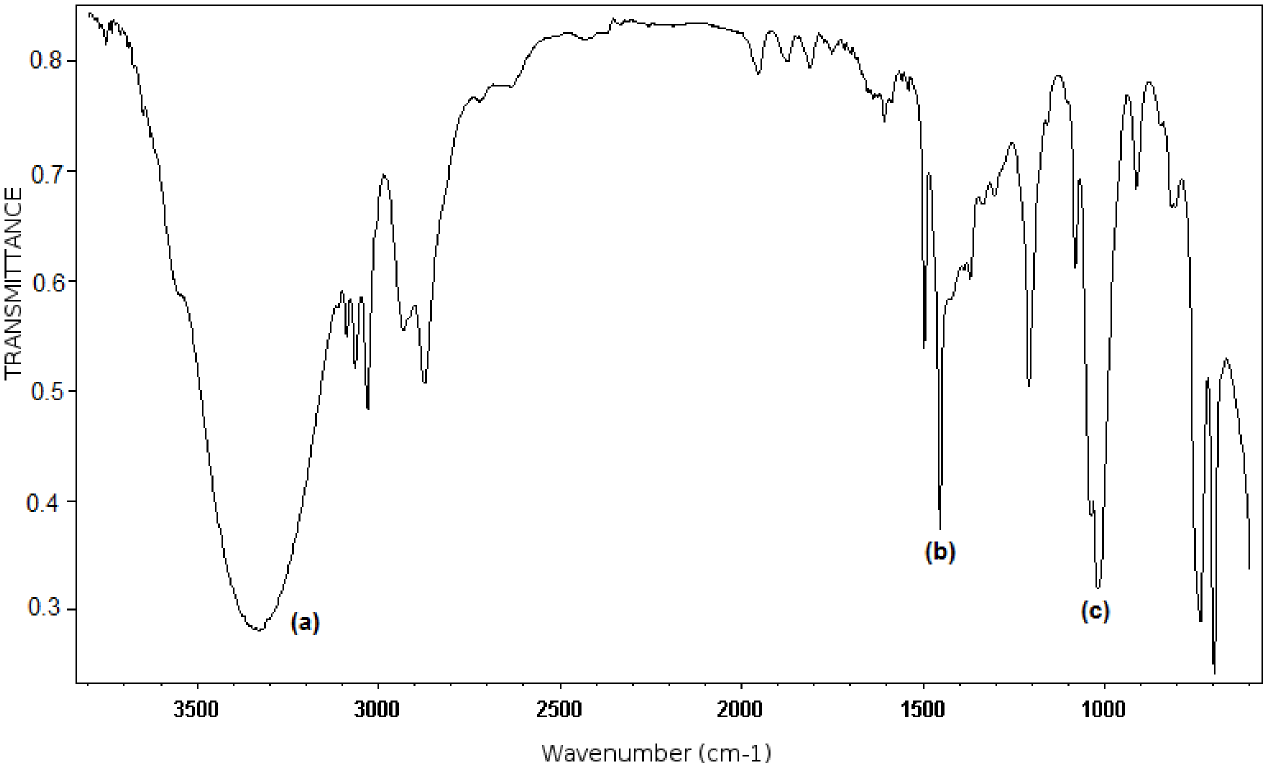


Fig. 5.1

(a) **Use the table of characteristic infra-red absorption frequencies in the *Data Booklet* to** identify the infra-red absorption range shown by benzyl alcohol.

IR region	Wavenumbers/ cm^{-1}	Functional groups present
(a)	3200 – 3600	(Primary) alcohol
(b)	1475 – 1625	Benzene
(c)	970 – 1260	(Primary) alcohol

[3]

(b) The student carried out reflux of benzyl alcohol with acidified potassium dichromate and the product **A** obtained was analysed using spectrometer. Fig. 5.2 shows the IR spectrum obtained.

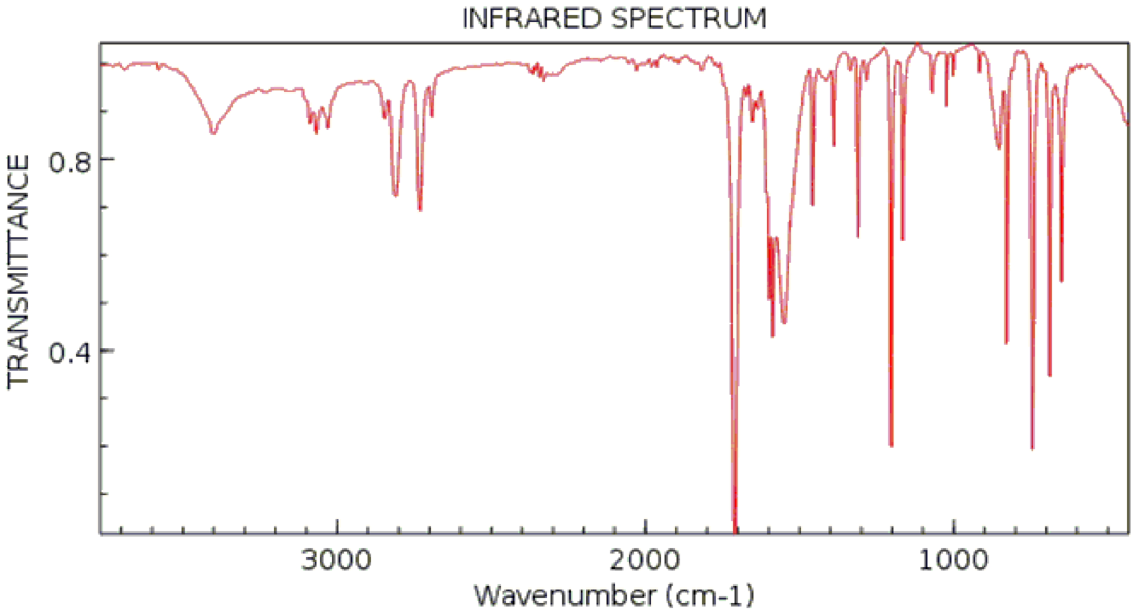
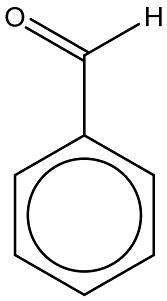


Fig. 5.2

By comparing the two infra-red spectra, suggest two differences from the infra-red spectra and draw the structure of the product **A** obtained.

Product **A:**



1. Peak (a) from Fig 5.1 is missing compared to Fig 5.2., indicating loss of –OH group
2. Presence of C=O at 1670–1740 cm^{-1} in Fig 5.2 compared to Fig 5.1, could be due to aldehyde group

Note: RCOOH is not acceptable as there is no O–H absorption from 2500-3000 cm^{-1} in Fig 5.2

[3]

(c) Suggest a simple chemical test that could be used to confirm benzyl alcohol $C_6H_5CH_2OH$ has been completely converted into product **A** in **(b)**.

Test : Add anhydrous $SOCl_2$, PCl_5 or Na(s)

Observations: Absence of HCl white fumes confirmed that there is no alcohol present or absence of effervescence of H_2 gas.

[2]

(d) A student wishes to determine the concentration of product **A** obtained. The student prepares 5 solutions of known concentrations, 0.0100, 0.0200, 0.0400, 0.0800 and 0.100 mol dm^{-3} of product **A**. 10 μL of each solution with the sample was used and a high performance liquid chromatogram was obtained. The peak areas of the chromatographs are given in the table below and a graph of concentration against peak area was obtained in Fig.5.3.

Solution concentration / mol dm^{-3}	0.0100	0.0200	0.0400	0.0800	0.100	sample
Peak area / cm^2	0.50	0.83	1.39	2.63	3.18	2.53

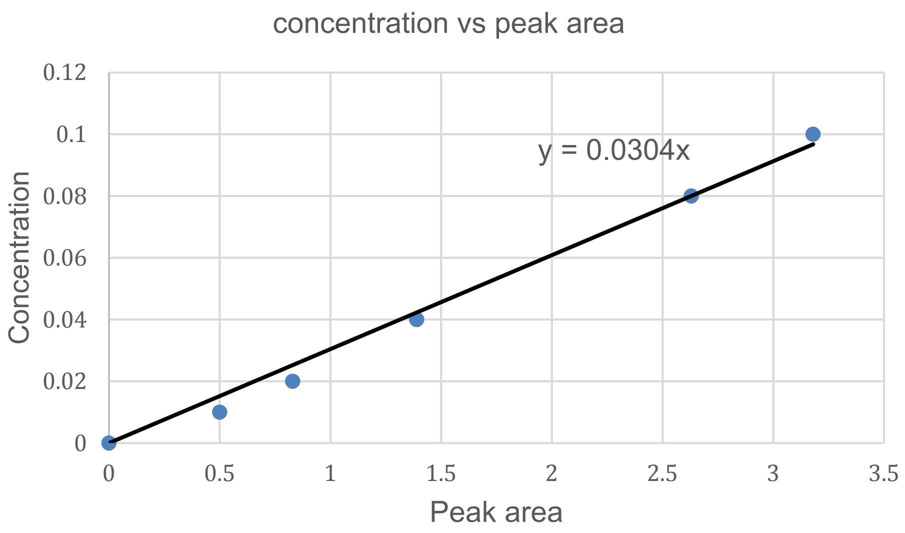


Fig. 5.3

(i) Using the peak area of the sample from the table and information from the graph, determine the concentration of product **A** in the sample.

Concentration of product **A** = 0.0304(2.53) = 0.0769 mol dm^{-3}

[1]

(ii) Suggest what the student can do to ensure high yield of product **A** from the reaction of benzyl alcohol with acidified potassium dichromate in **(b)**. Use Le Chatelier's Principle to explain your suggestion.

$C_6H_5CH_2OH + [O] \rightleftharpoons C_6H_5CHO$ (product **A**) + H_2O

Carry out immediate distillation of product **A**.

As product **A** is being removed, position of equilibrium shifts right to increase the concentration of product **A**, hence yield increases.

[2]

(e) Fig. 5.4 shows a Ritter reaction.

The Ritter reaction transforms a nitrile to amide using a strong acid and water as follows.

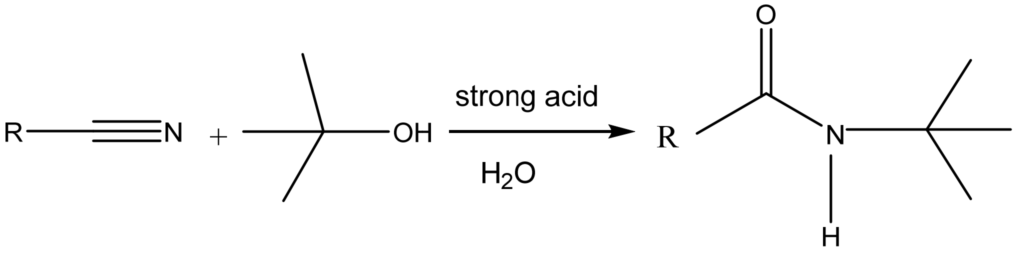
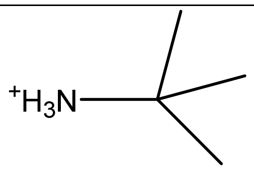


Fig. 5.4

(i) Side products will be formed from the Ritter reaction if heating was carried out.

Suggest the type of reaction which occurs and draw the structures of two side products formed.

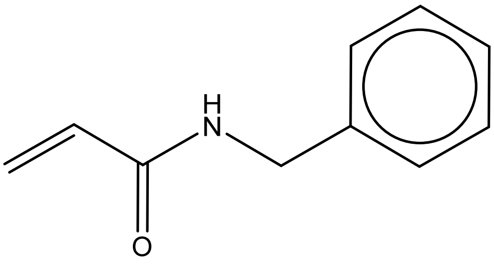
Type of reaction: Hydrolysis



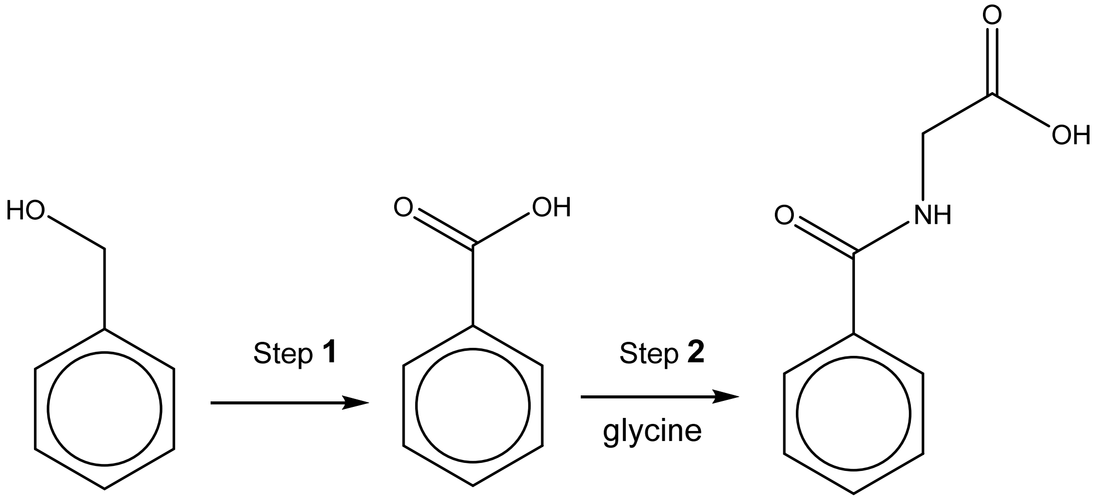
RCOOH

[3]

(ii) Benzyl alcohol, $C_6H_5CH_2OH$ undergoes Ritter reaction with CH_2CHCN as shown in Fig. 5.4. Draw the structure of the amide formed.



(f) Fig. 5.5 shows a possible process in the human body where benzyl alcohol is oxidised to benzoic acid, conjugated with amino acid, glycine in the liver, and excreted as benzoylaminoethanoic acid, as shown.



benzyl alcohol benzoic acid benzoylaminoethanoic acid

Fig 5.5

(i) Write an equation for the oxidation of benzyl alcohol to form benzoic acid. Use [O] to represent the formula of the oxidising agent.

$C_6H_5CH_2OH + 2[O] \rightarrow C_6H_5COOH + H_2O$

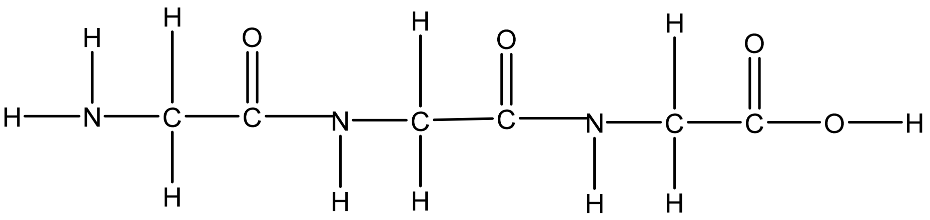
[1]

(ii) What type of reaction takes place in step **2**?

Condensation/Nucleophilic substitution

[1]

(iii) Draw the displayed formula of a tripeptide consisting of glycine only.



[1]

(iv) Benzoylaminoethanoic acid can be reduced by $LiAlH_4$ in dry ether at room temperature and hydrogen gas with nickel catalyst under high heat and pressure. The organic products formed in the two reactions are different. Compound **B** has a molecular mass of 151 and compound **C** has a molecular mass of 185.

Deduce the structures of **B** and **C**.

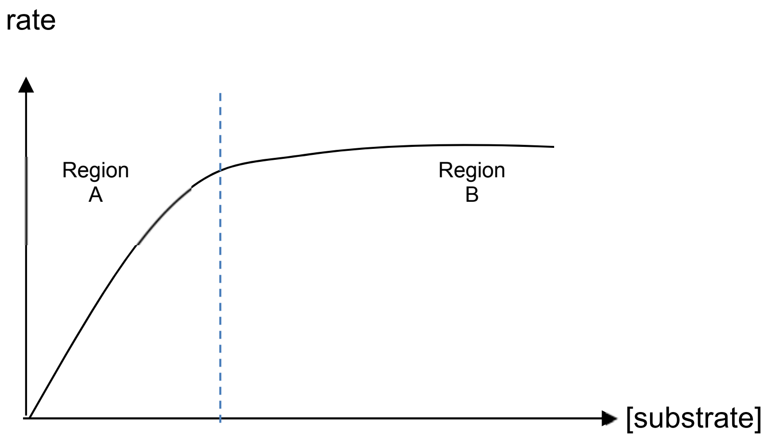
compound **B**

compound **C**

[2]

The synthesis of glycine in the liver is catalysed specifically by glycine synthase enzyme.

(v) Describe,with the aid of a sketch how the rate of synthesis of glycine is affected by the concentration of the substrate.



At low [substrate], the **active sites are not filled** and rate = k [substrate]; i.e. rate is proportional to [substrate] and the reaction is first order wrt [substrate] (region A).

At high [substrate], increasing its concentration has no effect at all on the rate of reaction; as **all the active sites are occupied**. i.e. reaction is zero order with respect to [substrate] (region B).

[3]

[Total: 23]

CANDIDATE'S NAME: ________________________________ CTG: ____________

YISHUN JUNIOR COLLEGE

2018 JC2 PRELIMINARY EXAMINATION

CHEMISTRY
HIGHER 2
Paper 3 Free Response

9729/03

MONDAY 10 SEPTEMBER 2018
1400hrs − 1600hrs
2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CTG on all the work that you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.

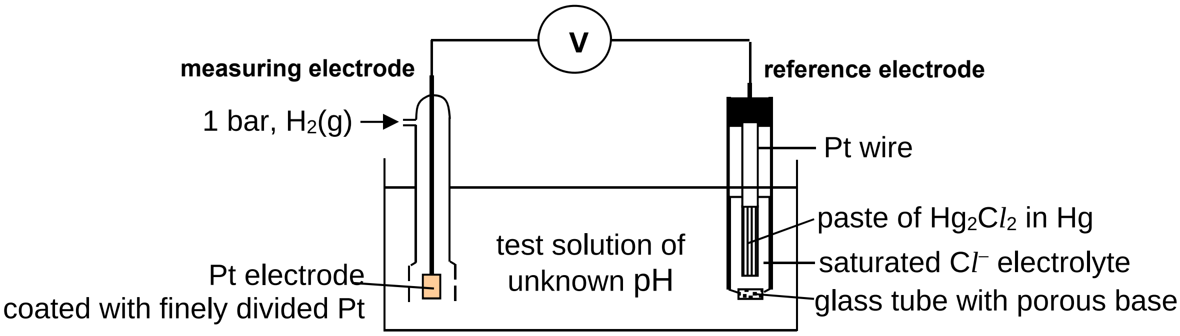
At the end of the examination, fasten all your work securely together with the cover page on top.
The number of marks is given in brackets [ ] at the end of each question or part question.

This question paper consists of **18** printed pages.

Section A (60 marks)

Answer **all** the questions in this section on the writing papers provided.

1 **(a)** A student designed an ion-specific probe to determine the concentration of H^+ ions in solution. He connected a hydrogen electrode to a calomel reference electrode, which comprises a paste of mercury(I) chloride, Hg_2Cl_2, and mercury in a saturated chloride electrolyte. The reference electrode is inserted into a glass tube with a porous base.



The hydrogen electrode, which is sensitive to H^+ ion concentration, is the measuring electrode. Therefore, this galvanic cell acts as a pH meter.

When both electrodes are in contact with the test solution, an electric current flows through the wire and mercury(I) chloride reacts to form liquid mercury and chloride ion at the reference electrode.

Under standard conditions, the E^θ_{cell} of the pH meter is +0.28 V.

(i) Suggest the use of the glass tube with a porous base in this experimental set-up. [1]

(ii) Identify the half-cell containing the anode. [1]

(iii) Construct the half equation for the reaction occurring at the reference electrode. [1]

(iv) Hence write an overall balanced equation for the pH meter. [1]

(v) Determine the ΔG^θ of this reaction and state the units. [2]

(vi) Explain why the cell potential would increase when the pH meter is placed in a solution of a higher pH. [1]

(b) The student used his probe in **(a)** to analyse a sample of mandelic acid, a bitter almond extract that is used as an antibacterial treatment.

The student obtained a cell potential reading, E_{cell}, of +0.41 V.

The *Nernst equation* can be used to calculate the concentration of H^+ ions detected by the probe:

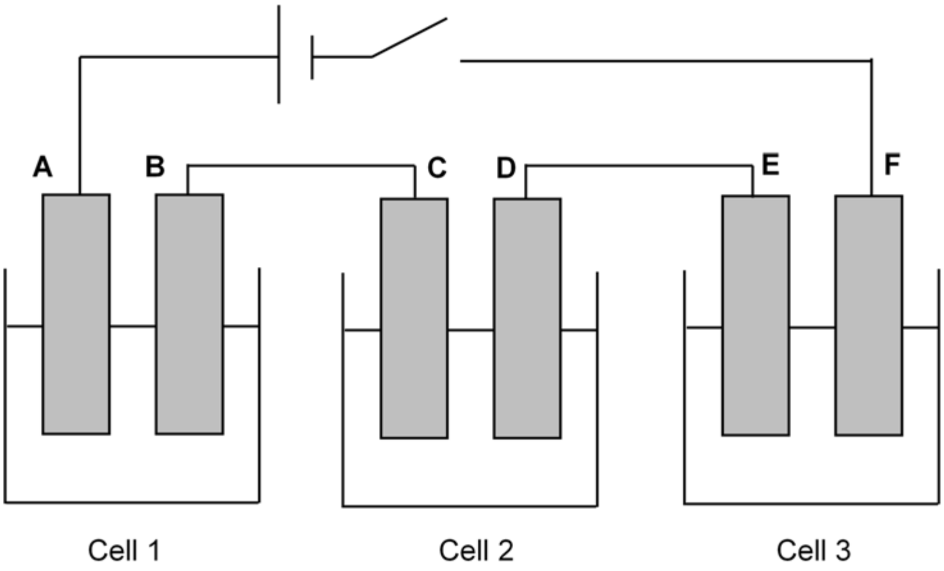
$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0592}{n}\log_{10}\left(\frac{[H^+]^2[Cl^-]^2}{P_{H_2}}\right)$$

where n is the number of moles of electrons transferred in the overall reaction,
$[H^+]$ is the concentration of hydrogen ions detected,
$[Cl^-]$ is the concentration of Cl^- ions,
P_{H_2} is the pressure, in bar, of hydrogen gas passed into the probe.

Assuming that the concentration of Cl^- is constant at 1 mol dm^{-3}, use the *Nernst equation* to calculate the concentration of H^+ ions in the solution and the pH of the solution.

[2]

(c) A current is passed through three cells connected in series as shown below.



Cell 1 contains lead electrodes, **A**, **B** and electrolyte $Pb(NO_3)_2(aq)$.

Cell 2 contains platinum electrodes, **C**, **D** and electrolyte NaBr(aq).

Cell 3 contains platinum electrodes, **E**, **F** and electrolyte containing $MnCl_x(aq)$.

(i) On closing the switch, write equations, including state symbols, for the reactions occurring at electrodes **A** and **D**.

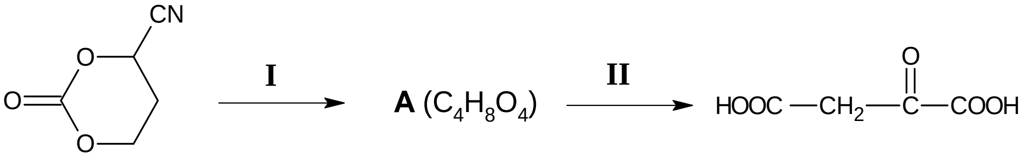
[2]

(ii) A current of 0.36 A was passed through the circuit for 30 minutes. 0.183 g of manganese was deposited in Cell 3. Determine the value of x in $MnCl_x$.

[3]

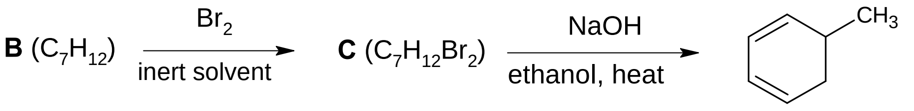
(d) Identify the structures of compounds **A**, **B**, **C** and **D** and suggest the reagents and conditions for each numbered steps **I**, **II** and **III** where possible.

(i)



[3]

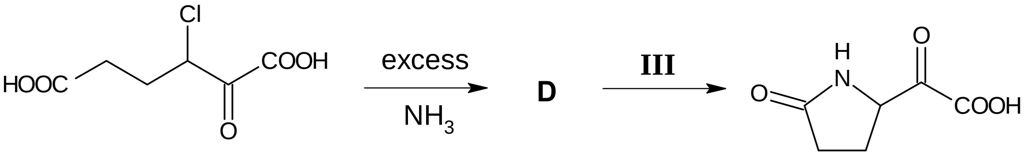
(ii)



only 1 product formed

[2]

(iii)



[2]

[Total: 21]

2 **(a)** Ethiopia is severely impacted by inadequate safe drinking water, where halogen contaminants such as chloride in drinking water, are the root cause of many common ailments such as low immunity and hypertension.

The Mohr's method is used to determine the chloride ion concentration of water samples from various sources such as seawater and stream.

A researcher retrieved a water sample from a stream and carried out Mohr's method, where the chloride ions present in the water sample is titrated against aqueous silver nitrate solution. As the aqueous silver nitrate is slowly added, a sparingly soluble white precipitate is formed. The indicator used in the titration is aqueous potassium chromate(VI), K_2CrO_4. The end-point of the titration is reached when any excess silver nitrate added results in the formation of a red-brown precipitate of Ag_2CrO_4.

The following are relevant K_{sp} values at 298 K:

silver salt	solubility product, K_{sp}
$AgCl$	2.00×10^{-10}
Ag_2CrO_4	1.10×10^{-12}

(i) Determine the concentration of Cl^-(aq) ions at the end-point of the titration.

[1]

(ii) Explain, with the aid of relevant equations, what would be observed if excess aqueous ammonia is added to the reaction mixture containing the white precipitate.

[2]

(iii) Determine the minimum concentration of CrO_4^{2-}(aq) ions in the titration mixture that is required to precipitate Ag_2CrO_4 immediately after the end-point.

[2]

(b) Oxygen gas, O_2, reacts with various period 3 elements to produce compounds for numerous uses. For example, aluminium oxide, Al_2O_3, is often used as a refractory material.

Element **X** forms a white oxide that is soluble in cold water. Its chloride dissolves in water to give a neutral solution.

Element **Y** forms an oxide which has the shape of trigonal planar around the central atom.

1 mole of the oxide of element **X** is added to an aqueous solution containing the same amount of the oxide of element **Y** to form a neutral solution.

Given that **X** and **Y** are period 3 elements, identify element **X** and the oxide of element **Y**. Give an equation to show the formation of the neutral solution.

[2]

(c) Reduction of ozone, O_3, produces the ozonide anion, O_3^-. Derivatives of this anion are explosive and must be stored at very low temperatures.

Potassium hydroxide reacts with ozone to produce the corresponding metal ozonide, oxygen gas and water.

(i) Suggest an equation for the reaction between potassium hydroxide and ozone. [1]

(ii) Draw a dot-and-cross diagram for ozone. Using VSEPR theory, explain the shape and bond angle of ozone. [3]

(iii) All the O–O bonds in ozone are found to have identical bond lengths.

Suggest an explanation for this observation. [1]

(d) Hydrogen reacts with nitrogen monoxide to give nitrogen and steam as shown.

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature and with the same concentration of NO for each experiment. The following results were obtained.

experiment	initial $[H_2]$ / mol dm^{-3}	initial rate of production of N_2 / mol dm^{-3} s^{-1}
1	1×10^{-3}	3×10^{-3}
2	2×10^{-3}	6×10^{-3}
3	3×10^{-3}	9×10^{-3}

(i) Using the above data, deduce the order of reaction with respect to $[H_2]$. Hence sketch a graph of initial rate against $[H_2]$.

[2]

(ii) The concentration of NO was halved and a new series of experiments were carried out at the same temperature. When a similar graph was plotted, the magnitude of the gradient decreases by 4 times compared to that obtained from the graph in **(d)(i)**.

Deduce the order of reaction with respect to [NO].

[1]

(iii) Hence write the rate equation for the reaction between H_2 and NO. Include the units for the rate constant.

[1]

(iv) The following mechanism was proposed for the reaction of hydrogen with nitrogen monoxide.

step 1: $2NO \rightleftharpoons N_2O_2$
step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

Identify the slow step which is consistent with the rate equation in **(d)(iii)**.

[1]

(v) Assuming that the reaction in **(d)** is exothermic, sketch a labelled energy profile diagram for the proposed mechanism in **(d)(iv)**. Indicate clearly the activation energy for each step.

[3]

[Total: 20]

3 **(a)** The protein, somatostatin has been used mainly for its anti-secretory effects in gastrointestinal disorders. Recently, its effects in the treatment of cancer have also been reported.

(i) Complete hydrolysis of a protein produces individual amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

State the reagents and conditions for the hydrolysis of a somatostatin molecule.

[1]

(ii) A somatostatin polypeptide, containing **fourteen** amino acids, produced the following fragments on hydrolysis.

Ser- Cys
Phe – Trp – Lys
Cys – Lys – Asn
Ala – Gly – Cys
Asn – Phe – Phe
Lys – Thr – Phe
Phe – Thr – Ser

Using the same 3-letter abbreviations as above, deduce the amino acid sequence of the polypeptide.

[2]

(iii) The complete hydrolysis of somatostatin is found to occur spontaneously at **high temperature**.

Suggest an explanation for this observation, taking into account the thermodynamic considerations of the reaction.

[2]

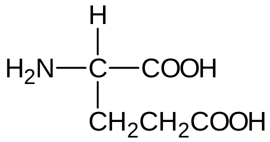
(b) Organophosphates, like carbon monoxide, are toxic to humans. When ingested, organophosphates inhibit the enzyme acetylcholinesterase, resulting in neuro poisoning. Carbon monoxide, on the other hand, inhibits the protein haemoglobin.

One possible treatment of neuro poisoning includes the use of a solution containing carbamates, with the general formula $ROCONR_2$. The carbamate administered can stabilise the enzyme by forming an enzyme–carbamate complex, which stops the organophosphates from binding to the enzyme's active site.

Explain, in terms of ligand strength and the type of reaction occurring, why carbamate can be used to treat neuro poisoning.

[2]

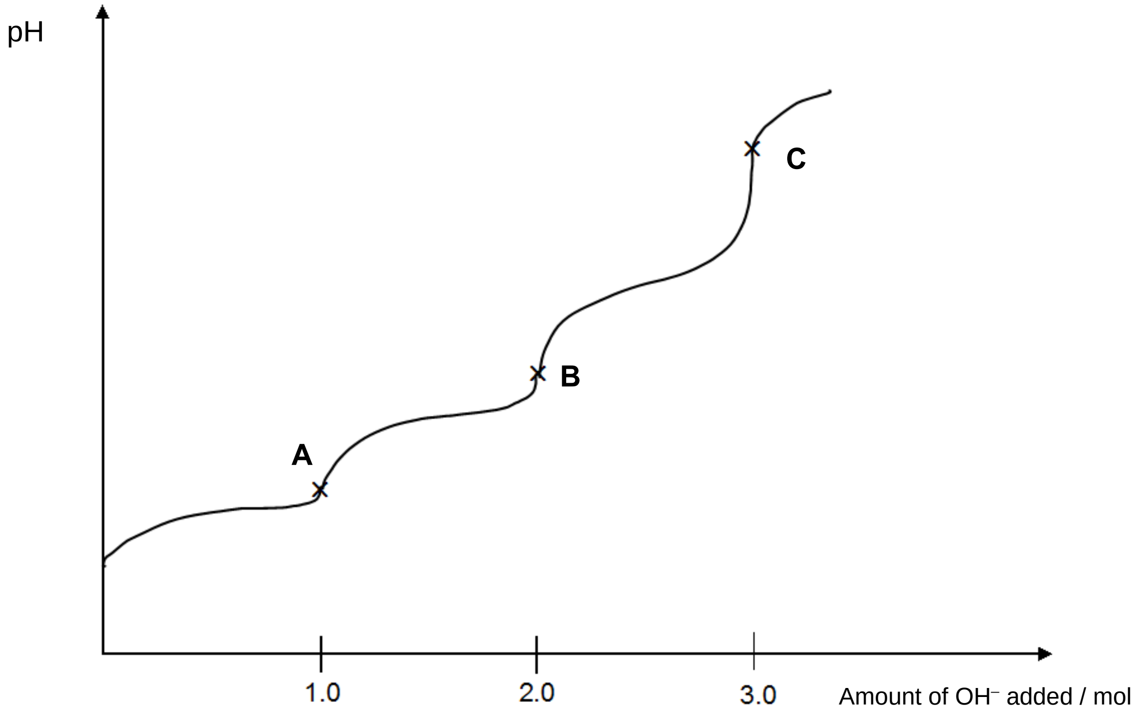
(c) Glutamic acid is used as a flavour enhancer and is responsible for umami, one of the five basic tastes of human sense of taste. It has the structure of



$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH_2COOH}{C}}-COOH$$

The pK_a values and titration curve of 1 mole of the protonated form of glutamic acid are as shown.

pK_a1 = 2.10
pK_a2 = 4.07
pK_a3 = 9.47



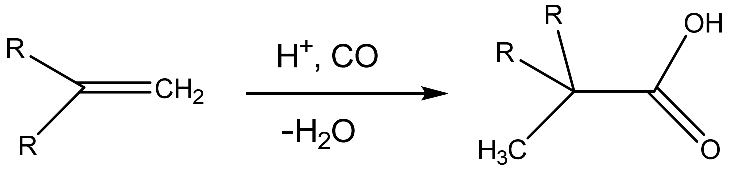
(i) Suggest the structures of **A**, **B** and **C**.

[2]

(ii) State the pH of the resultant solution when 1.5 moles of OH^- is added to the protonated glutamic acid.

[1]

(d) In the Koch reaction, carboxylic acids are formed from the acid catalysed reaction between alkenes and carbon monoxide.



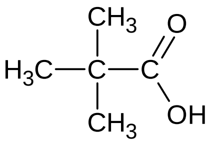
R = alkyl group

(i) Compound **A** has molecular formula $C_9H_{10}O$. It undergoes the Koch reaction to produce compound **B.**
Compound **A** also decolourises aqueous bromine to produce a white precipitate. When reacted with sodium metal, it produces a gas that extinguishes a lighted splint. It also reacts with acidified potassium manganate (VII), $KMnO_4$, to produce compound **C,** $C_8H_8O_2$. When treated with alkaline iodine, compound **C** produces a yellow precipitate. No precipitate was observed when Tollens' reagent was added to compound **C**.

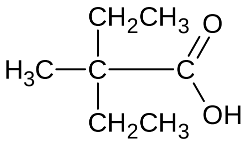
Suggest the structures of compounds **A**, **B** and **C**. Explain all the reactions involved.

[6]

(ii) Carboxylic acids, **D** and **E** could be formed using the Koch reaction.


$H_3C-C(CH_3)_2-COOH$

carboxylic acid **D**


$H_3C-C(CH_2CH_3)_2-COOH$

carboxylic acid **E**

Carboxylic acid **D** has a lower pKa value than carboxylic acid **E**. Explain the difference in their pKa values.

[3]

[Total: 19]

Section B (20 marks)

Answer **one** question from this section on the writing papers provided.

4 Organic molecules such as ethyne, C_2H_2, and ethylenediamine can function as ligands to transition metal ions.

ethyne

ethylenediamine

(a) A blue complex salt **A** has the molecular formula $NiN_5H_{17}OCl_2$ (M_r = 232.7).

1.00 g of **A** reacts completely with 25.00 cm^3 of 0.344 mol dm^{-3} silver nitrate solution.

When excess ethylenediamine was added to the blue solid **A**, a violet solution containing complex **B** was produced. **A** and **B** have the same coordination number.

(i) Calculate the amount of free chloride ions per mole of **A**.

[1]

(ii) State the full electronic configuration of the nickel ion. Draw fully-labelled diagrams of the orbitals which experience the greatest repulsion between the *d* electrons and the lone pair of electrons on the ligands.

[2]

(iii) With reference to your answer in **(a)(i)** and **(a)(ii)**, draw a three dimensional diagram to illustrate the shape of the complex ion in **A**.

[1]

(iv) Suggest a possible formula of the complex ion in **B**.

[1]

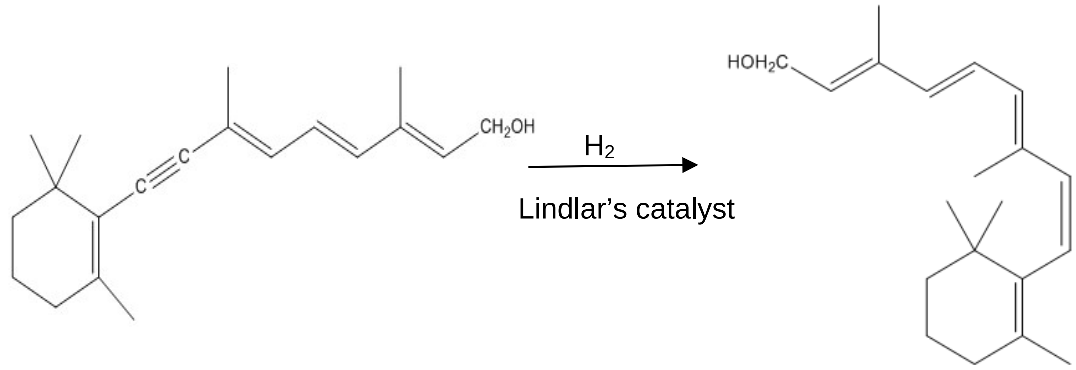
(b) State the hybridisation of the carbon atoms present in ethyne. Hence, in terms of orbital overlap, justify why ethyne can function as a ligand.

ethyne

[3]

(c) Alkynes are reduced to alkenes, using the Lindlar's catalyst, which are finely divided palladium metal precipitated onto a calcium carbonate support.

An example is in the synthesis of 7-cis-retinol.

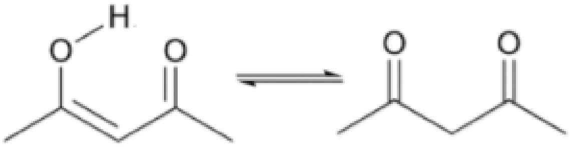


7-cis-retinol

(i) State the number of cis-trans isomers present in a molecule of 7-cis-retinol. [1]

(ii) Describe the mode of action by the Lindlar's catalyst. [3]

(d) Alkyne can also undergo hydration to form an enol which rapidly rearranges itself into a ketone. Such a rearrangement is known as ketone tautomerisation. An example is that of 2,4-pentanedione.



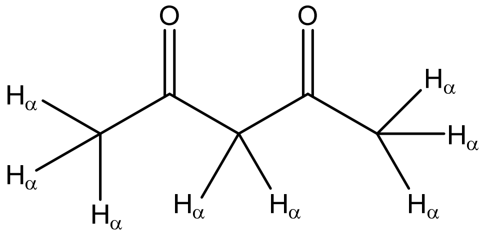
$K_{eq} = 0.315$

enol

ketone

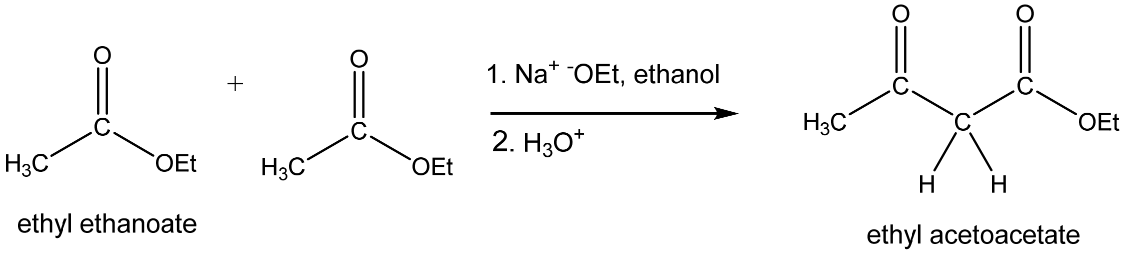
Using the data given, deduce if the tautomerisation reaction is spontaneous. [2]

(e) Carbonyl compounds, like 2,4-pentanedione contains acidic α hydrogen atoms.



Esters, like ketones and aldehydes, can also contain acidic α hydrogen atoms. When deprotonated by a suitable base, a carbonyl condensation reaction can occur.

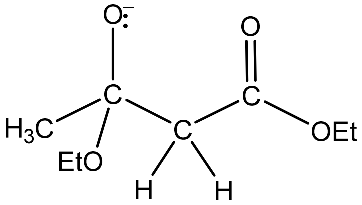
An example is the formation of ethyl acetoacetate from ethyl ethanoate.
(**Et : –CH_2CH_3**)



Part of the mechanism is described as follows:

Step 1:
A base, ethoxide ion ($^{-}$OEt), abstracts an acidic alpha hydrogen atom from the ethyl ethanoate molecule, yielding a RCH_2^- nucleophile.

Step 2:
The resultant RCH_2^- nucleophile adds to a second ester molecule, giving a tetrahedral alkoxide intermediate:



Step 3:
The tetrahedral intermediate expels the ethoxide ion to yield the new carbonyl compound, ethyl acetoacetate.

(i) Suggest the role of ethanol.

[1]

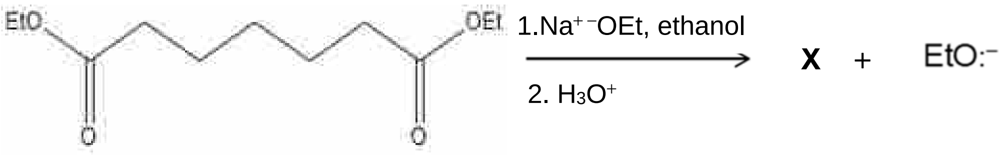
(ii) Suggest, with a reason, why the alpha hydrogen of the ester, ethyl ethanoate in Step 1 is acidic.

[1]

(iii) Using the information given, suggest the mechanism for the reaction. Show relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

(iv) Compound **X** can be synthesised from diethyl heptanedioate via the carbonyl condensation reaction.



diethyl heptanedioate

Suggest the structure of compound **X**.

[1]

[Total: 20]

5 **(a)** The following shows a series of reactions involving titanium compounds.

$$\mathrm{TiC}l_4 \xrightarrow[\mathbf{I}]{\text{conc HC}l} \underset{\text{colourless solution}}{[\mathrm{TiC}l_6]^{2-}} \xrightarrow[\mathbf{II}]{} \underset{\text{violet solution}}{[\mathrm{Ti(H_2O)_6}]^{3+}} \xrightarrow[\mathbf{III}]{} \underset{\text{orange solution}}{[\mathrm{TiC}l_6]^{3-}}$$

(i) Suggest the type of reaction for **II** and **III**.

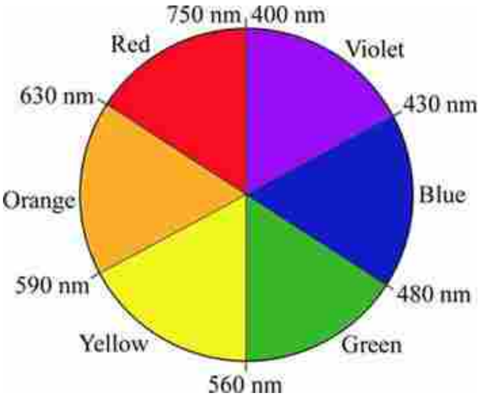
[2]

(ii) Explain why a solution of $[\mathrm{TiC}l_6]^{2-}$ is colourless while that of $[\mathrm{TiC}l_6]^{3-}$ is orange.

[2]

(iii) White light contains all the colours in the visible spectrum, and each of these colours is associated with a certain wavelength λ. The figure below shows a colour wheel with approximate wavelength values in nanometres for different colour light.

The formula relating energy gap between d orbitals, ΔE and wavelength λ is given as $\Delta E = \frac{hc}{\lambda}$, where *h* is the Planck's constant and c is the speed of light. As wavelength decreases, the energy gap increases.



Using the information given and those in **(a)**, deduce whether $[\mathrm{Ti(H_2O)_6}]^{3+}$ or $[\mathrm{TiC}l_6]^{3-}$ has a bigger energy gap between the d orbitals.

[1]

(iv) Explain why titanium forms complexes with different oxidation states while calcium is unable to do so.

[1]

(b) Organotitanium compounds such as CH_3TiCl_3 can function as nucleophiles. The methyl group, CH_3^-, acts as a nucleophile.

The reduction reaction of an ester, methyl propanoate, $C_2H_5COOCH_3$ with CH_3TiCl_3, followed by acidification produces a tertiary alcohol, $C_2H_5C(CH_3)_2OH$, as shown.

$$C_2H_5COOCH_3 + 2CH_3TiCl_3 \rightarrow C_2H_5C(CH_3)_2OH$$

(i) The mechanism is proposed as follows.

Step 1:
The nucleophile CH_3^- from CH_3TiCl_3 adds to the carbonyl carbon of the ester to form a tetrahedral alkoxide intermediate.

Step 2:
A ketone and a methoxide ion, CH_3O^- are produced from the alkoxide intermediate.

Step 3:
Another CH_3^- from CH_3TiCl_3 adds to the carbonyl carbon of the ketone to form another tetrahedral alkoxide intermediate.

Step 4:
Protonation of the alkoxide intermediate forms the product $C_2H_5C(CH_3)_2OH$.

Using the information given, suggest the mechanism for the reaction. Show relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[4]

(ii) Amides can also be reduced by organotitanium compounds to form the corresponding alcohol and amine. However, this reaction occurs at a slower rate as compared to that of an ester.

Suggest an explanation for this observation.

[1]

(iii) Suggest a simple chemical test to distinguish between $C_2H_5COOCH_3$ and $C_2H_5C(CH_3)_2OH$.

[2]

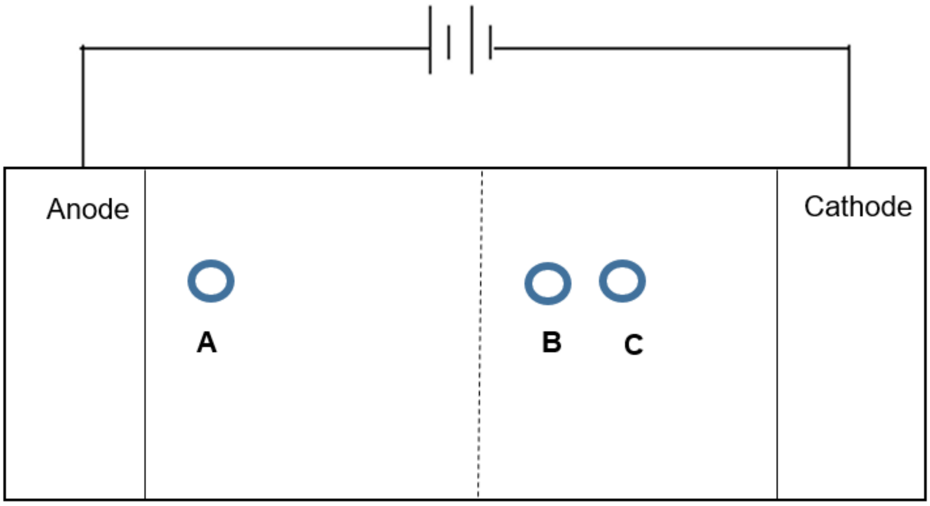
(c) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

amino acid	formula of side chain (R' in R'CH(NH_2)CO_2H)	isoelectric point
valine	-CH(CH_3)$_2$	6.00
glutamic acid	-CH_2CH_2COOH	3.15
asparagine	-CH_2CONH_2	5.41

At an intermediate pH, called the isoelectric point (*p*I), the amino acids will be *zwitterionic* and have *no* net charge.

An electrophoresis experiment is run on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.

The rate at which the amino acids move through the gel is inversely proportional to its mass.

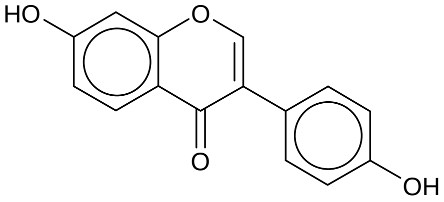


Original position of sample

Identify the structures **A**, **B** and **C**. Hence, explain the position of **B** relative to **C**.

[2]

(d) Soy beans, and especially the dofu made from them, are a good source of dietary isoflavenoids, which are claimed to help in the prevention of some cancers. The major isoflavenoid in soy is diadzein.



diazein

When diadzein is treated with H_2 and Ni, compound **D**, $C_{15}H_{14}O_4$, is formed. One mole of compound **D** reacts with three moles of sodium metal. **D** also dissolves in NaOH(aq). **D** reacts with acidified $K_2Cr_2O_7$ to give compound **E**, $C_{15}H_{12}O_4$, which gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Suggest a structural formula for **D** and for **E**, identifying any chiral carbon atoms. Explain the reactions which occur.

[5]

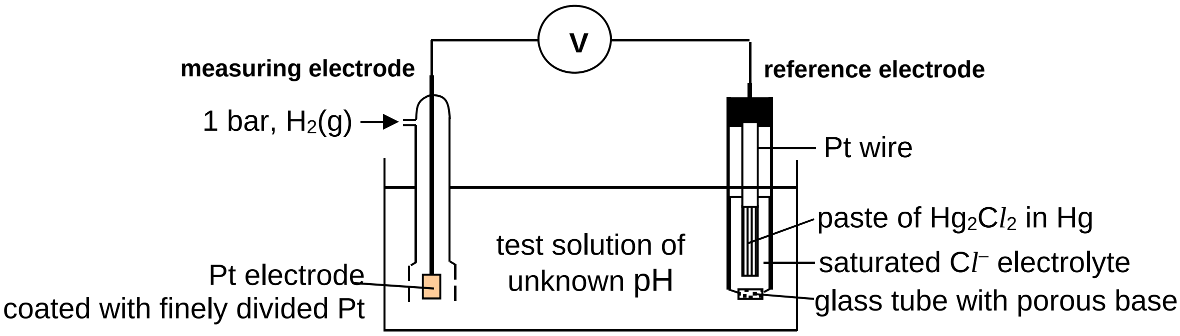
[Total: 20]

END OF PAPER

Section A (60 marks)

Answer **all** the questions in this section on the writing papers provided.

1 **(a)** A student designed an ion-specific probe to determine the concentration of H^+ ions in solution. He connected a hydrogen electrode to a calomel reference electrode, which comprises a paste of mercury(I) chloride, Hg_2Cl_2, and mercury in a saturated chloride electrolyte. The reference electrode is inserted into a glass tube with a porous base.



The hydrogen electrode, which is sensitive to H^+ ion concentration, is the measuring electrode. Therefore, this galvanic cell acts as a pH meter.

When both electrodes are in contact with the test solution, an electric current flows through the wire and mercury(I) chloride reacts to form liquid mercury and chloride ion at the reference electrode.

Under standard conditions, the $E^\ominus_{cell}$ of the pH meter is +0.28 V.

(i) Suggest the use of the glass tube with a porous base in this experimental set-up. [1]

To act as a salt bridge.

(ii) Identify the half-cell containing the anode. [1]

The half-cell with the hydrogen electrode contains the anode.

In the half-cell containing the calomel reference electrode, Hg^+ undergoes reduction to form Hg. Hence it contains the cathode.

(iii) Construct the half equation for the reaction occurring at the reference electrode. [1]

$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$

(iv) Hence write an overall balanced equation for the pH meter. [1]

$Hg_2Cl_2(s) + H_2(g) \rightarrow 2Hg(l) + 2Cl^-(aq) + 2H^+(aq)$

(v) Determine the ΔG^{θ} of this reaction and state the units.

[2]

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$

$\Delta G = -(2)(96500)(+0.28) = -54000 \text{ J mol}^{-1}$ or $-54.0 \text{ kJ mol}^{-1}$

(vi) Explain why the cell potential would increase when the pH meter is placed in a solution of a higher pH.

[1]

At a higher pH, there is lower $[H^+]$,

- equilibrium position in $2H^+(aq) + 2e \rightleftharpoons H_2(g)$ shifts to the left (OR eqm shifts to favour oxidation of H_2) and thus
- $E(H^+/H_2)$ becomes (more) negative.

Thus E_{cell} becomes more positive.

(b) The student used his probe in **(a)** to analyse a sample of mandelic acid, a bitter almond extract that is used as an antibacterial treatment.

The student obtained a cell potential reading, E_{cell}, of +0.41 V.

The *Nernst equation* can be used to calculate the concentration of H^+ ions detected by the probe:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n}\log_{10}\left(\frac{[H^+]^2[Cl^-]^2}{P_{H_2}}\right)$$

where n is the number of moles of electrons transferred in the overall reaction,
$[H^+]$ is the concentration of hydrogen ions detected,
$[Cl^-]$ is the concentration of Cl^- ions,
P_{H_2} is the pressure, in bar, of hydrogen gas passed into the probe.

Assuming that the concentration of Cl^- is constant at 1 mol dm^{-3}, use the *Nernst equation* to calculate the concentration of H^+ ions in the solution and the pH of the solution.

[2]

$$E = E^0_{cell} - \frac{0.0592}{n}\log\left(\frac{[H^+]^2[Cl^-]^2}{P_{H2}}\right)$$

$$0.41 = 0.28 - \frac{0.0592}{2}\log\left([H^+]^2\right)$$

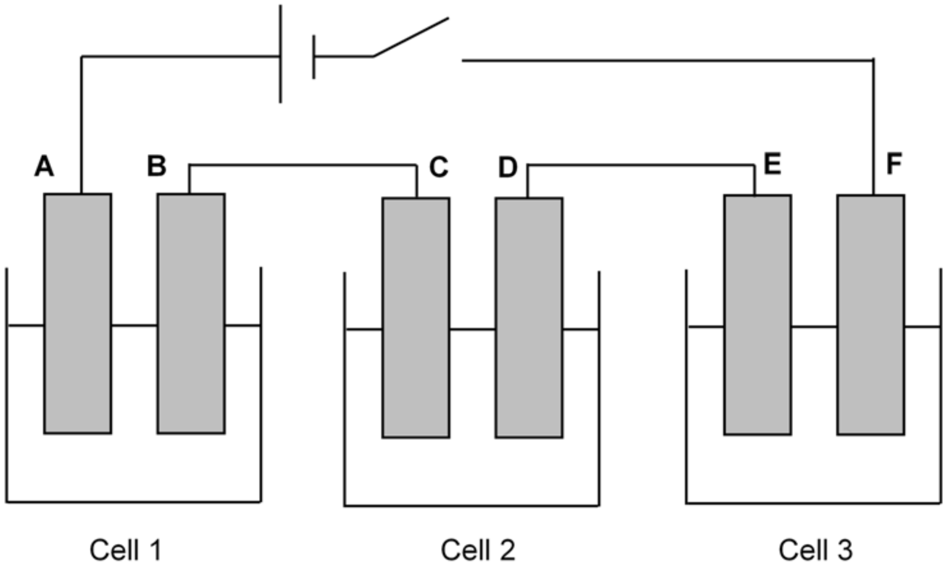
$$0.41 = 0.28 - \frac{0.0592}{2}\times 2\log[H^+]$$

$$\log[H^+] = -\frac{0.13}{0.0592}$$

$[H^+] = 6.37 \times 10^{-3}$ mol dm^{-3}

pH = $-\log(6.37 \times 10^{-3})$ = 2.20

(c) A current is passed through three cells connected in series as shown below.



Cell 1 contains lead electrodes, **A**, **B** and electrolyte $Pb(NO_3)_2(aq)$.

Cell 2 contains platinum electrodes, **C**, **D** and electrolyte NaBr(aq).

Cell 3 contains platinum electrodes, **E**, **F** and electrolyte containing $MnCl_x(aq)$.

(i) On closing the switch, write equations, including state symbols, for the reactions occurring at electrodes **A** and **D**.

[2]

A: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e$

D: $2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

(ii) A current of 0.36 A was passed through the circuit for 30 minutes. 0.183 g of manganese was deposited in Cell 3. Determine the value of x in $MnCl_x$.

[3]

Q = 0.36 x 30 x 60 = 648C

Amount of electrons transferred = 648/96500 = 0.0067150 mol

Amount of Mn deposited = 0.183/54.9 = 0.0033333 mol

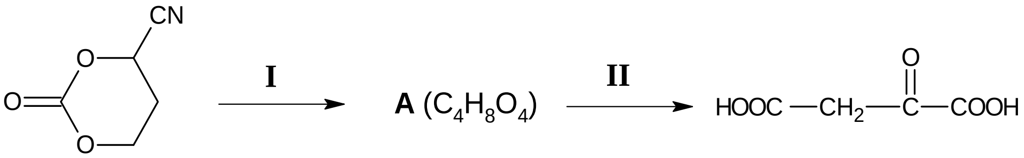
$Mn^{x+} + xe \rightarrow Mn$

$$\frac{n_e}{n_{Mn}} = \frac{0.0067150}{0.0033333} = 2$$

x=2

(d) Identify the structures of compounds **A**, **B**, **C** and **D** and suggest the reagents and conditions for each numbered steps **I**, **II** and **III** where possible.

(i)



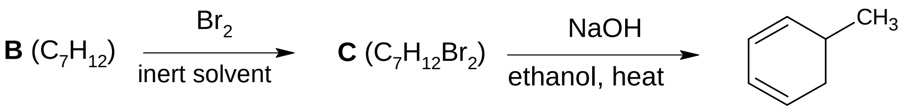
[3]

I: aqueous H_2SO_4, heat

II: $KMnO_4$ (or $K_2Cr_2O_7$), aqueous H_2SO_4, heat

A: $HOCH_2CH_2CHOH(COOH)$

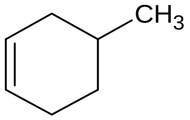
(ii)



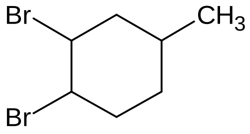
only 1 product formed

[2]

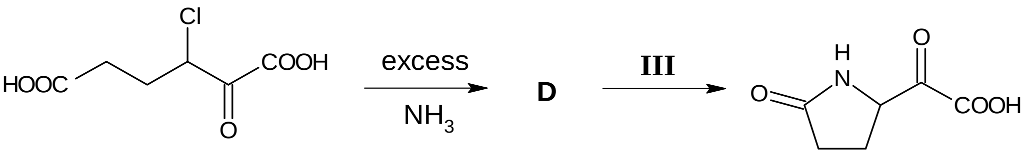
B:



C:

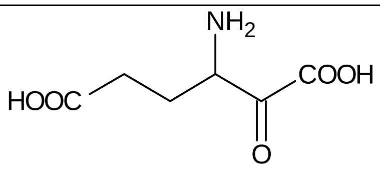


(iii)



[2]

D:



III: anhydrous PCl_5 (limited)

[Total: 21]

2 **(a)** Ethiopia is severely impacted by inadequate safe drinking water, where halogen contaminants such as chloride in drinking water, are the root cause of many common ailments such as low immunity and hypertension.

The Mohr's method is used to determine the chloride ion concentration of water samples from various sources such as seawater and stream.

A researcher retrieved a water sample from a stream and carried out Mohr's method, where the chloride ions present in the water sample is titrated against aqueous silver nitrate solution. As the aqueous silver nitrate is slowly added, a sparingly soluble white precipitate is formed. The indicator used in the titration is aqueous potassium chromate(VI), K_2CrO_4. The end-point of the titration is reached when any excess silver nitrate added results in the formation of a red-brown precipitate of Ag_2CrO_4.

The following are relevant K_{sp} values at 298 K:

silver salt	solubility product, K_{sp}
$AgCl$	2.00×10^{-10}
Ag_2CrO_4	1.10×10^{-12}

(i) Determine the concentration of Cl^-(aq) ions at the end-point of the titration.

[1]

At the end point, all the Cl^- in the solution would be precipitated out as $AgCl$.

Let x be the solubility of $AgCl$.
$K_{sp} = [Ag^+][Cl^-]$
$2.00 \times 10^{-10} = x^2$
$x = 1.41 \times 10^{-5}$ mol dm^{-3}

(ii) Explain, with the aid of relevant equations, what would be observed if excess aqueous ammonia is added to the reaction mixture containing the white precipitate.

[2]

$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ ------ (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

For $AgCl$, when ammonia is added, formation of soluble complex $Ag(NH_3)_2^+$ lowers the concentration of Ag^+ and causes position of equilibrium (1) to shift to the left. The ionic product $[Ag^+][Cl^-]$ < Ksp value and hence $AgCl$ dissolves.

(iii) Determine the minimum concentration of CrO_4^{2-}(aq) ions in the titration mixture that is required to precipitate Ag_2CrO_4 immediately after the end-point.

[2]

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

For precipitation of Ag_2CrO_4 just after end-point, ionic product = Ksp
$(1.41 \times 10^{-5})^2 [CrO_4^{2-}] = 1.10 \times 10^{-12}$
$[CrO_4^{2-}] = 5.53 \times 10^{-3}$ mol dm^{-3}

(b) Oxygen gas, O_2, reacts with various period 3 elements to produce compounds for numerous uses. For example, aluminium oxide, Al_2O_3, is often used as a refractory material.

Element **X** forms a white oxide that is soluble in cold water. Its chloride dissolves in water to give a neutral solution.

Element **Y** forms an oxide which has the shape of trigonal planar around the central atom.

1 mole of the oxide of element **X** is added to an aqueous solution containing the same amount of the oxide of element **Y** to form a neutral solution.

Given that **X** and **Y** are period 3 elements, identify element **X** and the oxide of element **Y**. Give an equation to show the formation of the neutral solution.

[2]

X: Na Oxide of **Y**: SO_3

$H_2SO_4 + Na_2O \rightarrow Na_2SO_4 + 2H_2O$

(c) Reduction of ozone, O_3, produces the ozonide anion, O_3^-. Derivatives of this anion are explosive and must be stored at very low temperatures.

Potassium hydroxide reacts with ozone to produce the corresponding metal ozonide, oxygen gas and water.

(i) Suggest an equation for the reaction between potassium hydroxide and ozone.

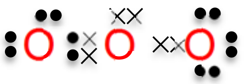
[1]

$4KOH + 4O_3 \rightarrow 4KO_3 + O_2 + 2H_2O$

Other balanced equations are also acceptable.

(ii) Draw a dot-and-cross diagram for ozone. Using VSEPR theory, explain the shape and bond angle of ozone.

[3]



There is 1 lone pair and 2 bond pairs of electrons on the central atom. Electron pairs are arranged as far apart as possible to minimize repulsion Hence it adopts a bent shape.

Repulsion between lone pair-bond pair electrons is greater than the bond pair-bond pair electrons. Hence the bond angle is 117° (or 118°).

(iii) All the O–O bonds in ozone are found to have identical bond lengths.

Suggest an explanation for this observation.

[1]

The pi electrons are delocalised over the 3 electronegative oxygen atoms.

(Any other phrasing related to resonance is acceptable.)

(d) Hydrogen reacts with nitrogen monoxide to give nitrogen and steam as shown.

$$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$$

In order to determine the rate equation for this reaction, an investigation was carried out at a constant temperature and with the same concentration of NO for each experiment. The following results were obtained.

experiment	initial $[H_2]$ / mol dm^{-3}	initial rate of production of N_2 / mol dm^{-3} s^{-1}
1	1×10^{-3}	3×10^{-3}
2	2×10^{-3}	6×10^{-3}
3	3×10^{-3}	9×10^{-3}

(i) Using the above data, deduce the order of reaction with respect to $[H_2]$. Hence sketch a graph of initial rate against $[H_2]$.

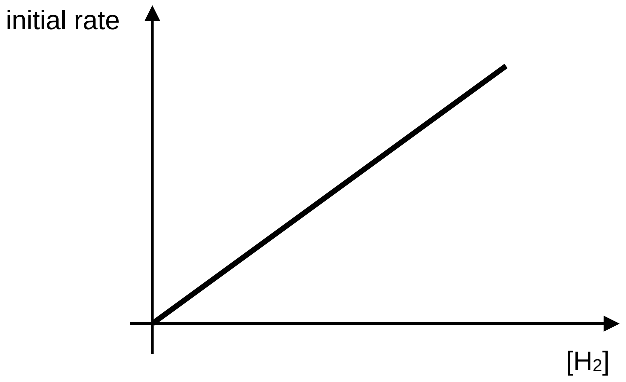
[2]

Let the rate equation be rate = k $[H_2]^x [NO]^y$

Comparing experiment 1 and 2,

$$\left(\frac{1\times10^{-3}}{2\times10^{-3}}\right)^x = \left(\frac{3\times10^{-3}}{6\times10^{-3}}\right)$$

x = 1



(ii) The concentration of NO was halved and a new series of experiments were carried out at the same temperature. When a similar graph was plotted, the magnitude of the gradient decreases by 4 times compared to that obtained from the graph in **(d)(i)**.

Deduce the order of reaction with respect to [NO].

[1]

When [NO] decreases by 2 times, rate decreases by 4 times.

Hence order of reaction wrt [NO] is 2.

(iii) Hence write the rate equation for the reaction between H_2 and NO. Include the units for the rate constant.

[1]

rate = k $[NO]^2 [H_2]$

units of k = $mol^{-2}\ dm^{6}\ s^{-1}$

(iv) The following mechanism was proposed for the reaction of hydrogen with nitrogen monoxide.

step 1: $2NO \rightleftharpoons N_2O_2$
step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$
step 3: $N_2O + H_2 \rightarrow N_2 + H_2O$

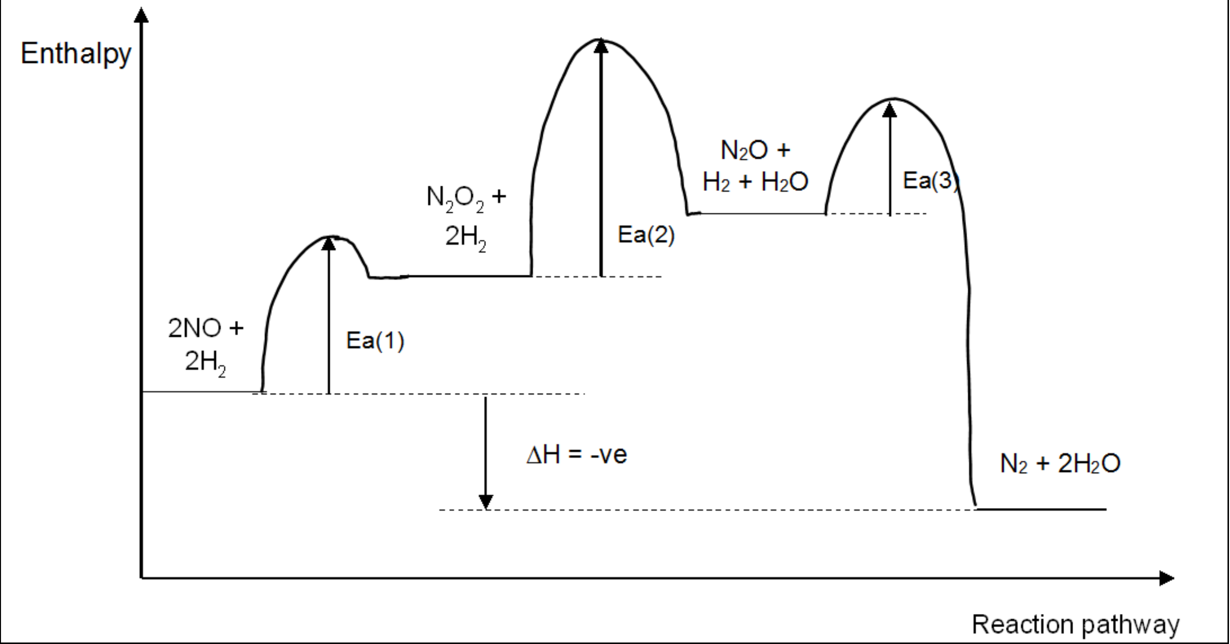
Identify the slow step which is consistent with the rate equation in **(d)(iii)**.

[1]

The second step is the slow step.

(v) Assuming that the reaction in **(d)** is exothermic, sketch a labelled energy profile diagram for the proposed mechanism in **(d)(iv)**. Indicate clearly the activation energy for each step.

[3]



- ✓ Axes correctly labelled
- ✓ 3 humps
- ✓ Ea(2) highest hump
- ✓ ΔH correctly shown
- ✓ All correct reactants, intermediates and products

[Total: 20]

3 **(a)** The protein, somatostatin has been used mainly for its anti-secretory effects in gastrointestinal disorders. Recently, its effects in the treatment of cancer have also been reported.

(i) Complete hydrolysis of a protein produces individual amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

State the reagents and conditions for the hydrolysis of a somatostatin molecule.

[1]

aqueous H_2SO_4 (or NaOH), heat under reflux

(ii) A somatostatin polypeptide, containing **fourteen** amino acids, produced the following fragments on hydrolysis.

Ser- Cys
Phe – Trp – Lys
Cys – Lys – Asn
Ala – Gly – Cys
Asn – Phe – Phe
Lys – Thr – Phe
Phe – Thr – Ser

Using the same 3-letter abbreviations as above, deduce the amino acid sequence of the polypeptide.

[2]

```
Ala- Gly –Cys
            Cys – Lys – Asn
                          Asn – Phe – Phe
                                      Phe – Trp – Lys
                                                  Lys – Thr – Phe
                                                              Phe – Thr – Ser
                                                                          Ser – Cys
```

Ala – Gly – Cys – Lys – Asn – Phe – Phe – Trp – Lys – Thr – Phe – Thr – Ser – Cys

(iii) The complete hydrolysis of somatostatin is found to occur spontaneously at **high temperature**.

Suggest an explanation for this observation, taking into account the thermodynamic considerations of the reaction.

[2]

- Both ΔS and ΔH are positive
- At higher T, $\Delta G < 0$ as $|T\Delta S| > |\Delta H|$

(b) Organophosphates, like carbon monoxide, are toxic to humans. When ingested, organophosphates inhibit the enzyme acetylcholinesterase, resulting in neuro poisoning. Carbon monoxide, on the other hand, inhibits the protein haemoglobin.

One possible treatment of neuro poisoning includes the use of a solution containing carbamates, with the general formula $ROCONR_2$. The carbamate administered can stabilise the enzyme by forming an enzyme–carbamate complex, which stops the organophosphates from binding to the enzyme's active site.

Explain, in terms of ligand strength and the type of reaction occurring, why carbamate can be used to treat neuro poisoning.

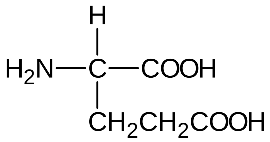
[2]

- Carbamate is a stronger ligand than organophosphate.

- It undergoes ligand exchange reaction and binds more strongly via dative bond to the enzyme to form a more stable complex.

- Hence, it stops the organophosphates from binding to the enzyme's active site.

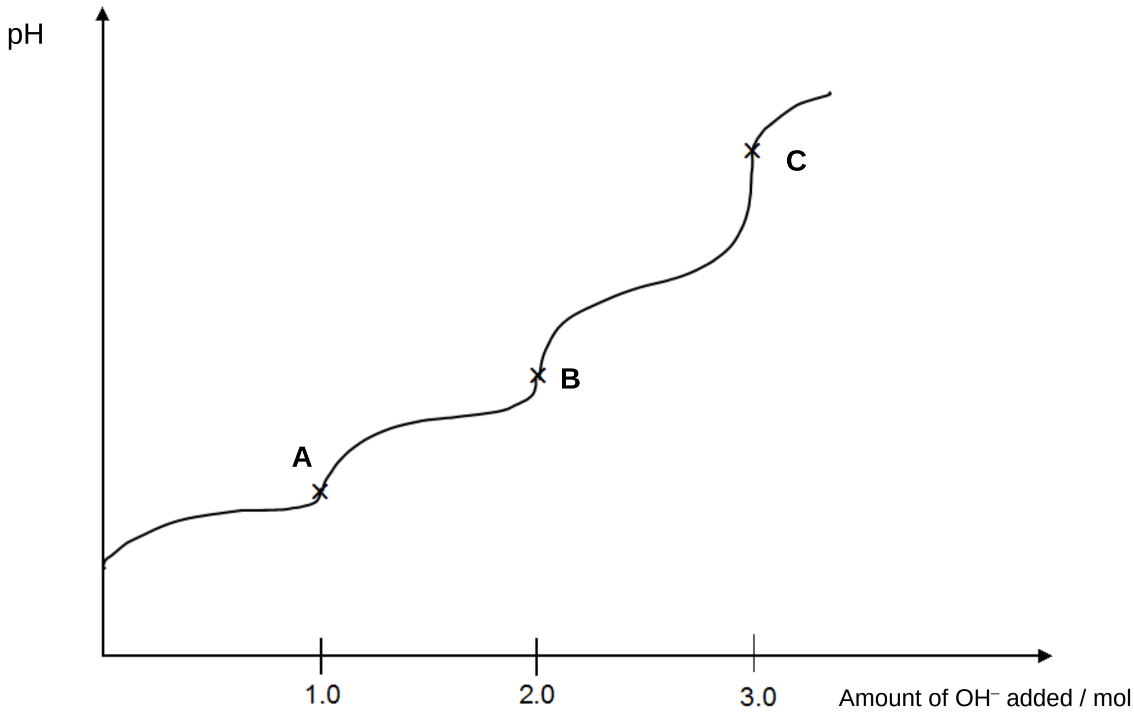
(c) Glutamic acid is used as a flavour enhancer and is responsible for umami, one of the five basic tastes of human sense of taste. It has the structure of



$$H_2N-CH(CH_2CH_2COOH)-COOH$$

The pK_a values and titration curve of 1 mole of the protonated form of glutamic acid are as shown.

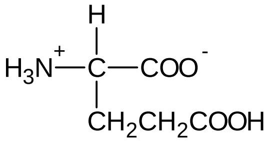
pK_a1 = 2.10
pK_a2 = 4.07
pK_a3 = 9.47



(i) Suggest the structures of **A**, **B** and **C**.

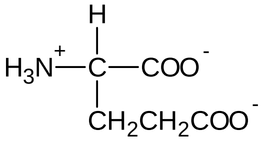
[2]

A:



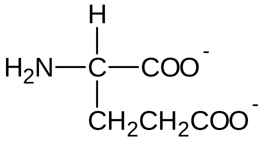
$H_3\overset{+}{N}-CH(CH_2CH_2COOH)-COO^-$

B:



$H_3\overset{+}{N}-CH(CH_2CH_2COO^-)-COO^-$

C:



$H_2N-CH(CH_2CH_2COO^-)-COO^-$

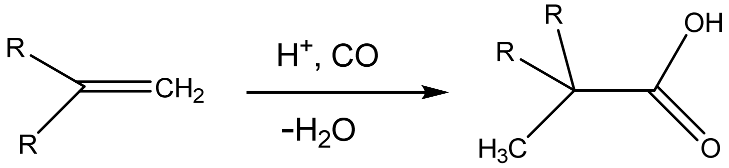
(ii) State the pH of the resultant solution when 1.5 moles of OH^- is added to the protonated glutamic acid.

[1]

Equimolar quantities of A and B are present.

$pH = pK_a2 = 4.07$

(d) In the Koch reaction, carboxylic acids are formed from the acid catalysed reaction between alkenes and carbon monoxide.



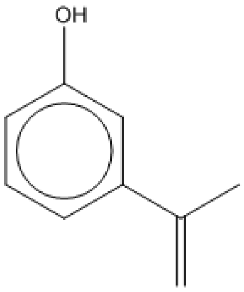
R = alkyl group

(i) Compound **A** has molecular formula $C_9H_{10}O$. It undergoes the Koch reaction to produce compound **B.**
Compound **A** also decolourises aqueous bromine to produce a white precipitate. When reacted with sodium metal, it produces a gas that extinguishes a lighted splint. It also reacts with acidified potassium manganate (VII), $KMnO_4$, to produce compound **C,** $C_8H_8O_2$. When treated with alkaline iodine, compound **C** produces a yellow precipitate. No precipitate was observed when Tollens' reagent was added to compound **C**.

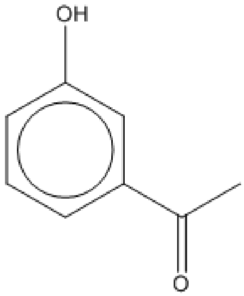
Suggest the structures of compounds **A**, **B** and **C**. Explain all the reactions involved.

[6]

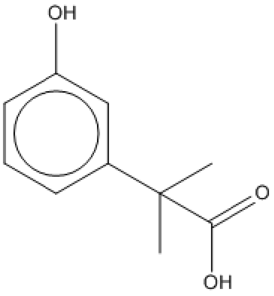
- ✓ High C:H ratio – suggest the presence of an aromatic ring
- ✓ Compound **A** undergoes Koch reaction – suggest presence of a –C=C– in compound **A** and a carboxylic acid functional group in compound **B**
- ✓ Compound **A** undergoes **electrophilic substitution** with aqueous bromine to produce a white precipitate – suggest the presence of phenol functional group
- ✓ Compound **A** undergoes **electrophilic addition** with aqueous bromine which gets decolourised – suggest the presence of –C=C– functional group
- ✓ Compound **A** undergoes **redox** reaction with Na(s) to produce hydrogen gas – suggest presence of phenol functional group
- ✓ Compound **A** undergoes **oxidation** with acidified $KMnO_4$ – suggest presence of an alkene
- ✓ Compound **C** undergoes **oxidation** with alkaline iodine – suggest presence of $–CH_3CO$ group
- ✓ Compound **C does not** undergo **oxidation** with Tollens' reagent – absence of aldehyde FG /presence of a ketone functional group



A

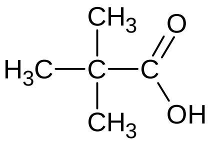


C

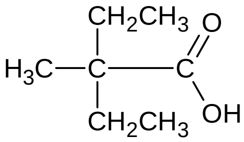


B

(ii) Carboxylic acids, **D** and **E** could be formed using the Koch reaction.



carboxylic acid **D**



carboxylic acid **E**

Carboxylic acid **D** has a lower pKa value than carboxylic acid **E**. Explain the difference in their pKa values.

[3]

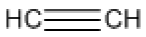
- Carboxylic acid **E** has a bigger alkyl group which is a stronger electron donating group
- which intensifies the negative charge of the conjugate base to a greater extent and destabilises it
- Carboxylic acid **E** dissociates to a less extent and produces less H^+ ions

[Total: 19]

Section B (20 marks)

Answer **one** question from this section on the writing paper provided.

4 Organic molecules such as ethyne, C_2H_2, and ethylenediamine can function as ligands to transition metal ions.



ethyne

ethylenediamine

(a) A blue complex salt **A** has the molecular formula $NiN_5H_{17}OCl_2$ (M_r = 232.7).

1.00 g of **A** reacts completely with 25.00 cm^3 of 0.344 mol dm^{-3} silver nitrate solution.

When excess ethylenediamine was added to the blue solid **A**, a violet solution containing complex **B** was produced. **A** and **B** have the same coordination number.

(i) Calculate the amount of free chloride ions per mole of **A**.

[1]

Amount of **A** = $\frac{1}{232.7}$
= 4.2974×10^{-3} mol

Amount of Ag^+ = $\frac{25}{1000} \times 0.344$
= 8.60×10^{-3} mol
= Amount of free Cl^-

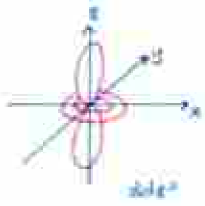
$$\frac{Amount\ of\ \boldsymbol{A}}{Amount\ of\ Cl^-} = \frac{4.2974 \times 10^{-3}}{8.60 \times 10^{-3}}$$
$$\approx \frac{1}{2}$$

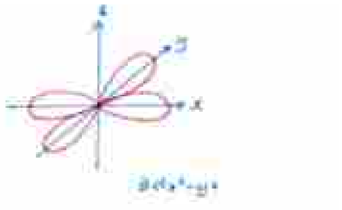
Hence, 1 mol of A contains **2 mol** of free chloride ions.

(ii) State the full electronic configuration of the nickel ion. Draw fully-labelled diagrams of the orbitals which experience the greatest repulsion between the *d* electrons and the lone pair of electrons on the ligands.

[2]

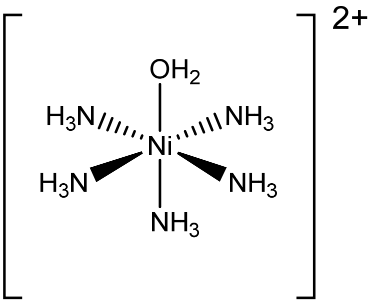
$Ni^{2+} = 1s^22s^22p^63s^23p^63d^8$





(iii) With reference to your answer in **(a)(i)** and **(a)(ii)**, draw a three dimensional diagram to illustrate the shape of the complex ion in **A**.

[1]



(iv) Suggest a possible formula of the complex ion in **B**.

[1]

Any of the following :

- $[Ni(NH_2CH_2CH_2NH_2)(NH_3)_4]^{2+}$
- $[Ni(NH_2CH_2CH_2NH_2)(H_2O)(NH_3)_3]^{2+}$
- $[\ [Ni((NH_2CH_2CH_2NH_2)_2(NH_3)_2]^{2+}$
- $[Ni(NH_2CH_2CH_2NH_2)_2(H_2O)(NH_3)]^{2+}$
- $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$

(b) State the hybridisation of the carbon atoms present in ethyne. Hence, in terms of orbital overlap, justify why ethyne can function as a ligand.

$HC\equiv CH$

ethyne

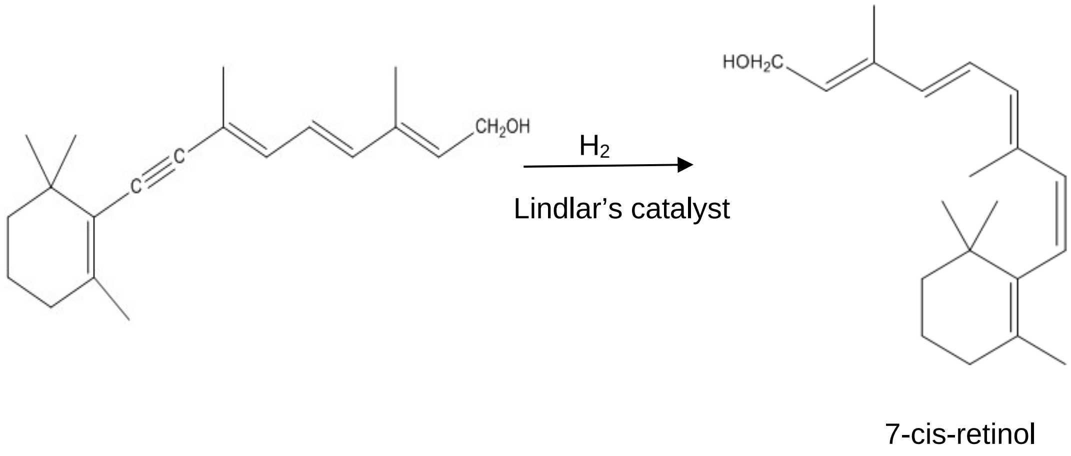
[3]

1. In ethyne, each of the carbon atom is sp hybridised.
2. The 2 unhybridised p orbital of the two carbon atoms, which is perpendicular to the plane of sp^2 hybrid orbitals, overlaps laterally or sideways to form 2 π bonds.

3. The electron density around the π bond is high, which allows ethyne to function as a ligand (or the pi electrons are not directly involved in holding the 2 carbon nuclei in place and since they are loosely held by the 2 carbon nuclei, they are available for reaction).

(c) Alkynes are reduced to alkenes, using the Lindlar's catalyst, which are finely divided palladium metal precipitated onto a calcium carbonate support.

An example is in the synthesis of 7-cis-retinol.



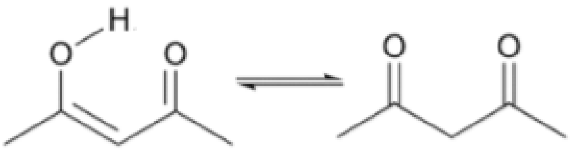
(i) State the number of cis-trans isomers present in a molecule of 7-cis-retinol. [1]

2^4 = **16**

(ii) Describe the mode of action by the Lindlar's catalyst. [3]

- ✓ Palladium functions as a heterogeneous catalyst.
- ✓ Availability of partially filled d orbitals in palladium metal allows reactant molecules to adsorb onto metal surface.
- ✓ This weakens the bonds within the reactants.
- ✓ Reactant molecules are also brought closer together, increasing surface concentration on the catalyst.
- ✓ As such, activation energy is lowered.
- ✓ Once the products are formed, the product molecules are desorbed from the metal surface.

(d) Alkyne can also undergo hydration to form an enol which rapidly rearranges itself into a ketone. Such a rearrangement is known as ketone tautomerisation. An example is that of 2,4-pentanedione.



$K_{eq} = 0.315$

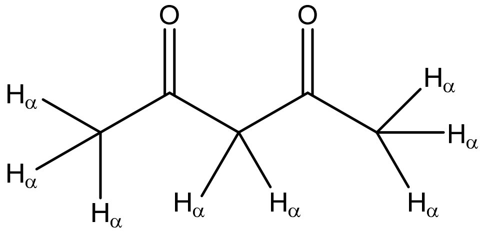
enol ketone

Using the data given, deduce if the tautomerisation reaction is spontaneous.

[2]

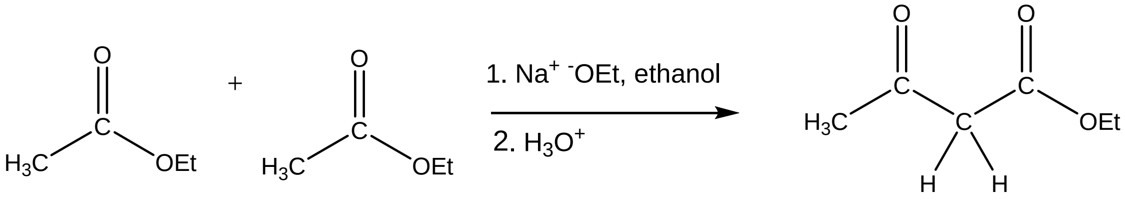
K < 1, suggest that position of equilibrium lies to the left.
$\Delta G>0$, Not spontaneous

(e) Carbonyl compounds, like 2,4-pentanedione contains acidic α hydrogen atoms.



Esters, like ketones and aldehydes, can also contain acidic α hydrogen atoms. When deprotonated by a suitable base, a carbonyl condensation reaction can occur.

An example is the formation of ethyl acetoacetate from ethyl ethanoate.
(Et : –CH_2CH_3)



ethyl ethanoate ethyl acetoacetate

Part of the mechanism is described as follows:

Step 1:
A base, ethoxide ion ($^{-}$OEt), abstracts an acidic alpha hydrogen atom from the ethyl ethanoate molecule, yielding a RCH_2^- nucleophile.

Step 2:
The resultant RCH_2^- nucleophile adds to a second ester molecule, giving a tetrahedral alkoxide intermediate:

Step 3:
The tetrahedral intermediate expels the ethoxide ion to yield the new carbonyl compound, ethyl acetoacetate.

(i) Suggest the role of ethanol.

[1]

Organic solvent

(ii) Suggest, with a reason, why the alpha hydrogen of the ester, ethyl ethanoate in Step 1 is acidic.

[1]

The conjugate base produced is stabilised by the electron withdrawing ester functional group (or by resonance)

(iii) Using the information given, suggest the mechanism for the reaction. Show relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

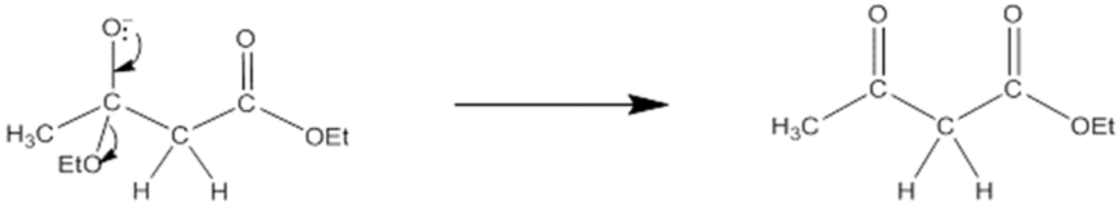
[3]

A base, ethoxide ion ($^{-}$OEt), abstracts an acidic alpha hydrogen atom from the ethyl ethanoate molecule, yielding a RCH_2^- nucleophile.

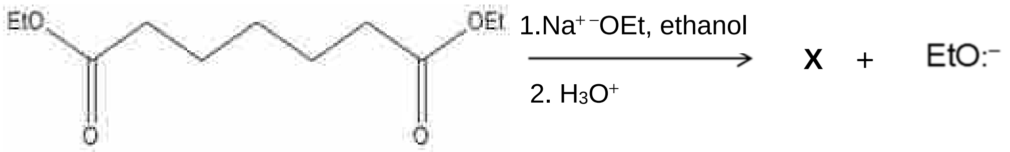
+ EtOH

Step 2:
The resultant RCH_2^- nucleophile adds to a second ester molecule, giving a tetrahedral alkoxide intermediate:

Step 3:
The tetrahedral intermediate expels the ethoxide ion to yield the new carbonyl compound, ethyl acetoacetate.



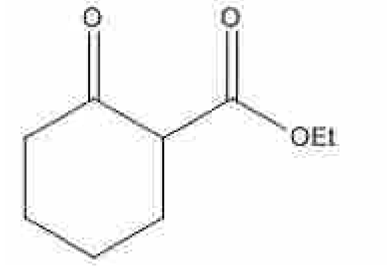
(iv) Compound **X** can be synthesised from diethyl heptanedioate via the carbonyl condensation reaction.



diethyl heptanedioate

Suggest the structure of compound **X**.

[1]



[Total: 20 m]

5 **(a)** The following shows a series of reactions involving titanium compounds.

$$TiCl_4 \xrightarrow[\text{I}]{\text{conc HCl}} \underset{\text{colourless solution}}{[TiCl_6]^{2-}} \xrightarrow[\text{II}]{} \underset{\text{violet solution}}{[Ti(H_2O)_6]^{3+}} \xrightarrow[\text{III}]{} \underset{\text{orange solution}}{[TiCl_6]^{3-}}$$

(i) Suggest the type of reaction for **II** and **III**.

[2]

II: reduction or redox

III: ligand exchange

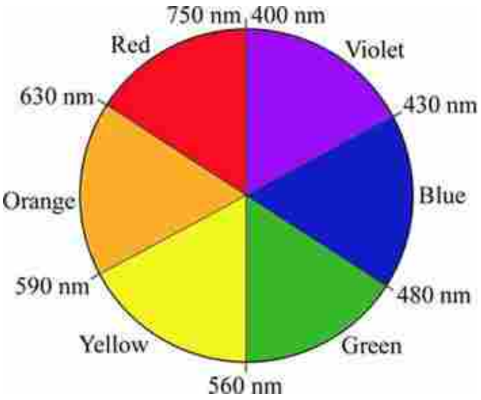
(ii) Explain why a solution of $[TiCl_6]^{2-}$ is colourless while that of $[TiCl_6]^{3-}$ is orange. [2]

Ti^{4+} in $[TiCl_6]^{2-}$ has empty *d* orbitals while Ti^{3+} in $[TiCl_6]^{3-}$ contains partially filled *d* orbitals.

Hence electron can be promoted from lower energy *d* orbital to the higher energy *d* orbital (*d*–*d* transition) for $[TiCl_6]^{3-}$ but not for $[TiCl_6]^{2-}$.

(iii) White light contains all the colours in the visible spectrum, and each of these colours is associated with a certain wavelength λ. The figure below shows a colour wheel with approximate wavelength values in nanometres for different colour light.

The formula relating energy gap between d orbitals, ΔE and wavelength λ is given as $\Delta E = \frac{hc}{\lambda}$, where h is the Planck's constant and c is the speed of light. As wavelength decreases, the energy gap increases.



Using the information given and those in **(a)**, deduce whether $[Ti(H_2O)_6]^{3+}$ or $[TiCl_6]^{3-}$ has a bigger energy gap between the d orbitals. [1]

Violet $[Ti(H_2O)_6]^{3+}$ absorbs in the yellow region while orange $[TiCl_6]^{3-}$ absorbs in the blue region. Blue colour has a shorter wavelength than yellow and thus indicates a bigger energy gap between the 2 sets of orbitals.

(iv) Explain why titanium forms complexes with different oxidation states while calcium is unable to do so. [1]

Ti can show variable oxidation states as the energy difference between the 3*d* and 4s orbitals of titanium is relatively small. With sufficient energy, the 4s and inner 3*d* electrons can be removed.

(b) Organotitanium compounds such as CH_3TiCl_3 can function as nucleophiles. The methyl group, CH_3^-, acts as a nucleophile.

The reduction reaction of an ester, methyl propanoate, $C_2H_5COOCH_3$ with CH_3TiCl_3, followed by acidification produces a tertiary alcohol, $C_2H_5C(CH_3)_2OH$, as shown.

$$C_2H_5COOCH_3 + 2CH_3TiCl_3 \rightarrow C_2H_5C(CH_3)_2OH$$

(i) The mechanism is proposed as follows.

Step 1:
The nucleophile CH_3^- from CH_3TiCl_3 adds to the carbonyl carbon of the ester to form a tetrahedral alkoxide intermediate.

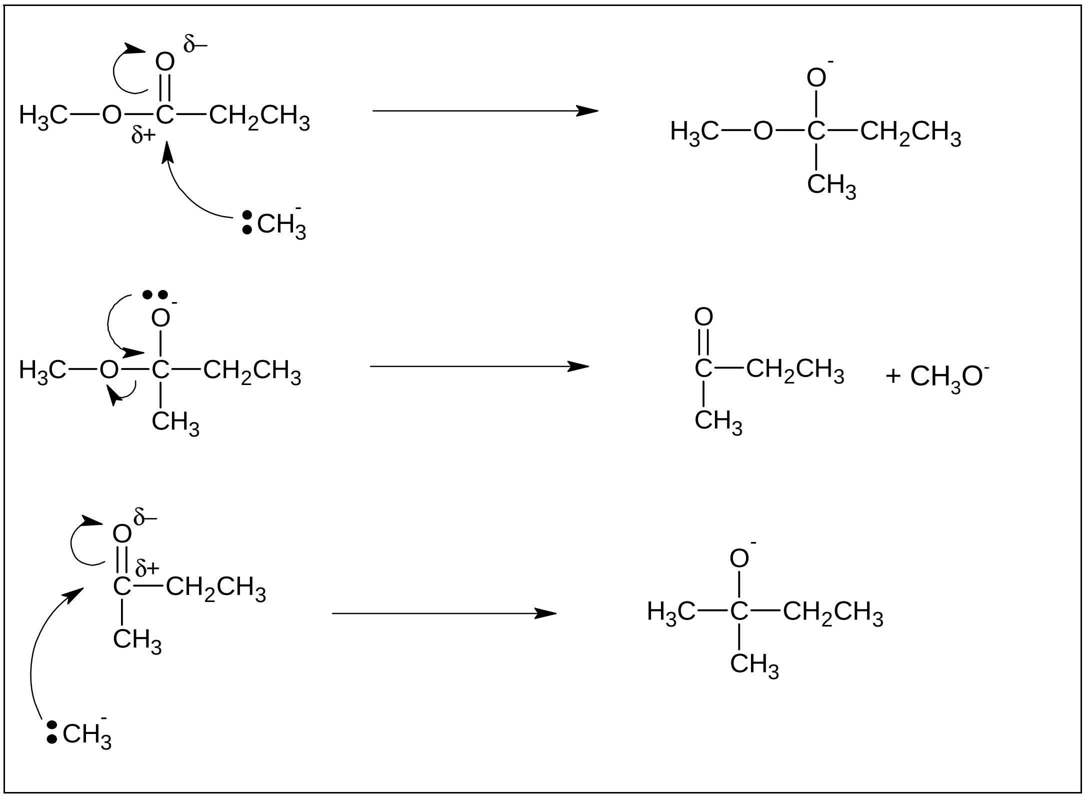
Step 2:
A ketone and a methoxide ion, CH_3O^- are produced from the alkoxide intermediate.

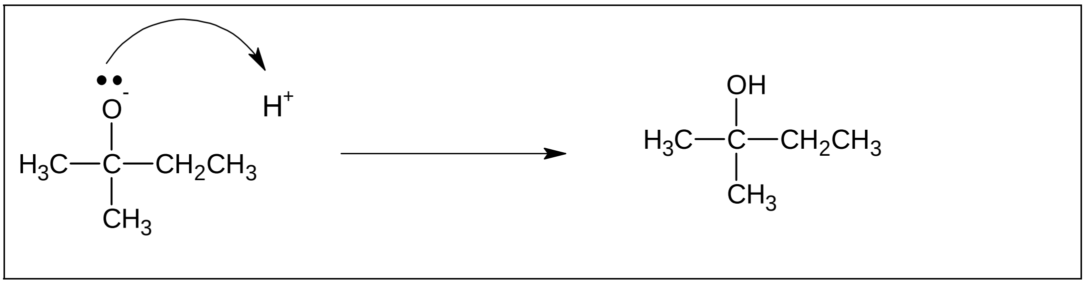
Step 3:
Another CH_3^- from CH_3TiCl_3 adds to the carbonyl carbon of the ketone to form another tetrahedral alkoxide intermediate.

Step 4:
Protonation of the alkoxide intermediate forms the product $C_2H_5C(CH_3)_2OH$.

Using the information given, suggest the mechanism for the reaction. Show relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[4]





(ii) Amides can also be reduced by organotitanium compounds to form the corresponding alcohol and amine. However, this reaction occurs at a slower rate as compared to that of an ester.

Suggest an explanation for this observation.

[1]

Oxygen is more electronegative than nitrogen, hence the carbonyl carbon of the ester is more electron deficient compared to that of the amide. Hence the ester is more susceptible to nucleophilic attack by the reducing agent.

(iii) Suggest a simple chemical test to distinguish between $C_2H_5COOCH_3$ and $C_2H_5C(CH_3)_2OH$.

[2]

test: anhydrous PCl_5

observations: white fumes of HCl observed for $C_2H_5C(CH_3)_2OH$ and no fumes observed for $C_2H_5COOCH_3$

Other alternatives are acceptable eg Na test.

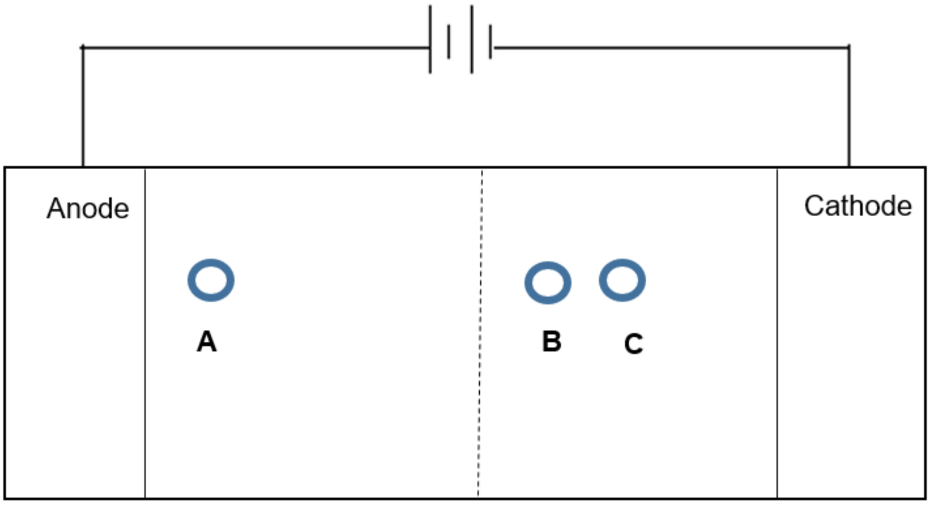
(c) The following amino acids are some of the amino acids present in the primary sequence of haemoglobin.

amino acid	formula of side chain (R' in $R'CH(NH_2)CO_2H$)	isoelectric point
valine	$-CH(CH_3)_2$	6.00
glutamic acid	$-CH_2CH_2COOH$	3.15
asparagine	$-CH_2CONH_2$	5.41

At an intermediate pH, called the isoelectric point (pI), the amino acids will be *zwitterionic* and have *no* net charge.

An electrophoresis experiment is run on a solution containing the above three amino acids at pH 5.00. The relative positions of the amino acids are shown in the diagram below.

The rate at which the amino acids move through the gel is inversely proportional to its mass.



Original position of sample

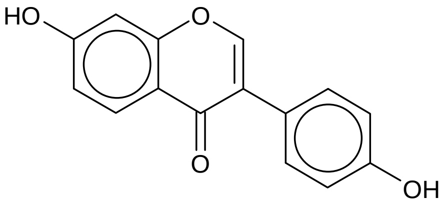
Identify the structures **A**, **B** and **C**. Hence, explain the position of **B** relative to **C**.

[2]

A: Glutamic acid; **B**: Asparagine ; **C** : Valine

Asparagine has a larger molecular mass than valine. Since, the rate in which the amino acids move through the gel is inversely proportional to its mass, asparagine will migrate to the cathode at a slower rate.

(d) Soy beans, and especially the dofu made from them, are a good source of dietary isoflavenoids, which are claimed to help in the prevention of some cancers. The major isoflavenoid in soy is diadzein.

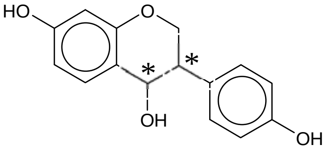
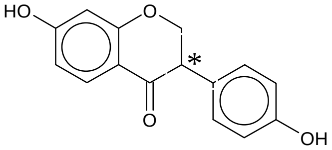


diadzein

When diadzein is treated with H_2 and Ni, compound **D**, $C_{15}H_{14}O_4$, is formed. One mole of compound **D** reacts with three moles of sodium metal. **D** also dissolves in NaOH(aq). **D** reacts with acidified $K_2Cr_2O_7$ to give compound **E**, $C_{15}H_{12}O_4$, which gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Suggest a structural formula for **D** and for **E**, identifying any chiral carbon atoms. Explain the reactions which occur.

[5]

D	**E**
	

Structures of **D** and **E** with chiral carbon correctly identified

The alkene and ketone in diadzein undergoes reduction with H_2 and Ni to form **D**.

1 mole of **D** undergoes redox with 3 moles of Na as it has 3 –OH groups.

D dissolves in NaOH(aq) as it contains acidic phenol and undergoes acid-base reaction.

The secondary alcohol in **D** is oxidised to ketone.

E contains a ketone group thus it gives an orange precipitate with 2,4-DNPH via condensation reaction.

[Total: 20]

END OF PAPER

Candidate's name ………………………………….………. CTG ………..…….

YISHUN JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS 2018

CHEMISTRY 9729/4

HIGHER 2

6 August 2018

2 hours 30 minutes

Paper 4 Practical Test

Candidates answer on the Question Paper.
No Additional Materials are required.

READ THESE INSTRUCTIONS FIRST

Write your name and CTG in the spaces provided on this cover page.

Give details of the practical shift and laboratory, where appropriate, in the box provided.

Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Shift
Laboratory

For Examiner's Use	
1	**/41**
2	**/14**
Total	
	/ 55

Qualitative Analysis Notes are printed on pages 18 and 19.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

This question paper consists of **19** printed pages.

Answer **all** the questions in the spaces provided.

1 Determination of concentration of sulfuric acid

Both group 1 carbonates and hydroxides are bases which neutralise sulfuric acid as shown by the equations below.

$M_2CO_3 + H_2SO_4 \rightarrow M_2SO_4 + H_2O + CO_2$
$2MOH + H_2SO_4 \rightarrow M_2SO_4 + 2H_2O$

FA 1 is dilute solution of sulfuric acid, H_2SO_4
FA 2 is 0.550 mol dm^{-3} sodium hydroxide, NaOH
FA 3 is anhydrous powder of an unknown group 1 carbonate

In this question, you will perform an experiment to determine the concentration of the sulfuric acid solution by means of a graphical method and hence, determine the relative atomic mass of an unknown group 1 element.

You will first prepare a standard solution of the group 1 carbonate, **FA 4**, using its anhydrous powder, **FA 3**.

You will then add different volumes of **FA 4** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the amount of the group 1 carbonate solution you add will only partially neutralise the sulfuric acid.

You will then complete the neutralisation of each mixture by titration with sodium hydroxide, **FA 2**.

In **1(c)**, you will use your volumes of **FA 2** and **FA 4** to plot a graph which will enable you to determine the concentration of the sulfuric acid solution and hence, determine the relative atomic mass of the unknown group 1 element.

(a) Preparation of **FA 4**

1. Weigh accurately about 10.0g of **FA 3** into an empty weighing bottle. Record all weighings in the space provided. Make certain that your recorded results show the precision of your working.
2. Transfer the contents of the weighing bottle into a 250 cm^3 beaker and rinse the weighing bottle with deionised water and transfer the rinsing into the beaker. Repeat the rinsing to ensure all **FA 3** has been transferred.
3. Add 100 cm^3 of deionised water to dissolve **FA 3**.
4. Transfer **all** of the solution to a graduated flask and make up the solution to 250 cm^3 with deionised water and mix thoroughly.

Results

[1]

(b) Preparation and titration of the reaction mixture

Notes: You will perform each titration **<u>once</u>** only. Great care must be taken that you do not overshoot the end-point.

You should aim not to exceed 25 minutes for this experiment.

1. Fill the burette labelled '**FA 2**' with **FA 2**.
2. Fill the burette labelled '**FA 4**' with **FA 4**.
3. Pipette 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
4. Add 6.00 cm^3 of **FA 4** into the same conical flask from step 3.
5. Thoroughly swirl the mixture.
6. Add 2 to 3 drops of methyl orange indicator to the conical flask.
7. Titrate the mixture in the conical flask with **FA 2** until an orange colour is obtained.
8. Repeat steps 3 to 7 until four more aliquots using the following volumes of 9.50 cm^3, 13.00 cm^3, 17.00 cm^3 and 20.00 cm^3 of **FA 4** have been titrated. Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Results

[2]

(c) Plot a graph of the volumes of **FA 2** added, on the *y*-axis, against the volumes of **FA 4** added on the *x*-axis on the grid in **Fig 1.1.**

You should choose scales for the axes which allow you to determine by extrapolation
- the volume of **FA 4** required, **V_{max}(FA 4)**, to completely react with 25.0 cm^3 of **FA 1** if no **FA 2** is added;
- the volume of **FA 2** required, **V_{max}(FA 2)**, to completely react with 25.0 cm^3 of **FA 1** if no **FA 4** is added.

Draw the line of best fit, taking into account all your plotted points. Hence obtain values for **V_{max}(FA 4)** and **V_{max}(FA 2)**.

Fig 1.1

V_{max}(FA 4) =………………………. **V_{max}(FA 2) = ………………………….**

[7]

(d) Suggest an explanation on the direction of the slope of your graph.

[1]

Calculations

(e) **(i)** Using appropriate data from your graph in **(c)**, calculate the concentration of sulfuric acid in **FA 1**.

[2]

(ii) Using your answer in **(e)(i)** and appropriate data from your graph in **(c)**, calculate the concentration of group 1 carbonate in **FA 4**.

[2]

(iii) Hence, calculate the relative atomic mass of M.
[A_r: O = 16.0; C = 12.0]

[2]

(f) A student performs this experiment. Unknowingly, he uses a sample of **FA 3** which is slightly damp. State and explain the effect on the relative atomic mass of M calculated in **e(iii)**.

....

....

....

....

....

.... [2]

Turn over

(g) Determination of concentration of sulfuric acid using gravimetric analysis

A student performed an experiment to determine the concentration of sulfuric acid using its density. The student weighed the mass of an empty 250 cm^3 volumetric flask and recorded the mass Table 1.1. He used a pipette to transfer 25.0 cm^3 of sulfuric acid, **FA 1** into the flask and then re-weigh it. He then recorded the mass of the flask and **FA 1** in Table 1.1.

Table 1.1

Mass of flask and **FA 1** / g	122.22
Mass of flask / g	96.62
Mass of **FA 1**/ g	

(i) Calculate the mass and hence the density of sulfuric acid in **FA 1** in g cm^{-3}. Leave your calculated density to 3 decimal places.

[2]

(ii) Use **Fig. 1.2** and your answer in **g(i)**, deduce the concentration of sulfuric acid in **FA 1** in mol dm^{-3}.

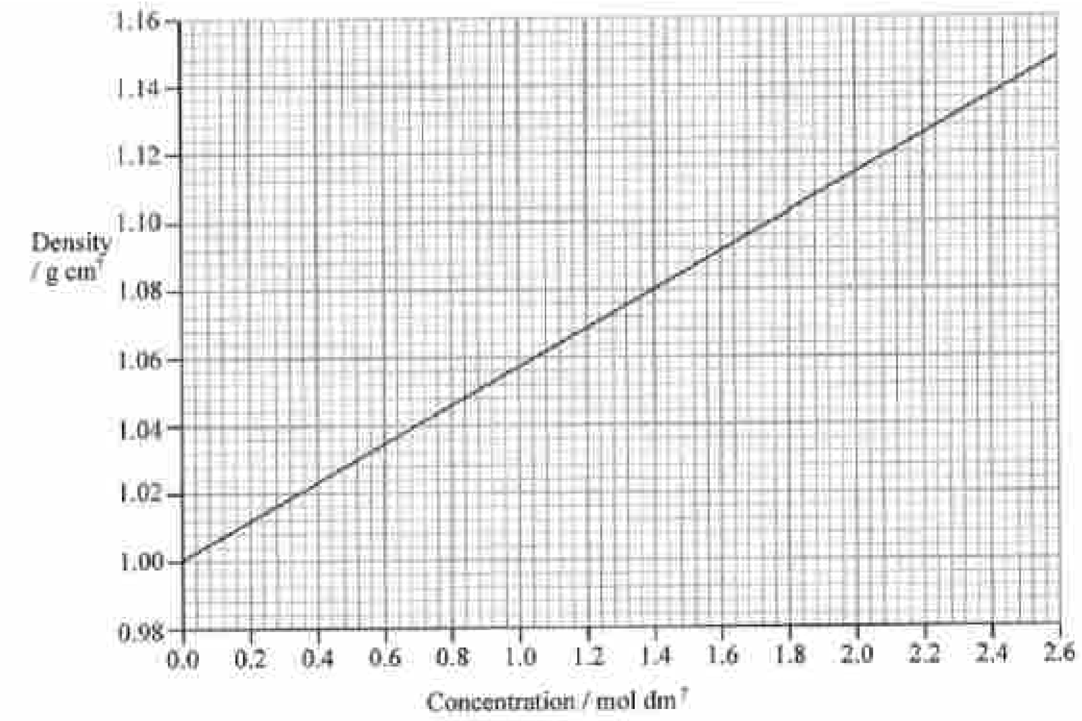


Fig. 1.2

concentration of sulfuric acid in **FA 1** = **…………………………**

[1]

(h) **Determination of concentration of sulfuric acid using thermochemistry**

The neutralisation between a base and sulfuric acid is exothermic. Heat released is sufficient to allow the maximum temperature, ΔT_{max}, to be determined within a few minutes.

In this question, you are to perform an experiment to determine a value, ΔT_{max}. You will then use your value, ΔT_{max} to determine the concentration of sulfuric acid.

You will carry out the following instructions to obtain a value of ΔT_{max}.

1. Use a 25.0 cm^3 pipette, transfer **FA 1** into a polystyrene cup held securely in a beaker. Record the temperature to 1 decimal place in the table provided.
2. Use a measuring cylinder, measure 100 cm^3 of **FA 2**. Record the temperature to 1 decimal place. Calculate the weighted average temperature, T_{ave} of T_{FA1} and T_{FA2} to 1 decimal place.
3. Add **FA 2** carefully and quickly to **FA 1** in the cup, stir and record the maximum temperature reached, again to 1 decimal place.

$$\text{Weighted average temperature, } T_{ave} = \frac{(V_{FA1} \text{ X } T_{FA1}) + (V_{FA2} \text{ X } T_{FA2})}{V_{FA1} + V_{FA2}}$$

Temperature of **FA 1** before mixing, T_{FA1} / ^oC	
Temperature of **FA 2** before mixing, T_{FA2} / ^oC	
Weighted average temperature, T_{ave} / ^oC	
Maximum temperature reached, T_{max} / ^oC	
ΔT_{max} / ^oC	

[2]

(i) Use the equation below to find the concentration of the acid:

Concentration = 0.161 × ΔT_{max}

Concentration = **…………………………………**

[1]

(ii) Instead of adding **FA 2** to **FA 1** to determine ΔT_{max}, the student added barium hydroxide, $Ba(OH)_2$ of the same concentration and volume. Explain the impact on the value of ΔT_{max}.

.... [2]

Turn over

(i) Planning

The exothermic reaction between an acid and metal hydroxide can be used to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration* and can be used to calculate the concentration of an acid solution.

The procedure from **1(h)** could be further improved to obtain a more accurate value for the concentration of sulfuric acid in **FA 1**.

Plotting ΔT_{max} against volumes of **FA 2** gives two best-fit lines. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(i) Plan an investigation, based on the information above, to determine the equivalence-point for the neutralisation between **FA 1** and **FA 2** and hence the concentration of sulfuric acid in **FA 1**.

You may assume you are provided with

- 250 cm^3 solution of dilute sulfuric acid, **FA 1**,
- 250 cm^3 of 0.550 mol dm^{-3} sodium hydroxide, NaOH, **FA 2**,
- graph paper,
- the equipment normally found in the school or college laboratory.

In your plan you should include brief details of

- the apparatus you would use, bearing in mind the levels of precision they offer,
- the procedure that you would follow and the measurements that you would take,
- how you would recognise the equivalence-point had been passed,
- provide a sketch of the graph that you expect to obtain,
- how you would determine the concentration of sulfuric acid,
- state a safety precaution and suggest how do you minimise the risks involved.

[8]

(ii) State and explain one consideration to be taken when deciding the minimum volume of **FA 1** to be used.

[1]

(iii) Describe how you would use your graph in **1i(i)** to determine the enthalpy change of neutralisation between **FA 1** and **FA 2.**

[2]

(iv) How, if at all, will $\Delta T_{\max}$ vary if you use half the volumes of the original **FA 1** and **FA 2**. Explain your answer.

[2]

(v) Provide a reason why this method is preferred to that in **1(h)**.

....

....

.... [1]

[Total: 41]

Turn over

2 Investigation of some chemical reactions involving metal ions

FA 5 is a solid metal carbonate with the formula, XCO_3.
FA 6 is an aqueous solution containing one cation and one anion.

(a) Perform the tests described in **Table 2.1**, and record your observations in the table. Test and identify any gases evolved.

Table 2.1

	tests	observations
1	Place a spatula of solid **FA 5** in a test-tube. Hold the test-tube in a holder. Heat the test-tube strongly until no further changes are seen. Keep the residue for test 2.	
2	To the residue from test 1, add sufficient amount of **FA 1** to dissolve the residue completely. Filter the mixture if necessary. Keep the filtrate for tests 3 and 4.	
3	Add ten drops of the solution obtained from test 2 to a test-tube. Add aqueous NH_3 to this test-tube, until no further change.	

4	Add ten drops of the solution from test 2 to a test-tube. Then add 5 drops of aqueous potassium iodide and shake the mixture thoroughly. To the mixture, add 5 drops of aqueous sodium thiosulfate.	
5	Add a drop of **FA 6** solution onto a universal indicator paper.	
6	Add 1cm depth of **FA 6** to a test tube. Then add a spatula of **FA 3** to the test tube.	
7	To 1 cm depth of **FA 6**, add 10 drops of nitric acid followed by 10 drops of aqueous barium chloride.	

[5]

(b) Consider your observation in **Table 2.1**.

(i) Suggest the identities of the cations in **FA 5** and **FA 6** and the anion in **FA 6**.

Cation in **FA 5** : ……………………………………………………………………..

Cation in **FA 6** : ……………………………………………………………………..

Anion in **FA 6** : ……………………………………………………………………..

[2]

(ii) A student carried out test 1 using **FA 3**, it is unlikely for the same observation to be observed for this test. Suggest an explanation to account for this difference.

[2]

(iii) Test 4 in **Table 2.1** shows a redox reaction to take place.

Some relevant redox half-equations are given in Table 2.2.

Table 2.2

half equation	E^{θ} / V
$X^{2+} + e^- \rightleftharpoons X^+$	+0.15
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Using the information in **Table 2.2**, calculate E^{θ}_{cell} for the reaction shown in your observation in test 4. Suggest a reason for the deviation from the prediction of E^{θ}_{cell} value calculated.

[2]

(iv) Write an equation to account for the observation to test 5 in **Table 2.1**.

[1]

(v) Use your answer to **(iv)** to account for the observations to test 6 in **Table 2.1.**

[2]

[Total: 14]

Turn over

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

END OF PAPER 4

Candidate's name ………………………………….………. CTG ……….…….

YISHUN JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS 2018

Answers

CHEMISTRY
9729/4

HIGHER 2
6 August 2018
2 hours 30 minutes

Paper 4 Practical Test

Candidates answer on the Question Paper.
No Additional Materials are required.

READ THESE INSTRUCTIONS FIRST

Write your name and CTG in the spaces provided on this cover page.

Give details of the practical shift and laboratory, where appropriate, in the box provided.

Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Shift
Laboratory

For Examiner's Use	
1	/41
2	/14
Total	
	/ 55

Qualitative Analysis Notes are printed on pages 18 and 19.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

This question paper consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

1 Determination of concentration of sulfuric acid

Both group 1 carbonates and hydroxides are bases which neutralise sulfuric acid as shown by the equations below.

$M_2CO_3 + H_2SO_4 \rightarrow M_2SO_4 + H_2O + CO_2$
$2MOH + H_2SO_4 \rightarrow M_2SO_4 + 2H_2O$

FA 1 is dilute solution of sulfuric acid, H_2SO_4
FA 2 is 0.550 mol dm^{-3} sodium hydroxide, NaOH
FA 3 is anhydrous powder of an unknown group 1 carbonate

In this question, you will perform an experiment to determine the concentration of the sulfuric acid solution by means of a graphical method and hence, determine the relative atomic mass of an unknown group 1 element.

You will first prepare a standard solution of the group 1 carbonate, **FA 4**, using its anhydrous powder, **FA 3**.

You will then add different volumes of **FA 4** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the amount of the group 1 carbonate solution you add will only partially neutralise the sulfuric acid.

You will then complete the neutralisation of each mixture by titration with sodium hydroxide, **FA 2**.

In **1(c)**, you will use your volumes of **FA 2** and **FA 4** to plot a graph which will enable you to determine the concentration of the sulfuric acid solution and hence, determine the relative atomic mass of the element in the unknown group 1 carbonate, **FA 3** .

(a) Preparation of **FA 4**

1. Weigh accurately about 10.0g of **FA 3** into an empty weighing bottle. Record all weighings in the space provided. Make certain that your recorded results show the precision of your working.
2. Transfer the contents of the weighing bottle into a 250 cm^3 beaker and rinse the weighing bottle with deionised water and transfer the rinsing into the beaker. Repeat the rinsing to ensure all **FA 3** has been transferred.
3. Add 100 cm^3 of deionised water to dissolve **FA 3**.
4. Transfer **all** of the solution to a graduated flask and make up the solution to 250 cm^3 with deionised water and mix thoroughly.

Results

Mass of weighing bottle and **FA 3** / g	
Mass of empty weighing bottle / g	
Mass of **FA 3** / g	9.990

OR
mass of FA3 used (with Tare function) = 10.049 g
mass recorded to 3 dp + header + units + mass reading ranges from 9.950 to 10.049 g: 1 mark

[1]

(b) Preparation and titration of the reaction mixture

Notes: You will perform each titration **once** only. Great care must be taken that you do not overshoot the end-point.

You should aim not to exceed 25 minutes for this experiment.

1. Fill the burette labelled '**FA 2**' with **FA 2**.
2. Fill the burette labelled '**FA 4**' with **FA 4**.
3. Pipette 25.0 cm^3 of **FA 1** into a 250 cm^3 conical flask.
4. Add 6.00 cm^3 of **FA 4** into the same conical flask from step 3.
5. Thoroughly swirl the mixture.
6. Add 2 to 3 drops of methyl orange indicator to the conical flask.
7. Titrate the mixture in the conical flask with **FA 2** until an orange colour is obtained.
8. Repeat steps 3 to 7 until four more aliquots using the following volumes of 9.50 cm^3, 13.00 cm^3, 17.00 cm^3 and 20.00 cm^3 of **FA 4** have been titrated. Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Results

volume of **FA 4** used / cm^3	6.00	9.50	13.00	17.00	20.00
final burette reading / cm^3	27.90	23.00	40.90	12.50	20.70
initial burette reading / cm^3	0.00	0.00	23.30	0.00	12.40
volume of **FA 2** used / cm^3	27.90	23.00	17.60	12.50	8.30

[2]

(c) Plot a graph of the volumes of **FA 2** added, on the *y*-axis, against the volumes of **FA 4** added on the *x*-axis on the grid in **Fig 1.1.**

You should choose scales for the axes which allow you to determine by extrapolation

- the volume of **FA 4** required, **V_{max}(FA 4)**, to completely react with 25.0 cm^3 of **FA 1** if no **FA 2** is added;
- the volume of **FA 2** required, **V_{max}(FA 2)**, to completely react with 25.0 cm^3 of **FA 1** if no **FA 4** is added.

Draw the line of best fit, taking into account all your plotted points. Hence obtain values for **V_{max}(FA 4)** and **V_{max}(FA 2)**.

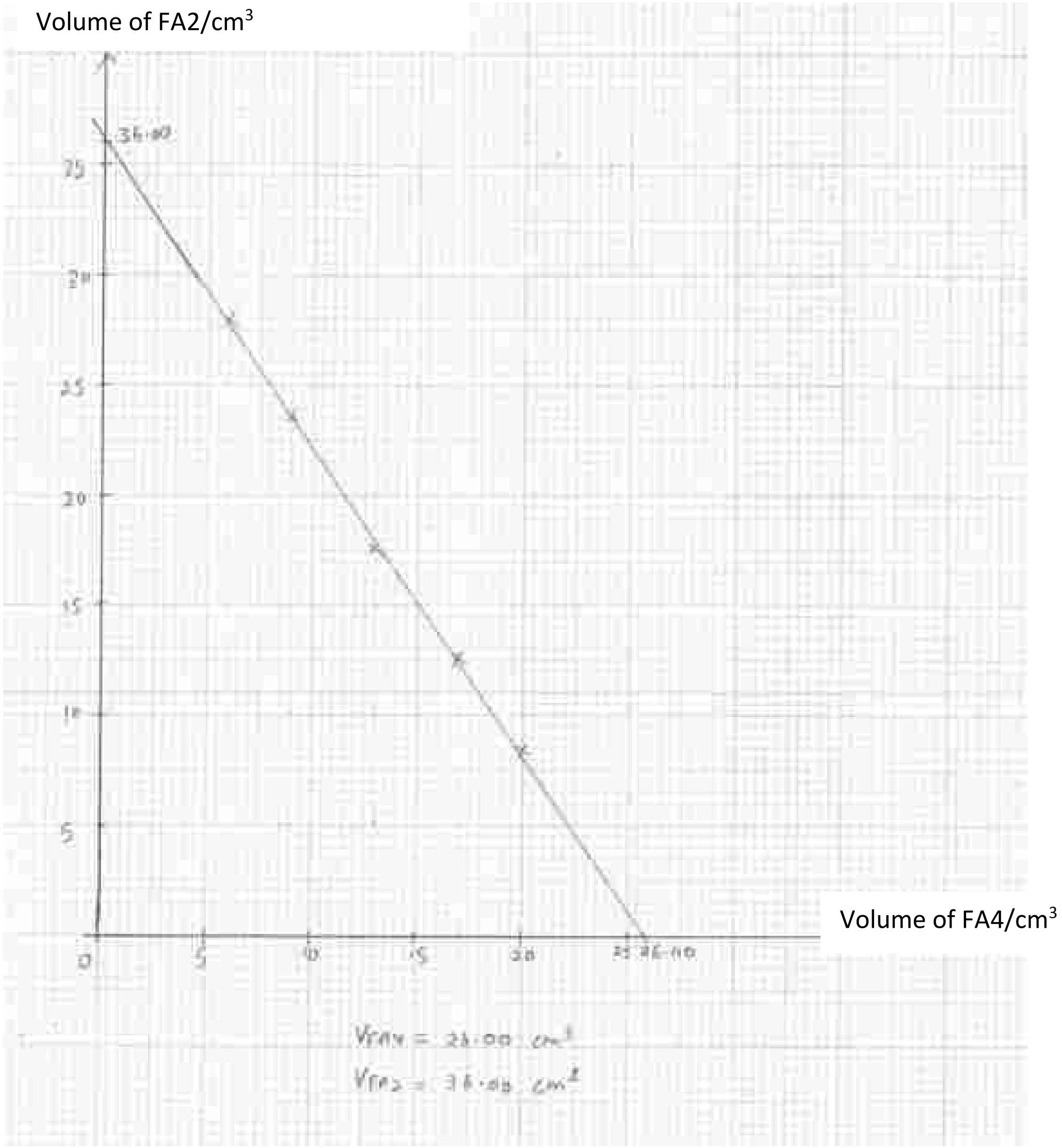


Fig 1.1

V_{max}(FA 4) =…26.00 cm^3…… **V_{max}(FA 2) =** …36.00 cm^3……

[7]

(d) Suggest an explanation on the direction of the slope of your graph.

Negative gradient or downward sloping line as when volume of M_2CO_3 increases, volume of NaOH needed to neutralise remaining H_2SO_4 decreases.

[1]

Calculations

(e) **(i)** Using appropriate data from your graph in **(c)**, calculate the concentration of sulfuric acid in **FA 1**.

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

$$\frac{C_{H_2SO_4} \times V_{H_2SO_4}}{C_{NaOH} \times V_{NaOH}} = \frac{1}{2}$$

$$C_{H_2SO_4} = \frac{\frac{1}{2} \times 0.550 \times 36.00}{25.0} = 0.396 \text{ mol dm}^{-3}$$

Or

$$n_{NaOH} = 0.550 \times \frac{36.00}{1000} = 0.0198 \text{ mol}$$

$$n_{H_2SO_4} = \frac{1}{2} \times n_{NaOH} = \frac{1}{2} \times 0.0198 = 0.009900 \text{ mol}$$

$$C_{H_2SO_4} = \frac{0.00900}{\frac{25.0}{1000}} = 0.396 \text{ mol dm}^{-3}$$

[2]

(ii) Using your answer in **(e)(i)** and appropriate data from your graph in **(c)**, calculate the concentration of group 1 carbonate in **FA 4**.

$M_2CO_3 + H_2SO_4 \rightarrow M_2SO_4 + CO_2 + H_2O$

$$\frac{C_{M_2O_3} \times V_{M_2O_3}}{C_{H_2SO_4} \times V_{H_2SO_4}} = \frac{1}{1}$$

$$C_{M_2O_3} = \frac{0.396 \times 25.0}{26.00} = 0.38076 \text{ moldm}^{-3} = 0.381 \text{ moldm}^{-3}$$

OR

$$n_{H_2SO_4} = 0.009900 \text{ mol}$$

$$n_{M_2O_3} = n_{H_2SO_4} = 0.009900 \text{ mol}$$

$$C_{M_2O_3} = \frac{0.00990}{\frac{26.00}{1000}} = 0.38076 \text{ moldm}^{-3} = 0.381 \text{ moldm}^{-3}$$

[2]

(iii) Hence, calculate the relative atomic mass of M.
[A_r: O = 16.0; C = 12.0]

$n_{M_2O_3} = 0.38076 \times \frac{250}{1000} = 0.095190$ mol

M_r of $M_2O_3 = \frac{10.194}{0.095192}$ = 107.091 = 107.1

A_r of M = $\frac{107.091 - (12.0 + 16.0 \times 3)}{2}$ = 23.55 = 23.6

[2]

(f) A student performs this experiment. Unknowingly, he uses a sample of **FA 3** which is slightly damp. State and explain the effect on the relative atomic mass of M calculated in **e(iii)**.

Presence of moisture makes actual mass of M_2CO_3 added lower than expected.

Calculated concentration of M_2CO_3 or H_sSO_4 is higher and hence the A_r of M calculated is lower.

[2]

(g) **Determination of concentration of sulfuric acid using gravimeteric analysis**

A student performed an experiment to determine the concentration of sulfuric acid using its density. The student weighed the mass of an empty 250 cm^3 volumetric flask and recorded the mass Table 1.1. He used a pipette to transfer 25.0 cm^3 of sulfuric acid, **FA 1** into the flask and then re-weigh it. He then recorded the mass of the flask and **FA 1** in Table 1.1.

Table 1.1

Mass of flask and **FA 1** / g	122.22
Mass of flask / g	96.62
Mass of **FA 1** / g	25.60

(i) Calculate the mass and hence the density of sulfuric acid in **FA 1** in g cm^{-3}. Leave your calculated density to 3 decimal places.

mass = 25.60 g
density = $\frac{25.6}{25.0} = 1.024$ gcm^{-3}

[2]

(ii) Use **Fig. 1.2** and your answer in **g(i)**, deduce the concentration of sulfuric acid in **FA 1** in mol dm^{-3}.

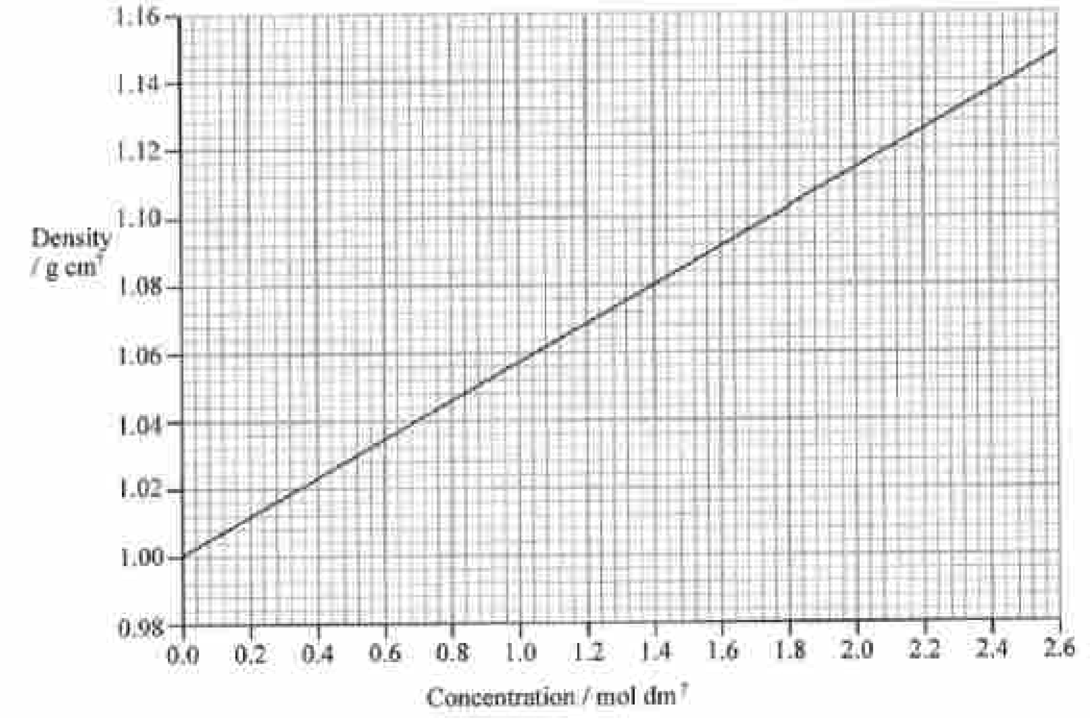


Fig. 1.2

concentration of sulfuric acid in **FA 1** = 0.400 mol dm^{-3}
(0.38 – 0.42, within ½ square)

[1]

(h) **Determination of concentration of sulfuric acid using thermochemistry**

The neutralisation between a base and sulfuric acid is exothermic. Heat released is sufficient to allow the maximum temperature, ΔT_{max}, to be determined within a few minutes.

In this question, you are to perform an experiment to determine a value, ΔT_{max}. You will then use your value, ΔT_{max} to determine the concentration of sulfuric acid.

You will carry out the following instructions to obtain a value of ΔT_{max}.

1. Use a 25.0 cm^3 pipette, transfer **FA 1** into a polystyrene cup held securely in a beaker. Record the temperature to 1 decimal place in the table provided.
2. Use a measuring cylinder, measure 100 cm^3 of **FA 2**. Record the temperature to 1 decimal place. Calculate the weighted average temperature, T_{ave} of T_{FA1} and T_{FA2} to 1 decimal place.
3. Add **FA 2** carefully and quickly to **FA 1** in the cup, stir and record the maximum temperature reached, again to 1 decimal place.

$$\text{Weighted average temperature, } T_{ave} = \frac{(V_{FA1} \text{ X } T_{FA1}) + (V_{FA2} \text{ X } T_{FA2})}{V_{FA1} + V_{FA2}}$$

Temperature of **FA 1** before mixing, T_{FA1} / °C	31.0
Temperature of **FA 2** before mixing, T_{FA2} / °C	29.0
Weighted average temperature, T_{ave} / °C	29.4
Maximum temperature reached, T_{max} / °C	32.0
ΔT_{max} / °C	2.6

[2]

(i) Use the equation below to find the concentration of the acid:

Concentration = 0.161 × ΔT_{max}

Concentration = 0.419 mol dm^{-3}

[1]

(ii) Instead of adding **FA 2** to **FA 1** to determine ΔT_{max}, the student added barium hydroxide, $Ba(OH)_2$ of the same concentration and volume. Explain the impact on the value of ΔT_{max}.

Limiting reagent is H_2SO_4 although the base is changed from NaOH to $Ba(OH)_2$.

The number of moles of water formed is the same.

Since the total volume after mixing **FA 1** and **FA 2** remains the same, the amount of heat released is the same, ΔT_{max} is the same.

[2]

(i) Planning

The exothermic reaction between an acid and metal hydroxide can be used to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration* and can be used to calculate the concentration of an acid solution.

The procedure from **1(h)** could be further improved to obtain a more accurate value for the concentration of sulfuric acid in **FA 1**.

Plotting ΔT_{max} against volumes of **FA 2** gives two best-fit lines. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(i) Plan an investigation, based on the information above, to determine the equivalence-point for the neutralisation between **FA 1** and **FA 2** and hence the concentration of sulfuric acid in **FA 1**.

You may assume you are provided with

- 250 cm^3 solution of dilute sulfuric acid, **FA 1**,
- 250 cm^3 of 0.550 mol dm^{-3} sodium hydroxide, NaOH, **FA 2**,
- graph paper,
- the equipment normally found in the school or college laboratory.

In your plan you should include brief details of

- the apparatus you would use, bearing in mind the levels of precision they offer,
- the procedure that you would follow and the measurements that you would take,
- how you would recognise the equivalence-point had been passed,
- provide a sketch of the graph that you expect to obtain,
- how you would determine the concentration of sulfuric acid,
- state a safety precaution and suggest how do you minimise the risks involved.

1. Use a burette, transfer 30.00 cm^3 of **FA 1** into a styrofoam cup placed in a beaker.
2. Use a thermometer, measure the initial temperature of **FA 1**.
3. Using a second burette, transfer 40.00 cm^3 of **FA 2** into a second styrofoam cup placed in a beaker.
4. Use a thermometer, measure the initial temperature of **FA 2**.
5. Calculate the weighted average temperature of **FA 1** and **FA 2**.
6. Add **FA 2** into the Styrofoam cup containing **FA 1**. Cover the Styrofoam cup with the lid.
7. Use the thermometer to stir the mixture and measure the maximum temperature (ΔT_{max}) of the mixture using the thermometer
8. Note the value of ΔT_{max}
9. Wash the Styrofoam cup thoroughly and dry it

10. Repeat steps 1 to 8 using 10 cm^3 of **FA 1** and 60 cm^3 of **FA 2**, 20 cm^3 of **FA 1** and 50 cm^3 of **FA 2**, 40 cm^3 of **FA 1** and 30 cm^3 of **FA 2**, 50 cm^3 of **FA 1** and 20 cm^3 of **FA 2**.

11. Tabulate the volumes of **FA 1** and **FA 2**, and ΔT_{max}

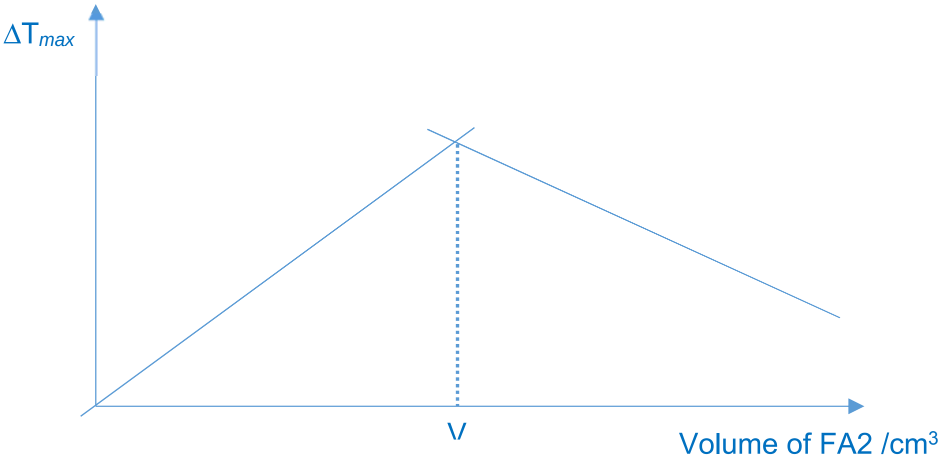
12. Plot the graph of ΔT_{max} against volume of FA2.

13. From the graph, the volume of **FA 2**, V which gives the highest ΔT_{max} is the exact volume of NaOH which is required to neutralise with H_2SO_4 from **FA 1**.The intersection of the two straight lines will be the neutralisation volume of H_2SO_4.

14. From the plot, when the ΔT_{max} begins to decrease, the neutralisation has passed.

15. $C_{H_2SO_4} = \frac{1}{2} \times \frac{\text{VFA2 X 0.550}}{\text{Vtotal- VFA2 at equivalence}}$

16. The H_2SO_4 or NaOH of high concentration is corrosive. Wear gloves to avoid skin contact.



[8]

(ii) State and explain one consideration to be taken when deciding the minimum volume of **FA 1** to be used.

Enough solution to cover the bulb of thermometer so that the change in temperature of the solution could be measured quickly without heat lost.

OR

The volume of FA1 used must produce a significant change in temperature so that the percentage error of the thermometer can be kept low.

[1]

(iii) Describe how you would use your graph in **1i(i)** to determine the enthalpy change of neutralisation between **FA 1** and **FA 2.**

Using maximum change in temperature, ΔT_{max} from the graph, calculate, heat of released from neutralisation using, q = mcΔT.

Using the volume of H_2SO_4 which causes ΔT_{max}, calculate no. of moles of H_2SO_4, n, and the number of moles of water is 2n ; Enthalpy of neutralisation, $\Delta H = -(q/2n)$.

[2]

(iv) How, if at all, will ΔT_{max} vary if you use half the volumes of the original **FA 1** and **FA 2**. Explain your answer.

ΔH of neutralisation is constant. Half the volumes of original **FA 1** and **FA 2** will half the number of moles of water.

$\Delta H_{neutralisation} = -\frac{\frac{1}{2}V \times C \times \Delta T}{\frac{1}{2}n\ of\ water}$; with constant $\Delta H_{neutralisation}$, ΔT_{max} will be the same.

[2]

(v) Provide a reason why this method is preferred to that in **1(h)**.

This method makes use of more data points and is more accurate.

[1]

[Total: 41]

2 Investigation of some chemical reactions involving metal ions

FA 5 is a solid metal carbonate with the formula, XCO_3.
FA 6 is an aqueous solution containing one cation and one anion.

(a) Perform the tests described in Table 2.1, and record your observations in the table. Test and identify any gases evolved.

Table 2.1

	tests	observations
1	Place a spatula of solid **FA 5** in a test-tube. Hold the test-tube in a holder. Heat the test-tube strongly until no further changes are seen. Keep the residue for test 2.	Green solid turned black upon heating. Gas evolved formed white ppt with limewater. Water condensed at upper part of test tube
2	To the residue from test 1, add sufficient amount of **FA 1** to dissolve the residue completely. Keep this solution for tests 3 and 4.	Black solid dissolved to give a pale blue solution. (If solid from test 1 is not completely decomposed, effervescence will be seen here but not a marking point for this.)
3	Add ten drops of the solution obtained from test 2 to a test-tube. Add aqueous NH_3 to this test-tube, until no further change.	Blue ppt formed. Soluble in excess NH_3 to give a dark blue solution.
4	Add ten drops of the solution from test 2 to a test-tube. Then add about 1 cm depth of aqueous potassium iodide and shake the mixture thoroughly. To the mixture, add 1 cm depth of aqueous sodium thiosulfate.	White (off white) ppt formed in brown solution or brown ppt. White (off white) ppt in colourless solution (brown solution decolourised, white ppt seen).
5	Test the **FA 6** solution with the universal indicator paper.	Universal indicator turned orange, pH = 3.
6	Add 1cm depth of **FA 6** to a test tube. Then add a spatula of **FA 3** to the test tube.	Effervescence observed and gas evolved formed white ppt with limewater. White ppt seen.
7	To 1 cm depth of **FA 6**, add 10 drops of nitric acid followed by 10 drops of aqueous barium chloride.	White ppt formed.

[5]

(b) Consider your observation in **Table 2.1**.

(i) Suggest the identities of the cations in **FA 5** and **FA 6** and the anion in **FA 6**.

Cation in **FA 5** : Cu^{2+}

Cation in **FA 6** : Al^{3+}

Anion in **FA 6** : SO_4^{2-}

[2]

(ii) A student carried out test 1 using **FA 3**, it is unlikely for the same observation to be observed for this test. Suggest an explanation to account for this difference.

FA 3 is a group 1 carbonate.

Charge density of group 1 cation is lower, hence it has lower polarising power.

Electron cloud of CO_3^{2-} is less polarised.

Thermal stability of group 1 carbonate is higher, hence does not get

decomposed.

[2]

(iii) Test 4 in **Table 2.1** shows a redox reaction to take place.
Some relevant redox half-equations are given in Table 2.2.

Table 2.2

half equation	E^θ / V
$X^{2+} + e^- \rightleftharpoons X^+$	+0.15
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Using the information in **Table 2.2**, calculate E^θ_{cell} for the reaction shown in your observation in test 4. Suggest a reason for the deviation from the prediction of E^θ_{cell} value calculated.

$E^\theta_{cell} = +0.15 - (+0.54) = -0.39$ V

Reaction should not be spontaneous due to negative E^θ_{cell}.

Due the precipitation of CuI, [Cu^+] dropped, equilibrium of $Cu^{2+} + e \rightleftharpoons Cu^+$

shifts right, favouring reduction.

$E^\theta_{(Cu^{2+}/Cu^+)}$ becomes more positive, E^θ_{cell} becomes more positive.

[2]

(iv) Write an equation to account for the observation to test 5 in **Table 2.1**.

$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H_3O^+$

[1]

(v) Use your answer to **(iv)** to account for the observations to test 6 in **Table 2.1.**

The formation of H_3O^+ from **FA 6** reacts with CO_3^{2-} from **FA 3** produces $CO_2(g)$.

$CO_3^{2-} + 2H_3O^+ \rightarrow 3H_2O + CO_2$

Further hydrolysis of Al^{3+} produces $Al(OH)_3$ which accounts for the white ppt seen.

[2]

[Total: 14]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

END OF PAPER 4

Yishun Junior College
JC2 Preliminary Examinations 2018
H2 Chemistry Practical P4 Preparation List

FA 1 – 0.400 mol dm^{-3} H_2SO_4 ; each student 200 cm^3 in labelled bottle

FA 2 – 0.550 mol dm^{-3} NaOH ; each student 250 cm^3 in labelled bottle

FA 3 – solid Na_2CO_3; each student around 12g. Solid to be placed in clean dry bottle with spatula for student to scoop. Total mass to purchase 5000g. (bought as $CuCO_3$. $Cu(OH)_2$)

FA 4 – student to prepare own standard solution of **FA 3**

FA 5 – 2 g of solid Copper(II) carbonate per student labelled in plastic bottle. (Total mass for all 1000g)

FA 6 – 8 cm^3 of aqueous aluminium sulfate labelled in stoppered plastic bottle (16.661g/250 cm^3; or 333.33g in 5 litre= 0.20M)

21 students in each lab –6 weighing balances

8 students in each lab – 2 weighing balances

Access arrangement – 1 weighing balance

QA reagents
1. limewater
2. aqueous ammonia
3. potassium iodide
4. aqueous sodium thiosulfate
5. aqueous barium chloride
6. Wash bottle filled with deionised water
7. Dilute nitric acid

Apparatus list
Q1. For each student

- 1 empty plastic weighing bottle
- 2 X 250 cm^3 beaker
- 250 cm^3 volumetric flask
- 1 X 50 ml burette labelled FA 2
- 1 X 50 ml burette labelled FA 4
- 1 X 25 ml pipette and filler
- 2 X 250 ml conical flask
- 1 thermometer, gradation 0.2°C
- 1 X 100 ml measuring cylinder
- 1 styrofoam cup (200 cm^3)
- 1 small bottle of methyl orange

Q2. For each student

- 6 hard glass test tubes
- 2 small test tubes for limewater test
- 1 test tube holder
- 1 test tube rack
- 1 test tube cleaning brush
- 1 bunsen burner
- 1 bunsen burner lighter
- 1 safety goggles
- 1 heat proof mat
- 6 plastic droppers
- 2 spatula
- 1 glass rod
- 1 plastic bottle containing filter paper strips, blue and red litmus papers
- 2 strips of universal indicator paper
- 1 universal indicator paper chart
- 2 pieces of paper towels

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

Paper 1 Multiple Choice **19 September 2018**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your Exam Number, name and CT group on the Multiple Choice Answer Sheet.

There are **thirty** questions. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choices in **soft pencil** on the separate Multiple Choice Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. No mark will be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **8** printed pages.

1 The Avogadro constant is *L*. How many neutrons are present in 24 dm^3 of chlorine gas, measured at r.t.p?

A 17*L** **B** 18.5*L* **C** 37*L* **D** 71*L*

2 A carbon sample contains a mixture of ^{12}C and ^{14}C isotopes. When 1.000 g of this sample is burned completely in $^{16}O_2$. The mass of CO_2 formed is 3.629 g.

What is the percentage by mass of the ^{12}C isotope in this sample?

A 85.0% **B** 88.6% **C** 90.0% **D** 91.4%

3 When phosphoryl chloride, $POCl_3$, dissolves in water, it gives a mixture of phosphoric acid and hydrochloric acid. How many moles of sodium hydroxide would be needed to neutralise the solution formed by adding one mole of $POCl_3$ to excess water?

A 3 **B** 4 **C** 5 **D** 6

4 Which of the following pairs have similar shapes and the first species has a smaller bond angle than the second species?

1 $SiCl_4$, PF_4^+

2 PH_3, NH_3

3 SO_3^{2-}, CO_3^{2-}

A 1 only **B** 2 only

C 1 and 2 only **D** 2 and 3 only

5 But-2-enedioic acid, $HC(CO_2H)=C(CO_2H)H$, exists as a pair of *cis*-*trans* isomers. The *cis* isomer has a lower melting point than the *trans* isomer.

Which of the following statements is correct about but-2-enedioic acid?

1 In the solid state, both the *cis* and *trans* isomers have the same density.

2 Intramolecular hydrogen bonding is present in the *cis* isomer.

3 The *cis* isomer is less polar than the *trans* isomer.

A 2 only **B** 1 and 2 only

C 1 and 3 only **D** 2 and 3 only

6 Which of the following statements about prop-1,2-diene, $H_2C=C=CH_2$, is **not** correct?

A The C=C in prop-1,2-diene is stronger than the C=C in ethene.

B The two π-bonds in prop-1,2-diene are perpendicular to each other.

C There are only two sp^2 hybridised carbon atoms in a prop-1,2-diene molecule.

D Prop-1,2-diene is a planar molecule.

7 Which of the following statements is **not** correct?

A Under very high pressure, HC*l* gas behaves more ideally than Cl_2 gas.

B Ideal gas molecules have zero size.

C Real gas molecules behave more ideally under low pressure and high temperature.

D There are no collisions between ideal gas molecules.

8 The lattice energies of the compounds, magnesium oxide, magnesium bromide, sodium oxide and sodium bromide are given below.

Which of the following values corresponds to the lattice energy of magnesium bromide?

A –752 kJ mol^{-1} **B** –2440 kJ mol^{-1}

C –2481 kJ mol^{-1} **D** –3790 kJ mol^{-1}

9 The enthalpy changes of formation of gaseous ethene and ethane are +52 kJ mol^{-1} and –85 kJ mol^{-1} respectively at 298 K.

Consider the following reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Which of the following statements is correct?

A $\Delta S_{reaction}$ is positive.

B The enthalpy change of the reaction is –137 kJ mol^{-1}.

C If ethene is converted to ethane via four stages instead of one as shown above, the enthalpy change of the reaction will be less exothermic.

D The addition of a catalyst will cause the enthalpy change of reaction to be more exothermic.

10 Ammonium chloride readily dissolves in water at room temperature. During the process, the temperature of the solution decreases.

Which of the following statements is correct?

1 Dissolution of ammonium chloride is favoured due to the entropy change.

2 Dissolution of ammonium chloride is not spontaneous at very low temperature.

3 The sum of the hydration energies of ammonium ion and chloride ion is less exothermic than the lattice energy of ammonium chloride.

A 1, 2 and 3 **B** 1 and 2 only

C 2 and 3 only **D** 1 only

11 Three experiments are conducted to determine the rate equation for a reaction between sulfuric acid and sodium thiosulfate. The volumes used and the time taken for the precipitate to form are shown below.

Experiment	Volume of H_2SO_4 / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time / s
1	20	20	20	30
2	40	20	0	15
3	x	20	0	15

What could be a suitable value for x?

A 5 **B** 10 **C** 20 **D** 30

12 Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5×10^9 years.

What would be the age of a rock sample, originally lead-free, in which the molar ratio of uranium to lead is now 1:7?

A 1.5×10^9 years

B 2.25×10^9 years

C 9.0×10^9 years

D 1.35×10^{10} years

13 A reversible reaction is catalysed.

Which of the following statements about this reaction are correct?

1 The catalyst alters the mechanism of the reaction.

2 The catalyst reduces the activation energy for both the forward and the backward reaction.

3 The catalyst alters the composition of the equilibrium mixture.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

14 Pure nitrosyl chloride gas, NOC*l*, was heated at 320 °C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas has dissociated according to the equation below and the total pressure was p atm.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

What is the numerical value of the equilibrium constant, K_p, at 320 °C?

A $\frac{17.9}{p}$ **B** $\frac{41.7}{p}$ **C** $0.0240p$ **D** $0.0276p$

15 What is the pH of the resultant solution when 100 cm^3 of 0.10 mol dm^{-3} aqueous NH_4Cl and 40 cm^3 of 0.15 mol dm^{-3} aqueous NaOH are mixed at 25 °C? (pK_b of NH_3 = 4.75)

A 4.57 **B** 4.93 **C** 9.07 **D** 9.43

16 The value of the solubility product, K_{sp}, of silver chromate(VI), Ag_2CrO_4, is 2.5×10^{-22} at 25 °C.

Which statement about silver chromate(VI) is correct?

A The units for K_{sp} of silver chromate(VI) are $mol^2\ dm^{-6}$.

B Addition of nitric acid will cause K_{sp} value of silver chromate(VI) to increase.

C Addition of nitric acid will cause the solubility of silver chromate(VI) to increase.

D The solubility of silver chromate(VI) in water is 1.58×10^{-11} mol dm^{-3}.

17 Which of the following changes does not alter the reduction potential measured for a Cl_2/Cl^- half-cell?

A Adding water into the half-cell.

B Placing the half-cell in an ice-water bath.

C Adding silver ions into the half-cell.

D Introducing an additional 1 bar of inert gas into the half-cell.

18 When a large current was passed through an aqueous copper(II) sulfate solution with two inert electrodes, there was liberation of x mol of copper and y dm^3 of oxygen, measured at r.t.p.

How many moles of electrons passed through the circuit?

A $x+\frac{y}{12}$ **B** $x+\frac{y}{6}$ **C** $2x+\frac{y}{12}$ **D** $2x+\frac{y}{6}$

19 Which of the following statements concerning the chlorine-containing compounds of period 3 elements is correct?

A PCl_3 and Cl_2O_7 are both acidic in nature due to their reactions with water.

B NaC*l* dissolves easily in water due to the favourable ion-dipole interactions and the compounds with the highest electrical conductivity in molten state is $AlCl_3$.

C The low boiling points of PCl_3 and Cl_2O_7 are due to the weak P–C*l* and C*l*–O bond energies.

D Both CCl_4 and $SiCl_4$ can dissolve in excess water completely to give an acidic solution.

20 When aqueous ammonia is added to a solution containing hexaaquairon(III) ions, $[Fe(H_2O)_6]^{3+}$, a red-brown precipitate is formed which does not dissolve in excess ammonia.

What is the role of the ammonia molecule in this reaction?

A Bronsted-Lowry base

B Lewis acid

C Ligand

D Reducing agent

21 Which types of stereoisomerism are shown by 2,4-dimethylhex-2-ene?

A enantiomerism only

B *cis-trans* isomerism only

C both *cis-trans* isomerism and enantiomerism

D neither *cis-trans* isomerism nor enantiomerism

22 A sample of ethene was added to a solution containing both Br_2(aq) and NaCl(aq). Which of the following products is **not** likely to be found in the reaction mixture?

A $CH_2(OH)CH_2Br$

B CH_2BrCH_2Cl

C $CH_2(OH)CH_2Cl$

D CH_2BrCH_2Br

23 Organic compound **X** gives a precipitate when warmed with aqueous silver nitrate. This precipitate dissolves when concentrated aqueous ammonia is added.

What could **X** be?

1 1-bromopropane
2 1-chloropropane
3 chlorobenzene

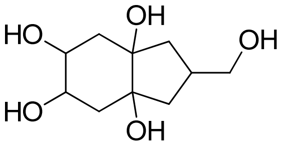
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

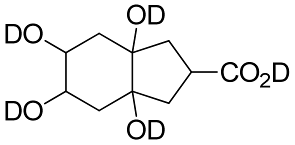
D 1 only

24 Deuterium, D, is an isotope of hydrogen. Which of the following is the product formed when the compound **Y** is distilled with $K_2Cr_2O_7$ in aqueous D_2SO_4?

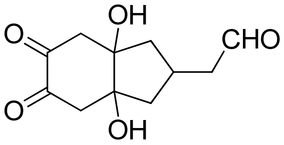


Compound **Y**

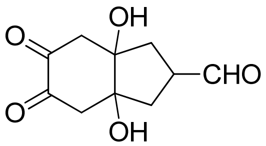
A



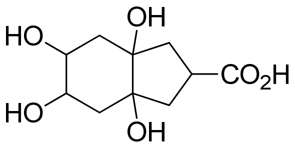
B



C



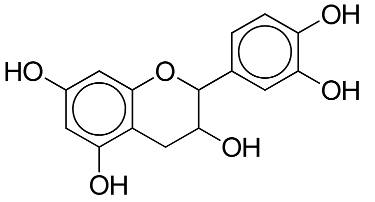
D



25 Starting with $C_6H_5COCH_3$, which two-stage process does **not** involve a condensation reaction?

	stage 1	**stage 2**
A	HCN with trace NaCN	NaOH
B	NH_2NH_2	NaOH
C	I_2 with NaOH	C_2H_5OH with conc. H_2SO_4
D	$NaBH_4$	CH_3COCl

26 Catechin is an antioxidant found in tea leaves, chocolates and red wine. It is often studied for its function as an inhibitor to the growth of cancer cells, amongst other health benefits.



catechin

Which of the following statements about catechin is correct?

A 1 mol of catechin reacts with 5 mol of NaOH.

B It can undergo electrophilic substitution with 2.5 mol of $Br_2(aq)$.

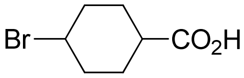
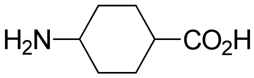
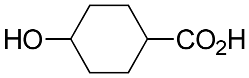
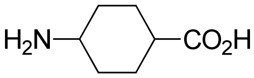
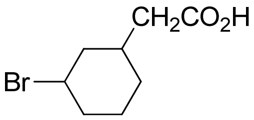
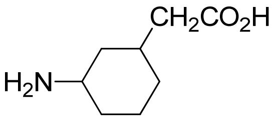
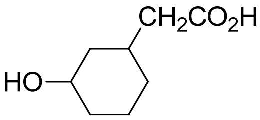
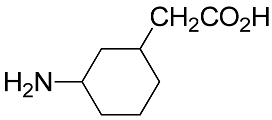
C It can undergo oxidation with hot alkaline $KMnO_4(aq)$.

D 1 mol of catechin reacts with 2 mol of Na_2CO_3.

27 The diagram below shows a reaction scheme for the formation of compound **Z**.

Compound **Z**

Which combination could be **X** and **Y**?

	X	**Y**
A		
B		
C		
D		

28 Equal amounts of two organic compounds, **P** and **Q**, were separately added to 100 cm^3 of water and the pH values of both solutions were determined. It was found that the pH of the aqueous solution of **P** is higher.

Which pairs of compounds could be **P** and **Q**?

	P	**Q**
1	CH_3CH_2OH	CH_3CO_2H
2	$CH_3CH_2NH_2$	$C_6H_5NH_2$
3	C_6H_5ONa	$C_6H_5CO_2Na$

A 1, 2 and 3

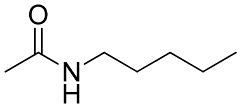
B 1 and 2 only

C 2 and 3 only

D 1 only

29 An amide, **M**, has the empirical formula $C_7H_{15}ON$. When **M** is hydrolysed by heating under reflux with dilute hydrochloric acid, a carboxylic acid with empirical formula C_2H_4O is obtained as one of the products.

What could be the skeletal formula of **M**?

1


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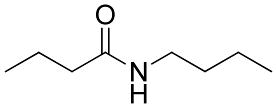

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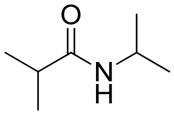


A 1, 2 and 3

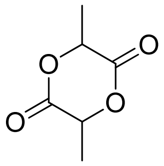
B 1 only

C 2 and 3 only

D 3 only

30 Which ester might be formed when lactic acid, $CH_3CH(OH)CO_2H$, is heated?

1 $CH_3CH(OH)CO_2CH(CH_3)CO_2H$

2


3 $CH_3CH(OH)CO_2CH(OH)CH_3$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Qn	Answer
1	**C**
2	**C**
3	**D**
4	**B**
5	**A**
6	**D**
7	**D**
8	**B**
9	**B**
10	**A**
11	**B**
12	**D**
13	**B**
14	**C**
15	**D**
16	**C**
17	**D**
18	**A**
19	**A**
20	**A**
21	**A**
22	**C**
23	**B**
24	**C**
25	**A**
26	**C**
27	**C**
28	**A**
29	**D**
30	**B**

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY **9729/02**

Paper 2 Structured **11 September 2018**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 20**
2	**/ 20**
3	**/ 20**
4	**/ 15**
Total	**/ 75**

This document consists of **20** printed pages.

Answer **all** the questions in the spaces provided.

1 **(a)** Bromine exists naturally as a mixture of two stable isotopes, ^{79}Br and ^{81}Br, in a 1:1 ratio.

(i) Write down the full electronic configuration of $^{79}Br^{2+}$.

.... [1]

(ii) Define the term *relative isotopic mass*.

....

.... [1]

(b) Chlorine atom exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in a 3:1 ratio. When equimolar amounts of bromine and chlorine were mixed together, an interhalogen compound, BrC*l*, is formed. The product mixture contains four species with three different mass numbers 114, 116 and 118. $^{79}Br^{35}Cl$ is one of the four species.

(i) With the help of the information given in **(a)**, state the species that corresponds to each mass number. Hence, calculate the relative abundance for each mass number.

mass number	species	relative abundance
114	$^{79}Br^{35}Cl$	
116		
118		

[3]

(ii) Explain whether BrC*l* or Cl_2 has a greater enthalpy change of vaporisation.

....

....

.... [1]

(iii) Suggest with a reason how the first ionisation energy of ^{79}Br is compared to ^{81}Br.

....

.... [1]

(c) Bromine reacts with an element **A** to form a compound with empirical formula **A**Br_3. The percentage by mass of **A** in **A**Br_3 is 4.31%. Calculate the relative atomic mass of **A**.

[1]

(d) Bromine and fluorine react to form the pale yellow liquid, bromine trifluoride, as shown in **Reaction 1**.

Reaction 1 $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$

Some thermochemical data are given below.

Standard enthalpy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–301
Standard Gibbs free energy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–241
Standard entropy of $Br_2(l)$, $S^{\ominus}(Br_2)$ / J mol^{-1} K^{-1}	152
Standard entropy of $BrF_3(l)$, $S^{\ominus}(BrF_3)$ / J mol^{-1} K^{-1}	178

(i) The above reaction is spontaneous at 298 K even though $\Delta S^{\ominus}$ is negative. Explain qualitatively why $\Delta H^{\ominus}$ is the predominant factor that causes the reaction to be spontaneous.

....

.... [1]

(ii) Sketch a graph to show how $\Delta G^{\ominus}$ varies with temperature in K for **Reaction 1**. Label the y–intercept.

[1]

(iii) Given that $\Delta S^\ominus = 2 \times S^\ominus(BrF_3) - [S^\ominus(Br_2) + 3 \times S^\ominus(F_2)]$ for **Reaction 1**, calculate the standard entropy of $F_2(g)$, $S^\ominus(F_2)$, at 298 K.

[2]

(e) Similar to water, liquid BrF_3 can be used as a solvent and it undergoes minimal self–ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

When $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$ react in BrF_3, an insoluble Ag_2SnF_6 is formed.

(i) Construct an equation for the reaction between $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$.

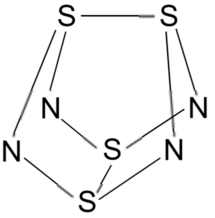
……………………………………………………………………………………………… [1]

(ii) State and draw the shapes of BrF_2^+ and BrF_4^-, including lone pairs of electrons.

BrF_2^+	BrF_4^-

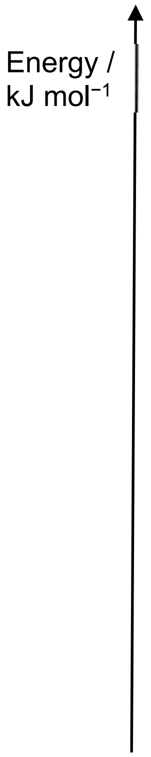
[2]

(f) One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent. A proposed structure of the molecule of S_4N_4 is shown below.



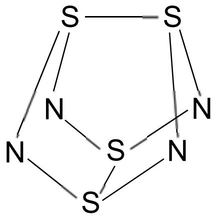
(i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4.

$\Delta H_f^\ominus[S_4N_4(g)] = +460$ kJ mol^{-1}
$\Delta H_{at}^\ominus[S(s)] = +279$ kJ mol^{-1}
$\Delta H_{at}^\ominus$[nitrogen] = +497 kJ mol^{-1}
Bond energy of (S–S) in S_4N_4 = +204 kJ mol^{-1}



[3]

(ii) The nitrogen atoms in S_4N_4 show their usual valency of 3. All four sulfur atoms have the same oxidation number. Add to the structure below to show which sulfur–nitrogen bonds are single bonds and which are double bonds.



[1]

(iii) Hence, explain why the calculated bond energy of sulfur–nitrogen bond in S_4N_4 from **(f)(i)** is between that of a S−N bond and a S=N bond.

……………………………………………………………………………………………

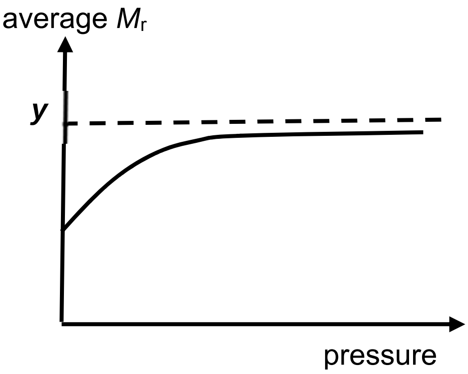
……………………………………………………………………………………… .[1]

[Total: 20]

2 **(a)** Dinitrogen tetraoxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other as shown below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(i) The diagram below shows the variation of the average molecular mass of the equilibrium mixture with pressure.



Predict a value for ***y*** and account for the shape of the graph.

....

....

....

.... [2]

0.0100 mol of inert N_2 with a partial pressure of 0.27 bar and 0.0500 mol of N_2O_4 were placed in a sealed vessel of volume 1.00 dm^3 and temperature of 50 °C. When equilibrium was established, the total pressure of all gases was 1.95 bar.

(ii) With reference to the *Data Booklet*, calculate the average molecular mass, M_r, of the N_2O_4/NO_2 equilibrium mixture. Give your answer to **three** significant figures.

[2]

(iii) Use your answer in **(a)(ii)** to calculate the mole fraction of NO_2 in the N_2O_4/NO_2 equilibrium mixture.

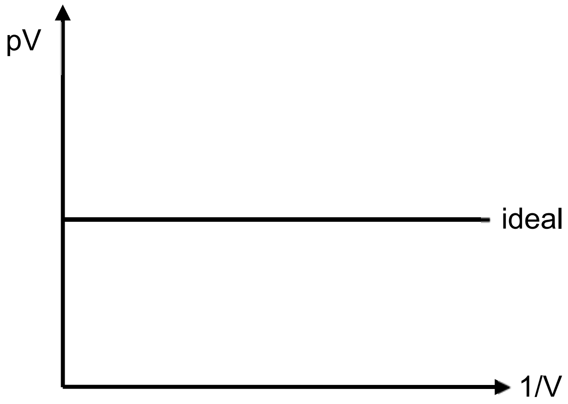
[1]

(iv) Write an expression for the equilibrium constant, K_c, for this N_2O_4/NO_2 equilibrium. Calculate the value of K_c and give its units.

[2]

(v) Sketch and label on the same axes, a graph of variation of pV against 1/V at constant temperature for 1 mol of

(I) N_2O_4, and
(II) NO_2.

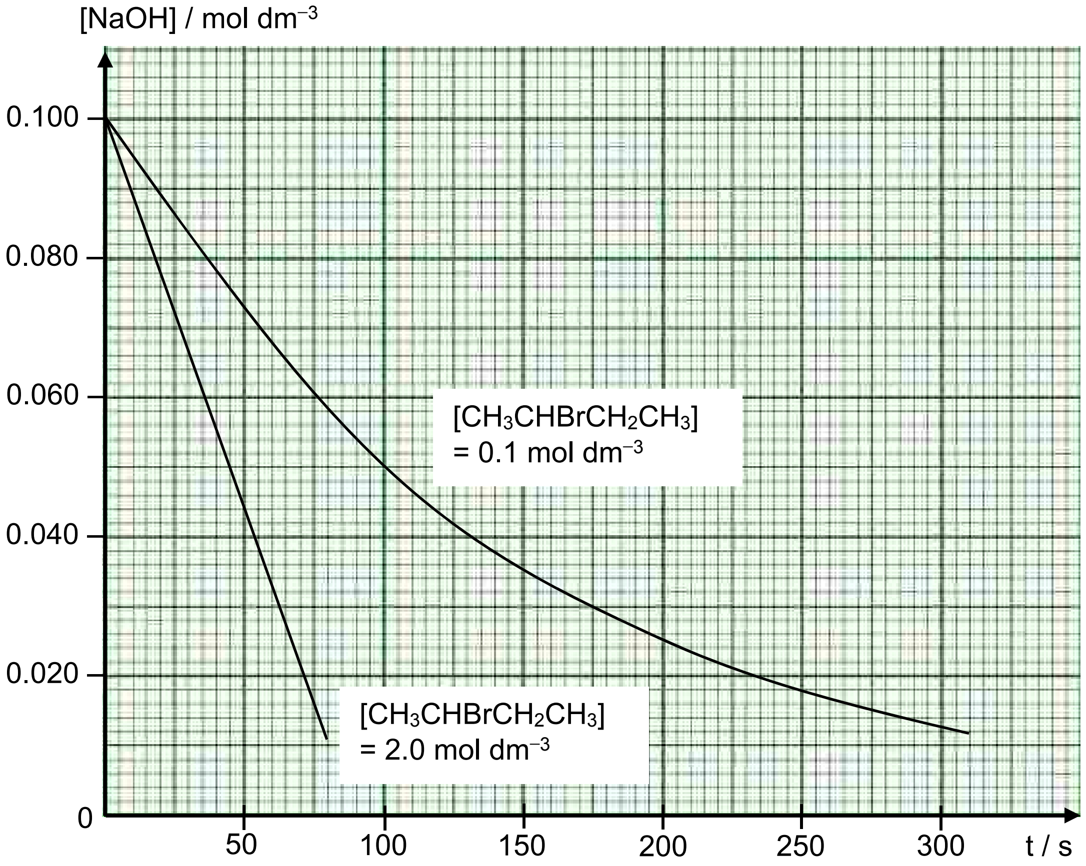


[1]

(b) 2–bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide. The kinetics of the reaction was determined by monitoring the change in concentration of sodium hydroxide with time.

Two sets of experiments were performed using different initial concentrations of 2–bromobutane while the initial concentration of sodium hydroxide was kept at 0.100 mol dm^{-3}.

The following graphs are obtained.



(i) Explain the terms *order of reaction* and *half–life*.

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…………………………………………………………………………………………… [2]

(ii) Use the graphs to determine the order of reaction with respect to

(I) NaOH, and

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

(II) $CH_3CHBrCH_2CH_3$

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… [2]

(iii) By determining the half–life for the graph of $[CH_3CHBrCH_2CH_3] = 0.1$ mol dm^{-3}, calculate the initial rate at t = 0 min, including its units.

[2]

(iv) Write two elementary equations to show how $CH_3CHBrCH_2CH_3$ and NaOH react.

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(v) $C_6H_5CH_2Br$ reacts with NaOH(aq) via an S_N1 mechanism. Suggest why this may be so.

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(c) 2–iodobutane, $CH_3CHICH_2CH_3$, exists as two enantiomers, **A** and **B**, which rotate plane–polarised light in opposite directions.

An optically pure sample containing only isomer **A** rotates plane–polarised light by an angle of +15.0°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in a mixture of ethanol and water. The product mixture is found to rotate plane–polarised light by an angle of −6.4°. The reaction is found to proceed by both the S_N1 and S_N2 mechanisms. If S_N1 and S_N2 mechanisms proceed in a ratio of 1:1, the percentage composition of **B** is 75%.

(i) Determine the percentage composition of **B** in the product mixture. Hence, deduce the predominant mechanism for the above reaction.

[2]

(ii) Describe the S_N2 mechanism for the reaction of $CH_3CHICH_2CH_3$ with $^{131}I^-$.

[2]

[Total: 20]

3 Nickel is widely used as components of fuel cells and batteries. It often occurs in ores along with iron as metal oxides. After the initial reduction of the ore with carbon, a nickel–iron alloy is formed. It can then be purified by an electrolysis technique.

(a) On the other hand, Group 2 metal oxides such as magnesium oxide, are not reduced by carbon. Use relevant data from the *Data Booklet* to explain why carbon can reduce oxides of nickel and iron but not magnesium oxide.

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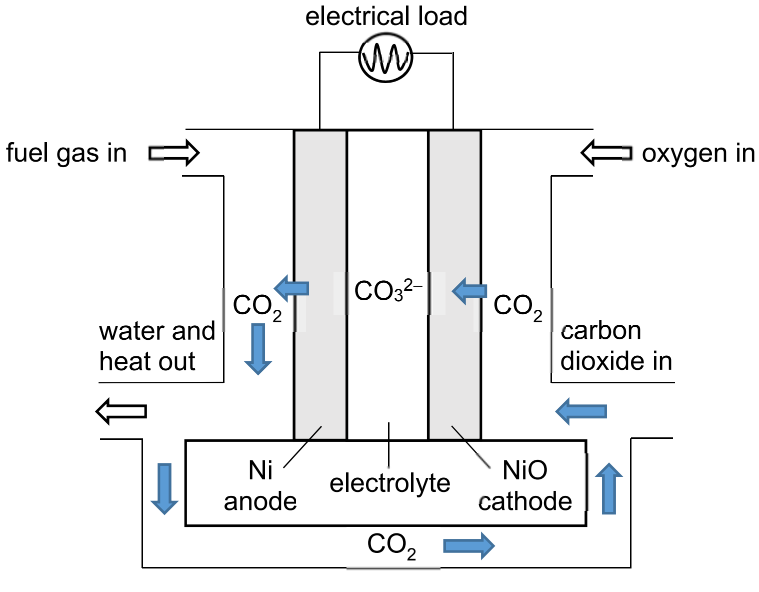
……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(b) Nickel and nickel(II) oxide are used as electrodes in molten carbonate fuel cells (MCFC).

MCFC operates at temperatures above 650 °C to ensure ionic conductivity of its electrolyte, which is a mixture of lithium carbonate and potassium carbonate.

The high temperature also allows fuel reforming which produces hydrogen gas at the anode for the electrochemical reaction. Fuel gases, such as natural gas and other higher hydrocarbons derived from biomass, could be used with MCFC. The CO_2 generated at the anode is recycled to the cathode where it is consumed as shown in the schematic diagram of MCFC below.



(i) When a hydrocarbon C_xH_y is used as the fuel gas, it undergoes fuel reforming with H_2O at the anode to produce hydrogen gas and carbon monoxide.

Write a balanced equation for the fuel reforming of the hydrocarbon, C_xH_y.

…………………………………………………………………………………… [1]

(ii) The fuel reforming is catalysed by the nickel. Explain the mode of action of the nickel catalyst.

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…………………………………………………………………………………………… [2]

(iii) Carbonates are generated at the cathode by the reaction between oxygen and carbon dioxide. The carbonate ions then diffuse across the electrolyte to the anode and react with hydrogen gas, generating steam and carbon dioxide.

Write the half–equations at both electrodes and hence give the overall equation for the MCFC.

Cathode: ……………………………………………………………………………..

Anode: ……………………………………………………………………………..

Overall: ……………………………………………………………………………..
[2]

(iv) The temperature of MCFC is kept constant.

With reference to your answer from **(b)(iii)**, state and explain the effect of increasing the partial pressure of oxygen on the cell potential of this MCFC.

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……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(c) Biomass from farms could be used to produce fuel gases for MCFC to power an ammonia–making plant for the farming community. The ammonia is manufactured in the following three–step process.

Step 1: Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

$$4LiOH \rightarrow 4Li + 2H_2O + O_2$$

Step 2: Reaction of lithium metal with nitrogen to form lithium nitride.

$$3Li + \tfrac{1}{2}N_2 \rightarrow Li_3N$$

Step 3: Reaction of lithium nitride with water to re–form lithium hydroxide and ammonia.

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Thus, the lithium hydroxide formed in **Step 3** can be re–used in **Step 1** and the process can be repeated.

(i) The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the cell potential by 0.60 V.

Use appropriate $E^\ominus$ values from the *Data Booklet* to calculate the minimum potential that should be applied in **Step 1**.

[2]

(ii) State the ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3**.

.... [1]

(iii) A farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a farm of 100 acres in a year.

[1 tonne = 10^6 g]

[2]

(d) Unlike lithium carbonate and potassium carbonate, a mixture of Group 2 carbonates consisting of magnesium carbonate and barium carbonate is **not** a suitable electrolyte for the molten carbonate fuel cell (MCFC) in **(b)**. For each of the carbonates, suggest a reason why it is not a suitable electrolyte.

Magnesium carbonate:

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

Barium carbonate:

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

[2]

(e) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} barium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.
[$K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; $K_{sp}(BaCO_3) = 5.1 \times 10^{-9}$ mol^2 dm^{-6}]

(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen.

[1]

(ii) Determine the concentration of the metal ion stated in **(e)(i)** when the other metal ion just begins to precipitate.

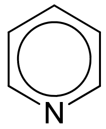
[2]

(iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective.

[1]

[Total: 20]

4 (a) Pyridine is an aromatic planar molecule similar to benzene. Unlike benzene, pyridine can act as a Bronsted–Lowry base and a nucleophile.



pyridine

(i) State the type of hybridisation of the nitrogen atom in pyridine.

…………………………………………………………………………………… [1]

(ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $CH_3CH_2NH_2$.

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… [1]

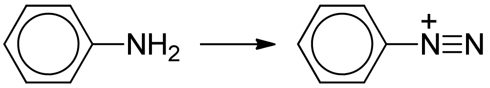
(iii) Write a balanced equation to show that pyridine is acting as

a Bronsted–Lowry base

a Lewis base but not a Bronsted–Lowry base

[2]

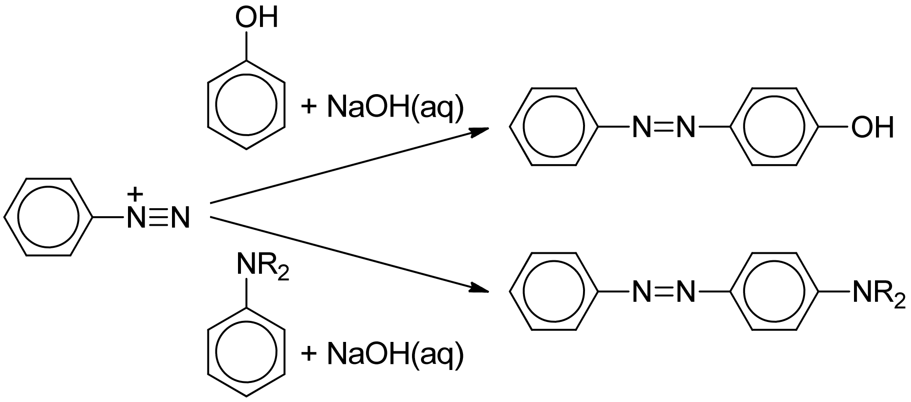
(b) Phenylamine and subsituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.



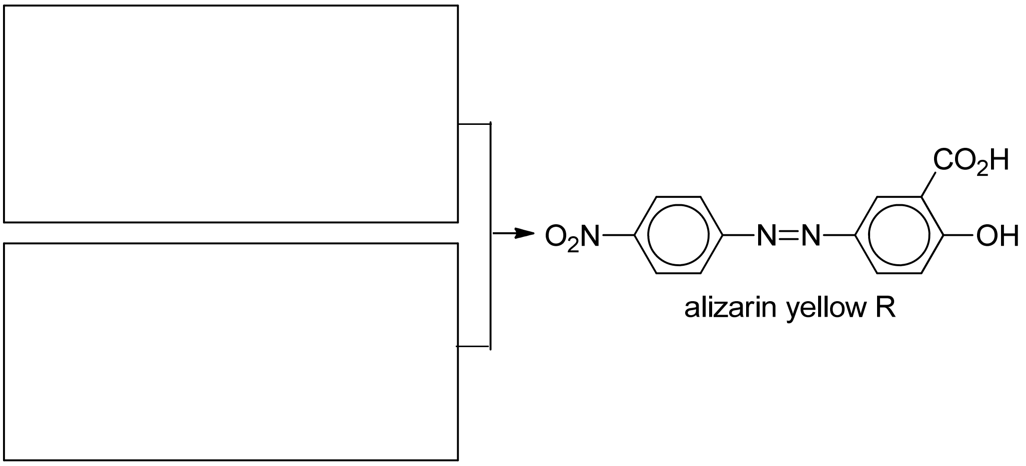
(i) State the type of reaction.

………………………………………………………………………………………… [1]

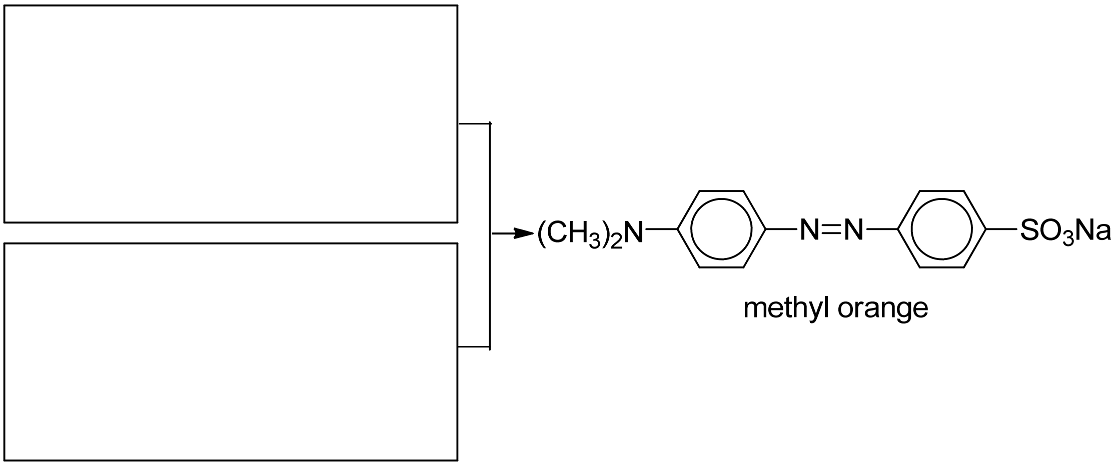
The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



(ii) Suggest the starting compounds needed to synthesise the following dyes. Draw their full structural formulae in the boxes provided.



alizarin yellow R



methyl orange

[4]

(iii) The benzene ring containing the NaO_3S- group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

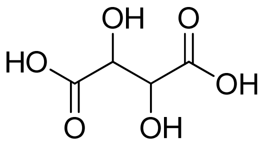
…………………………………………………………………………………………… [2]

(iv) Alizarin yellow R exhibits stereoisomerism and is a common indicator for acid−base titrations.

Draw the stereoisomers of alizarin yellow R.

[1]

(c) Tartaric acid is present in many plants.

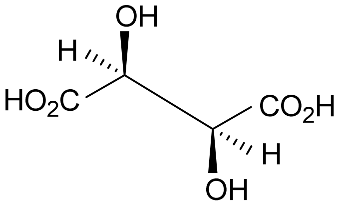


tartaric acid

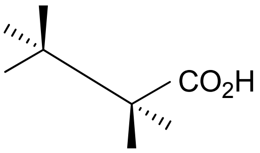
(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.

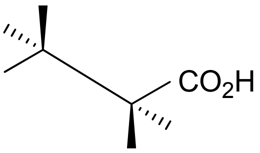
[1]

(ii) One stereoisomer of tartaric acid is shown below.



Complete the diagrams below to show two other stereoisomers of tartaric acid.





[2]

[Total: 15]

End of Paper

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/02

Paper 2 Structured **11 September 2018**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 20**
2	**/ 20**
3	**/ 20**
4	**/ 15**
Total	**/ 75**

This document consists of **20** printed pages.

Answer **all** the questions in the spaces provided.

1 **(a)** Bromine exists naturally as a mixture of two stable isotopes, ^{79}Br and ^{81}Br, in a 1:1 ratio.

(i) Write down the full electronic configuration of $^{79}Br^{2+}$.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$

[1]

(ii) Define the term *relative isotopic mass*.

Mass of an atom of isotope relative to $\frac{1}{12}$ the mass of an atom of carbon–12 isotope.

[1]

(b) Chlorine atom exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in a 3:1 ratio. When equimolar amounts of bromine and chlorine were mixed together, an interhalogen compound, BrC*l*, is formed. The product mixture contains four species with three different mass numbers 114, 116 and 118. $^{79}Br^{35}Cl$ is one of the four species.

(i) With the help of the information given in **(a)**, state the species that corresponds to each mass number. Hence, calculate the relative abundance for each mass number.

mass number	species	relative abundance
114	$^{79}Br^{35}Cl$	$\frac{1}{2} \times \frac{3}{4} = \frac{3}{8}$
116	$^{79}Br^{37}Cl$ and $^{81}Br^{35}Cl$	$(\frac{1}{2} \times \frac{1}{4}) + (\frac{1}{2} \times \frac{3}{4}) = \frac{1}{2}$
118	$^{81}Br^{37}Cl$	$\frac{1}{2} \times \frac{1}{4} = \frac{1}{8}$

[3]

(ii) Explain whether BrC*l* or Cl_2 has a greater enthalpy change of vaporisation.

BrC*l* has a greater enthalpy change of vaporisation as it has stronger instantaneous dipole–induced dipole interactions due to the greater number of electrons in the larger BrC*l* molecule.

OR

BrC*l* has a greater enthalpy change of vaporisation as it is polar with stronger permanent dipole–permanent dipole interactions than the instantaneous dipole–induced dipole interactions in Cl_2.

[1]

(iii) Suggest with a reason how the first ionisation energy of ^{79}Br is compared to ^{81}Br.

First ionisation energy of ^{79}Br is the same as that of ^{81}Br because they have the same number of protons.

[1]

(c) Bromine reacts with an element **A** to form a compound with empirical formula **A**Br_3. The percentage by mass of **A** in **A**Br_3 is 4.31%. Calculate the relative atomic mass of **A**.

Let A_r of A be y.

Element	**A**	**Br**
No. of moles/mol	$\frac{4.31}{y}$	$\frac{100-4.31}{79.9}$

Mole ratio of A : Br = 1 : 3 = $\frac{4.31}{y} : \frac{100-4.31}{79.9}$

No. of moles of Br atoms = 3 × no. of moles of A atoms

$\frac{100-4.31}{79.9} = 3 \times \frac{4.31}{y}$

$y = 10.8$

[1]

(d) Bromine and fluorine react to form the pale yellow liquid, bromine trifluoride, as shown in **Reaction 1**.

Reaction 1 $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$

Some thermochemical data are given below.

Standard enthalpy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–301
Standard Gibbs free energy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–241
Standard entropy of $Br_2(l)$, $S^\ominus(Br_2)$ / J mol^{-1} K^{-1}	152
Standard entropy of $BrF_3(l)$, $S^\ominus(BrF_3)$ / J mol^{-1} K^{-1}	178

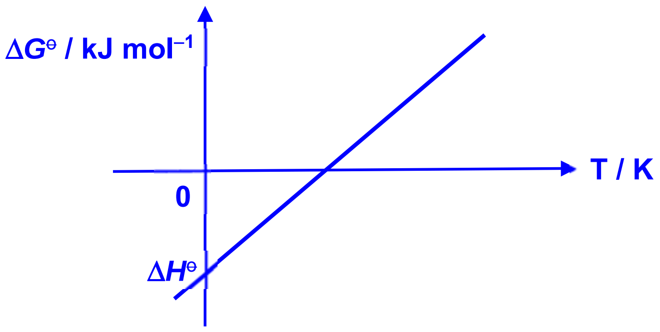
(i) The above reaction is spontaneous at 298 K even though $\Delta S^\ominus$ is negative. Explain qualitatively why $\Delta H^\ominus$ is the predominant factor that causes the reaction to be spontaneous.

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus < 0$ at 298 K

$\Delta H^\ominus$ is the predominant factor as it is exothermic (or negative) and drives the reaction.

[1]

(ii) Sketch a graph to show how $\Delta G^\ominus$ varies with temperature in K for **Reaction 1**. Label the y–intercept.



[1]

(iii) Given that $\Delta S^\ominus = 2 \times S^\ominus(BrF_3) - [S^\ominus(Br_2) + 3 \times S^\ominus(F_2)]$ for **Reaction 1**, calculate the standard entropy of $F_2(g)$, $S^\ominus(F_2)$, at 298 K.

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$
$$\Delta S^\ominus = (\Delta H^\ominus - \Delta G^\ominus) / T$$
$$= 2(-301 + 241) \times 10^3 / 298$$
$$= -403 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$-403 = 2(178) - [152 + 3S^\ominus(F_2)]$$
$$S^\ominus(F_2) = 202 \text{ J mol}^{-1} \text{ K}^{-1}$$

[2]

(e) Similar to water, liquid BrF_3 can be used as a solvent and it undergoes minimal self–ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

When $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$ react in BrF_3, an insoluble Ag_2SnF_6 is formed.

(i) Construct an equation for the reaction between $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$.

$$(BrF_2^+)_2(SnF_6^{2-}) + 2Ag^+(BrF_4^-) \rightarrow 4BrF_3 + Ag_2SnF_6$$

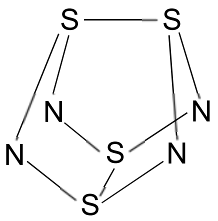
[1]

(ii) State and draw the shapes of BrF_2^+ and BrF_4^-, including lone pairs of electrons.

bent	**square planar**
BrF_2^+	BrF_4^-

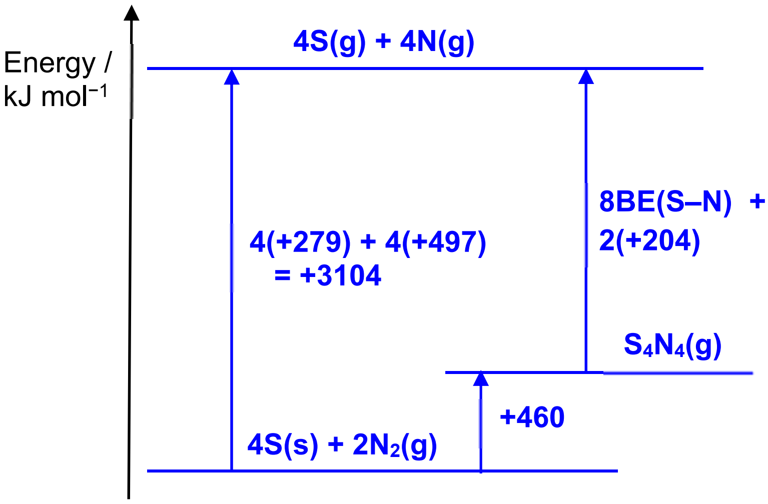
[2]

(f) One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent. A proposed structure of the molecule of S_4N_4 is shown below.



(i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4.

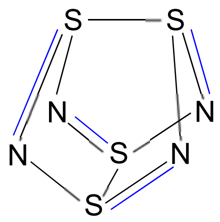
$\Delta H_f^\ominus[S_4N_4(g)] = +460\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus[S(s)] = +279\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus[\text{nitrogen}] = +497\ kJ\ mol^{-1}$
Bond energy of (S–S) in S_4N_4 = +204 kJ mol^{-1}



By Hess's Law,
$8BE(S–N) + 2(+204) = –(+460) + 3104$
$BE(S–N) = +279.5\ kJ\ mol^{-1}$

[3]

(ii) The nitrogen atoms in S_4N_4 show their usual valency of 3. All four sulfur atoms have the same oxidation number. Add to the structure below to show which sulfur–nitrogen bonds are single bonds and which are double bonds.



[1]

(iii) Hence, explain why the calculated bond energy of sulfur–nitrogen bond in S_4N_4 from **(f)(i)** is between that of a S−N bond and a S=N bond.

This is due to the delocalisation of pi electrons / formation of resonance structures between the two sulfur−nitrogen bonds in S−N−S / N−S−N.

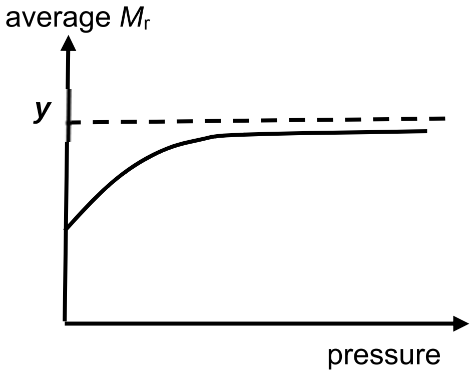
[1]

[Total: 20]

2 **(a)** Dinitrogen tetraoxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other as shown below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(i) The diagram below shows the variation of the average molecular mass of the equilibrium mixture with pressure.



Predict a value for ***y*** and account for the shape of the graph.

y = 2(14.0) + 4(16.0) = 92.0
By Le Chatelier's Principle, as pressure increases, the position of equilibrium would shift left to decrease the amount of gaseous molecules. Hence, more N_2O_4 will be produced and average M_r increases.

[2]

0.0100 mol of inert N_2 with a partial pressure of 0.27 bar and 0.0500 mol of N_2O_4 were placed in a sealed vessel of volume 1.00 dm^3 and temperature of 50 °C. When equilibrium was established, the total pressure of all gases was 1.95 bar.

(ii) With reference to the *Data Booklet*, calculate the average molecular mass, M_r, of the N_2O_4/NO_2 equilibrium mixture. Give your answer to **three** significant figures.

Mass of N_2O_4 initially = Total mass of N_2O_4 and NO_2 at equilibrium
= 0.0500 × 92.0
= 4.60 g

Total pressure of N_2O_4 and NO_2 at equilibrium
= 1.95 – 0.27
= 1.68 bar

$$pV = nRT = \frac{m}{M_r}RT$$
$$1.68 \times 10^5 \times 1.00 \times 10^{-3} = \frac{4.60}{M_r} \times 8.31 \times (273 + 50)$$
$$M_r = 73.5$$

[2]

(iii) Use your answer in **(a)(ii)** to calculate the mole fraction of NO_2 in the N_2O_4/NO_2 equilibrium mixture.

Let the mole fraction of NO_2 be z. Then the mole fraction of N_2O_4 is $(1 – z)$.

$$46z + 92(1 - z) = 73.5$$
$$z = 0.402$$

[1]

(iv) Write an expression for the equilibrium constant, K_c, for this N_2O_4/NO_2 equilibrium. Calculate the value of K_c and give its units.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Total number of moles of N_2O_4 and NO_2 at equilibrium
= 4.60 ÷ 73.5
= 0.0626 mol

n_{NO_2}
= 0.402 × 0.0626
= 0.0252 mol

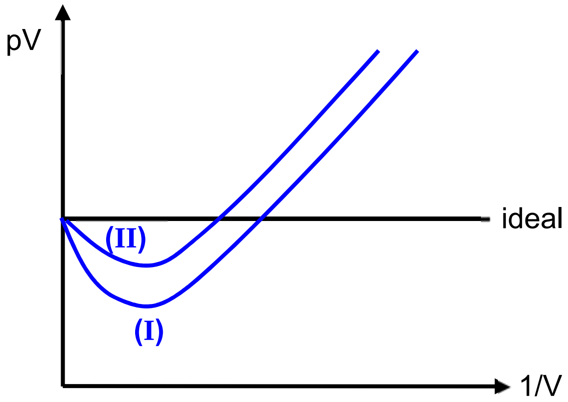
$n_{N_2O_4}$
= 0.0626 – 0.0252
= 0.0374 mol

$$K_c = \frac{(0.0252)^2}{0.0374}$$
$$= 0.0170 \text{ mol dm}^{-3}$$

[2]

(v) Sketch and label on the same axes, a graph of variation of pV against 1/V at constant temperature for 1 mol of

(I) N_2O_4, and
(II) NO_2.

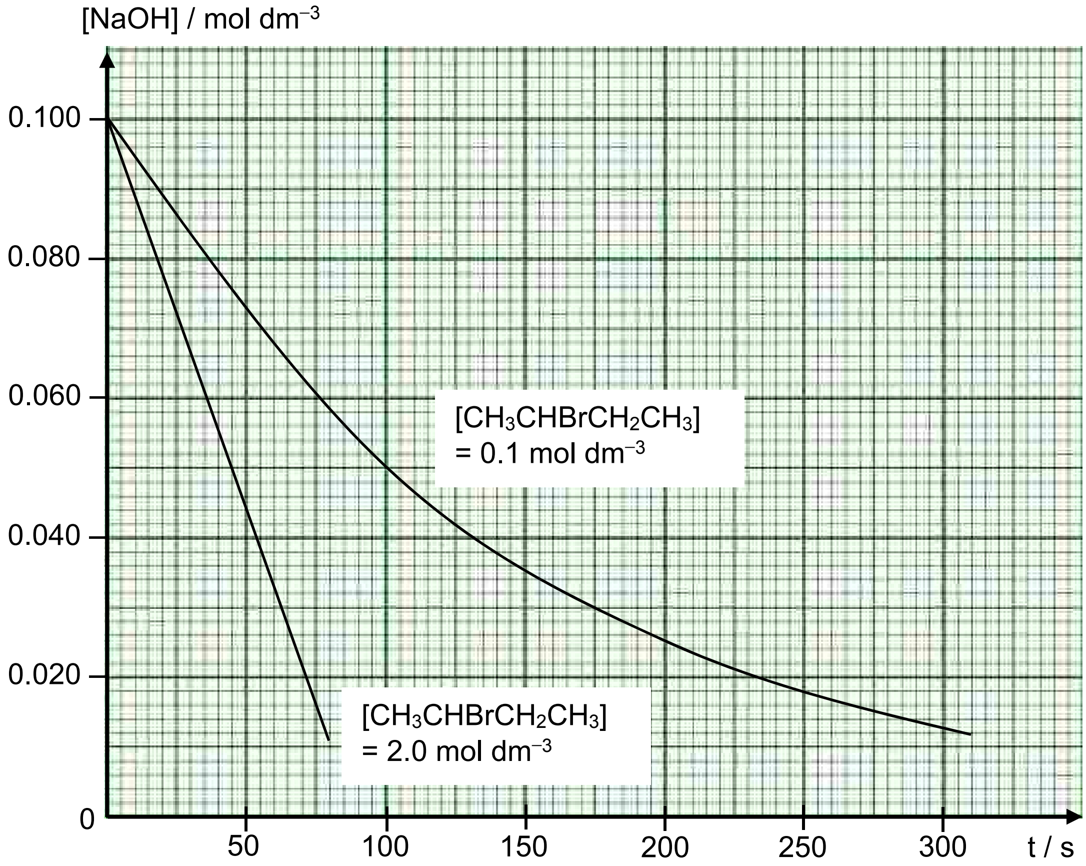


[1]

(b) 2–bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide. The kinetics of the reaction was determined by monitoring the change in concentration of sodium hydroxide with time.

Two sets of experiments were performed using different initial concentrations of 2–bromobutane while the initial concentration of sodium hydroxide was kept at 0.100 mol dm^{-3}.

The following graphs are obtained.



(i) Explain the terms *order of reaction* and *half–life*.

The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation.

The half–life ($t_{1/2}$) of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

[2]

(ii) Use the graphs to determine the order of reaction with respect to

(I) NaOH, and

When [$CH_3CHBrCH_2CH_3$] = 2.0 mol dm^{-3}, $CH_3CHBrCH_2CH_3$ is in excess and has pseudo zeroth order. From the graph of [$CH_3CHBrCH_2CH_3$] = 2.0 mol dm^{-3}, rate is a constant as seen from the constant gradient.

Thus, order of reaction wrt NaOH is zero.

(II) $CH_3CHBrCH_2CH_3$

From the graph of [$CH_3CHBrCH_2CH_3$] = 0.1 mol dm^{-3}, $t_{1/2}$ is constant.

Thus, order of reaction wrt $CH_3CHBrCH_2CH_3$ is one.

[2]

(iii) By determining the half–life for the graph of $[CH_3CHBrCH_2CH_3] = 0.1$ mol dm^{-3}, calculate the initial rate at t = 0 min, including its units.

$t_{1/2} = 100$ s
$k = \ln 2 \div 100$
$k = 6.93 \times 10^{-3}$ s^{-1}

Rate $= k\,[CH_3CHBrCH_2CH_3]$
$= 6.93 \times 10^{-3} \times 0.1$
$= 6.93 \times 10^{-4}$ mol dm^{-3} s^{-1}

[2]

(iv) Write two elementary equations to show how $CH_3CHBrCH_2CH_3$ and NaOH react.

$CH_3CHBrCH_2CH_3 \rightarrow CH_3\overset{+}{C}HCH_2CH_3 + Br^-$ slow

$CH_3\overset{+}{C}HCH_2CH_3 + OH^- \rightarrow CH_3CH(OH)CH_2CH_3$ fast

[1]

(v) $C_6H_5CH_2Br$ reacts with NaOH(aq) via an S_N1 mechanism. Suggest why this may be so.

The carbocation from $C_6H_5CH_2Br$ is resonance–stabilised as the positive charge can delocalise into the benzene ring.

[1]

(c) 2–iodobutane, $CH_3CHICH_2CH_3$, exists as two enantiomers, **A** and **B**, which rotate plane–polarised light in opposite directions.

An optically pure sample containing only isomer **A** rotates plane–polarised light by an angle of +15.0°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in a mixture of ethanol and water. The product mixture is found to rotate plane–polarised light by an angle of −6.4°. The reaction is found to proceed by both the S_N1 and S_N2 mechanisms. If S_N1 and S_N2 mechanisms proceed in a ratio of 1:1, the percentage composition of **B** is 75%.

(i) Determine the percentage composition of **B** in the product mixture. Hence, deduce the predominant mechanism for the above reaction.

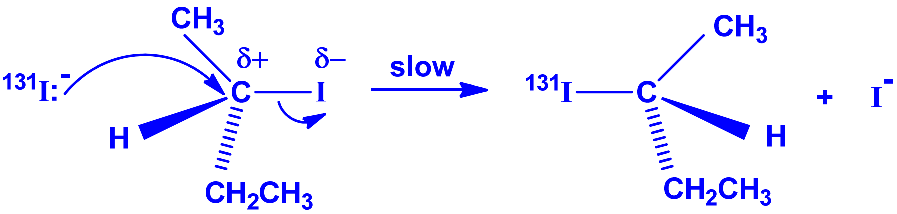
Let the percentage composition of B be *z*% and the percentage composition of A be (100 – *z*)%.

$$(-15.0°)\left(\frac{z}{100}\right) + (+15.0°)\left(\frac{100 - z}{100}\right) = -6.4°$$
$z = 71.3\%$

Since percenatge composition of B is less than 75 %, the predominant mechanism is S_N1.

[2]

(ii) Describe the S_N2 mechanism for the reaction of $CH_3CHICH_2CH_3$ with $^{131}I^-$.



[2]

[Total: 20]

3 Nickel is widely used as components of fuel cells and batteries. It often occurs in ores along with iron as metal oxides. After the initial reduction of the ore with carbon, a nickel–iron alloy is formed. It can then be purified by an electrolysis technique.

(a) On the other hand, Group 2 metal oxides such as magnesium oxide, are not reduced by carbon. Use relevant data from the *Data Booklet* to explain why carbon can reduce oxides of nickel and iron but not magnesium oxide.

From *Data Booklet*,
$E^\ominus(Mg^{2+}|Mg) = -2.38$ V
$E^\ominus(Ni^{2+}|Ni) = -0.25$ V
$E^\ominus(Fe^{2+}|Fe) = -0.44$ V
$E^\ominus(Fe^{3+}|Fe) = -0.04$ V

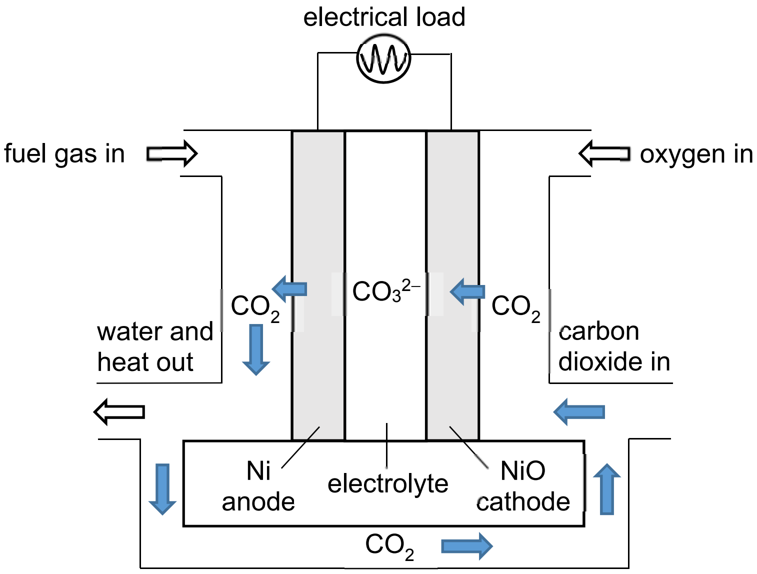
Standard reduction potential, $E^\ominus$, for nickel and iron are both much less negative than that of magnesium.

[2]

(b) Nickel and nickel(II) oxide are used as electrodes in molten carbonate fuel cells (MCFC).

MCFC operates at temperatures above 650 °C to ensure ionic conductivity of its electrolyte, which is a mixture of lithium carbonate and potassium carbonate.

The high temperature also allows fuel reforming which produces hydrogen gas at the anode for the electrochemical reaction. Fuel gases, such as natural gas and other higher hydrocarbons derived from biomass, could be used with MCFC. The CO_2 generated at the anode is recycled to the cathode where it is consumed as shown in the schematic diagram of MCFC below.



(i) When a hydrocarbon C_xH_y is used as the fuel gas, it undergoes fuel reforming with H_2O at the anode to produce hydrogen gas and carbon monoxide.

Write a balanced equation for the fuel reforming of the hydrocarbon, C_xH_y.

$C_xH_y + xH_2O \rightarrow (x + y/2)H_2 + xCO$

[1]

(ii) The fuel reforming is catalysed by the nickel. Explain the mode of action of the nickel catalyst.

Nickel is a heterogeneous catalyst.
Gaseous reactants are adsorbed on the Ni surface through forming weak bonds with the active sites of the catalyst.
This weakens the covalent bonds within the reactant molecules.
High concentration of reactants on the catalyst surface come into close contact with proper orientation for reaction to occur.
Products desorb from the surface of the catalyst.

[2]

(iii) Carbonates are generated at the cathode by the reaction between oxygen and carbon dioxide. The carbonate ions then diffuse across the electrolyte to the anode and react with hydrogen gas, generating steam and carbon dioxide.

Write the half–equations at both electrodes and hence give the overall equation for the MCFC.

Cathode: $O_2(g) + 2CO_2(g) + 4e^- \rightarrow 2CO_3^{2-}(l)$
Anode: $H_2(g) + CO_3^{2-}(l) \rightarrow H_2O(g) + CO_2(g) + 2e^-$
Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

[2]

(iv) The temperature of MCFC is kept constant.

With reference to your answer from **(b)(iii)**, state and explain the effect of increasing the partial pressure of oxygen on the cell potential of this MCFC.

Higher partial pressure of O_2 would cause the position of equilibrium of the overall reaction to shift to the right to decrease the amount of gaseous oxygen.
The cell potential becomes more positive. [2]

(c) Biomass from farms could be used to produce fuel gases for MCFC to power an ammonia–making plant for the farming community. The ammonia is manufactured in the following three–step process.

Step 1: Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

$$4LiOH \rightarrow 4Li + 2H_2O + O_2$$

Step 2: Reaction of lithium metal with nitrogen to form lithium nitride.

$$3Li + \tfrac{1}{2}N_2 \rightarrow Li_3N$$

Step 3: Reaction of lithium nitride with water to re–form lithium hydroxide and ammonia.

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Thus, the lithium hydroxide formed in **Step 3** can be re–used in **Step 1** and the process can be repeated.

(i) The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the cell potential by 0.60 V.

Use appropriate $E^\ominus$ values from the *Data Booklet* to calculate the minimum potential that should be applied in **Step 1**.

$E^\ominus(Li^+|Li) = -3.04$ V
$E^\ominus(O_2|OH^-) = +0.40$ V

$E^\ominus_{cell}$
$= |-3.04 - (+0.40)|$
$= 3.44$ V

Minimum potential
$= 3.44 + 0.60$
$= 4.04$ V

[2]

(ii) State the ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3**.

Ratio of Li : NH_3 = 3 : 1

[1]

(iii) A farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a farm of 100 acres in a year.

[1 tonne = 10^6 g]

Mass of NH_3 needed for 100 acres in a year
= $0.0770 \times 10^6 \times 100$
= 7.70×10^6 g

Amount of NH_3
= $7.70 \times 10^6 \div 17.0$
= 4.53×10^5 mol

Amount of Li required
= $3 \times 4.53 \times 10^5$
= 1.36×10^6 mol

Mass of Li required
= $1.36 \times 10^6 \times 6.9$
= 9.38×10^6 g
= 9.38 tonnes

[2]

(d) Unlike lithium carbonate and potassium carbonate, a mixture of Group 2 carbonates consisting of magnesium carbonate and barium carbonate is **not** a suitable electrolyte for the molten carbonate fuel cell (MCFC) in **(b)**. For each of the carbonates, suggest a reason why it is not a suitable electrolyte.

Magnesium carbonate:

Mg^{2+} ion has greater charge density than Group 1 ion and hence polarising the electron cloud of CO_3^{2-} to a greater extent. This causes lower thermal stability.

$MgCO_3$ may undergo thermal decomposition at the high operating temperature of the fuel cell, forming CO_2, depleting the source of CO_3^{2-}.

Barium carbonate:

$BaCO_3$ may have a higher melting point than the operating temperature.

There will be no charge carriers in the electrolyte if the carbonate does not melt.

[2]

(e) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} barium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.
[$K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$ $mol^2\ dm^{-6}$; $K_{sp}(BaCO_3) = 5.1 \times 10^{-9}$ $mol^2\ dm^{-6}$]

(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen.

Since K_{sp} of $BaCO_3$ is smaller (lower solubility), Ba^{2+} is precipitated first.

$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.1 \times 10^{-9}$
$0.100 \times [CO_3^{2-}] = 5.1 \times 10^{-9}$
$[CO_3^{2-}] = 5.1 \times 10^{-8}$ mol dm^{-3}

[1]

(ii) Determine the concentration of the metal ion stated in **(e)(i)** when the other metal ion just begins to precipitate.

$[CO_3^{2-}]$ when Mg^{2+} starts to precipitate
$= 3.5 \times 10^{-8} \div 0.100$
$= 3.5 \times 10^{-7}$ mol dm^{-3}

Using K_{sp} of $BaCO_3$,
$[Ba^{2+}] \times 3.5 \times 10^{-7} = 5.1 \times 10^{-9}$
$[Ba^{2+}] = 0.0146$ mol dm^{-3}

[2]

(iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective.

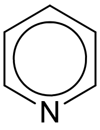
Percentage of Ba^{2+} ions remained
$= \frac{0.0146}{0.100} \times 100\%$ (ecf)
$= 14.6\% >> 1\%$

The above separation is not effective.

[1]

[Total: 20]

4 **(a)** Pyridine is an aromatic planar molecule similar to benzene. Unlike benzene, pyridine can act as a Bronsted–Lowry base and a nucleophile.



pyridine

(i) State the type of hybridisation of the nitrogen atom in pyridine.

sp^2 hybridisation

[1]

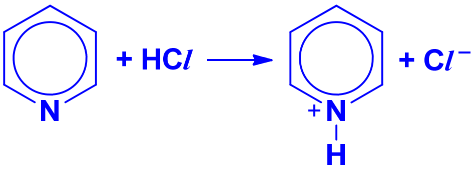
(ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $CH_3CH_2NH_2$.

The nitrogen atom in pyridine is sp^2 hybridised while that in ethylamine is sp^3 hybridised.
Hence, the lone pair of electrons in pyridine is less available for donation as it is more strongly attracted by / closer to the nucleus.

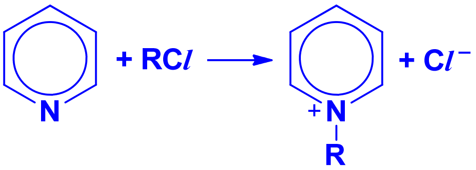
[1]

(iii) Write a balanced equation to show that pyridine is acting as

a Bronsted–Lowry base

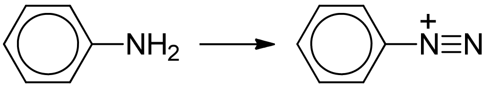


a Lewis base but not a Bronsted–Lowry base



[2]

(b) Phenylamine and subsituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.

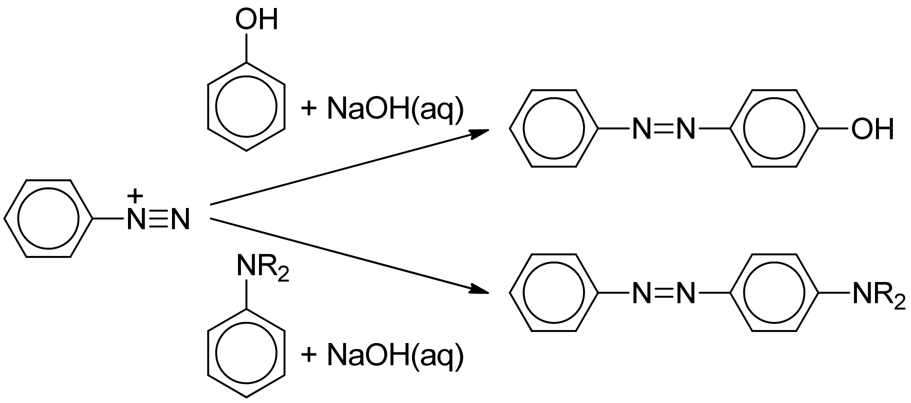


(i) State the type of reaction.

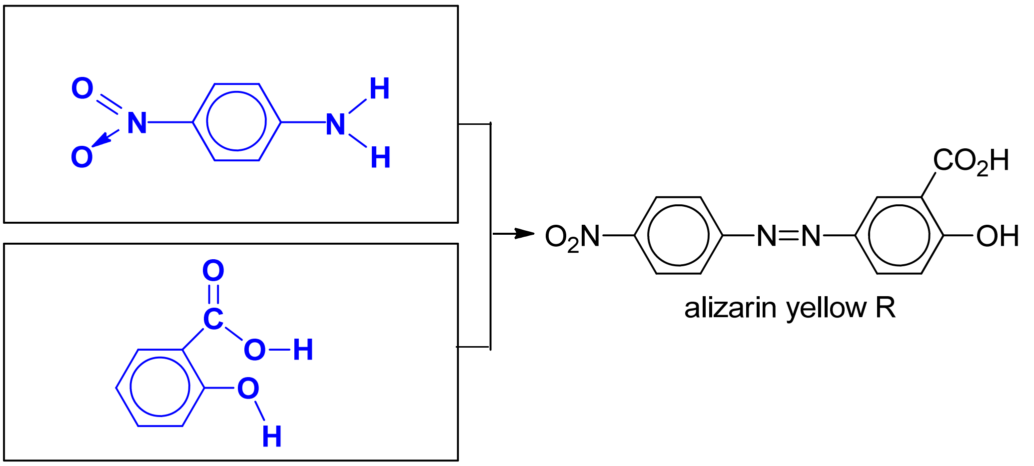
Oxidation

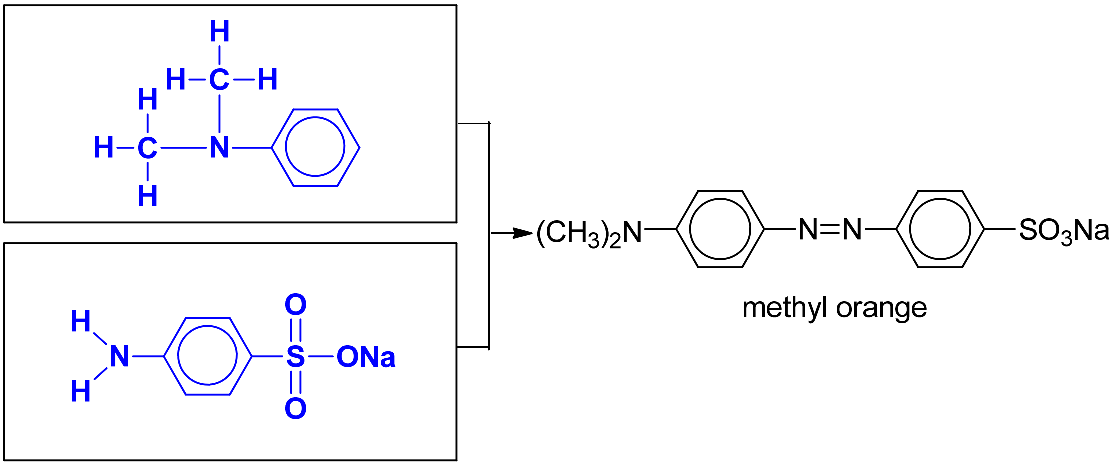
[1]

The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



(ii) Suggest the starting compounds needed to synthesise the following dyes. Draw their full structural formulae in the boxes provided.





[4]

(iii) The benzene ring containing the NaO_3S- group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

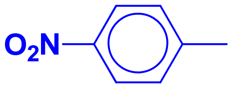
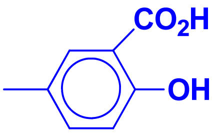
NaO_3S- group is an electron withdrawing group, making the benzene ring less electron–rich and less susceptible to electrophilic attack.

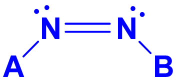
Lone pair of electrons on $-N(CH_3)_2$ can delocalise into the benzene ring, making the benzene ring more electron–rich and more susceptible to electrophilic attack.

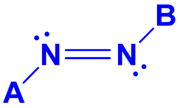
[2]

(iv) Alizarin yellow R exhibits stereoisomerism and is a common indicator for acid–base titrations.

Draw the stereoisomers of alizarin yellow R.

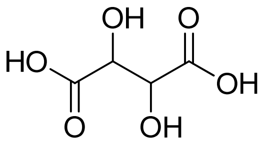
Let A be  . **Let B be**  .





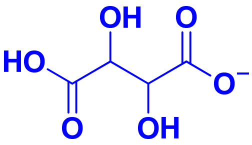
[1]

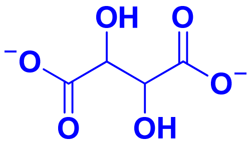
(c) Tartaric acid is present in many plants.



tartaric acid

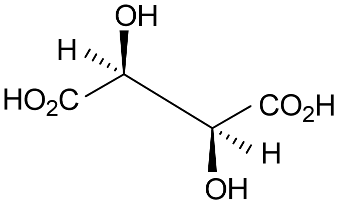
(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.



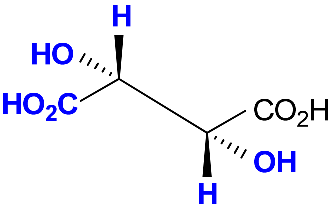


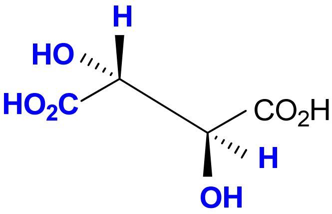
[1]

(ii) One stereoisomer of tartaric acid is shown below.



Complete the diagrams below to show two other stereoisomers of tartaric acid.





[2]

[Total: 15]

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/03

Paper 3 Free Response **17 September 2018**

Candidates answer on separate paper. **2 hours**

Additional Materials: Cover Page
Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
You must start the answer to each question on a fresh piece of writing paper.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** All the elements in the third period of the Periodic Table, sodium to sulfur, form chlorides by direct combination with chlorine. Aluminium chloride may be produced by passing a stream of chlorine over heated aluminium metal in a long hard–glass tube.

(i) With the aid of equations, explain the following observations when different amounts of water were added to solid aluminium chloride.

(I) When a limited amount of water was added, a white solid was formed together with steamy fumes.

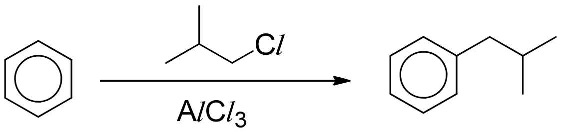
(II) When excess water was added, a solution of pH 3 was obtained. [2]

(ii) Both aluminium chloride and copper(I) complex solutions are colourless whereas a solution of copper(II) sulfate appears blue.
Explain these observations. [3]

(iii) Briefly describe the process of anodisation of aluminium. Write ion-electron equations for the reactions occurring at the anode and the cathode. [2]

(b) Compound **A** can be synthesised from benzene using aluminium chloride via a simple Friedel–Crafts alkylation as shown in **Reaction 1**. In addition, compound **B**, an isomer of compound **A** is also formed.

Reaction 1:



+ compound **B**

compound **A**

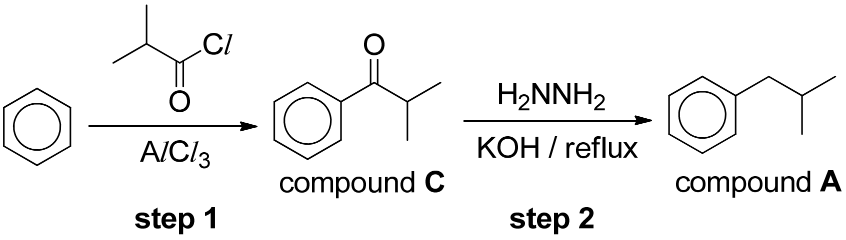
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

Draw the structure of compound **B**. Explain why the rearrangement of the carbocation is favoured. [2]

(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

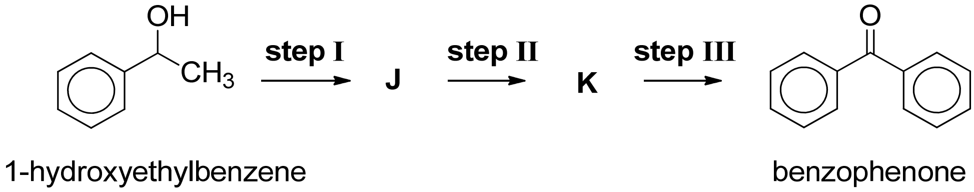
(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

Reaction 2:



(i) Draw the mechanism for **step 1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

(ii) Hence, suggest reagents and conditions for **steps I** to **III** in the following synthesis of benzophenone from 1-hydroxyethylbenzene. Give the structural formulae of **J** and **K**.



[4]

(d) A student wants to synthesise benzophenone using the reaction pathway illustrated in **(c)(ii)**. However, the solid sample of 1-hydroxyethylbenzene is contaminated with phenylamine. Briefly explain how you can separate 1-hydroxyethylbenzene from phenylamine via extraction. You are provided with

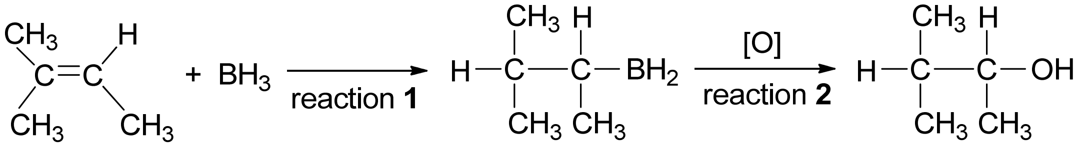
- ethanol, hexane, HC*l*(aq), NaOH(aq),
- separating funnel, and
- apparatus commonly found in a college laboratory.

[3]

[Total: 20]

2 **(a)** Borane, BH_3, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

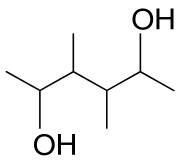
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

(ii) The product formed in reaction **1** contains a chiral centre. Explain whether the product formed rotates plane-polarised light. [2]

(iii) The diol **W** can be prepared by the same method as shown above.

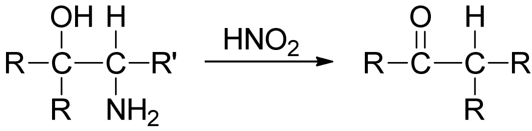


W

Draw the skeletal structure of the diene which could be used to prepare diol **W**. [1]

(b) A carbonyl compound, **Y**, $C_6H_{10}O$, can be synthesised from aminoalcohol, **X**, $C_6H_{13}ON$, in the presence of nitrous acid, HNO_2, via Tiffeneau-Demjanov Rearrangement.

The simplified illustration of the rearrangement is shown below.



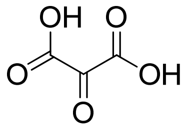
$$R\text{–}\overset{OH}{\underset{R}{C}}\text{–}\overset{H}{\underset{NH_2}{C}}\text{–}R' \xrightarrow{HNO_2} R\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{H}{\underset{R}{C}}\text{–}R'$$

Y produces a yellow precipitate with iodine in alkaline solution. Treatment of **Y** with hot acidified solution of potassium manganate(VII) produces **Z,** $C_5H_8O_3$, along with a gas that forms a white precipitate in limewater. **Y** was also observed to decolourise bromine in tetrachloromethane readily.

(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

(ii) With reference to the *Data Booklet*, identify an infra-red absorption range that will be shown by the functional group in **Y** but **not** in **X**. [1]

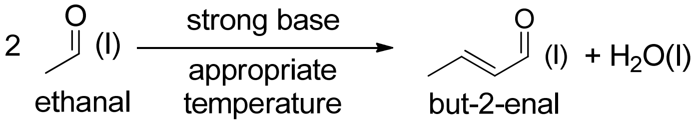
(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, $ClCH_2CHO$.



V

Give the reagents and conditions for each step. Draw the structural formulae of all the intermediates. [4]

(d) By either adjusting the reaction temperature or using a stronger base, ethanal can undergo Aldol Condensation reaction to form but-2-enal as shown below.



(i) With reference to the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

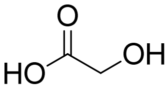
(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

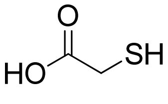
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

[Total: 20]

3 This question is about acids, bases and their derivatives.

(a) Glycolic acid and thioglycolic acid have very similar structures as shown below.


glycolic acid


thioglycolic acid

Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(i) Both oxygen and sulfur are Group 16 elements. Hence, suggest why the alcohol functional group of glycolic acid is a weaker acid than the –SH group of thioglycolic acid. [1]

(ii) Compare the first pK_a values of glycolic acid and thioglycolic acid. Explain its significance. [2]

(iii) Suggest the major species present in solutions of thioglycolic acid with the following pH values.

- pH 0
- pH 7
- pH 14 [2]

(iv) Assuming thioglycolic acid to be H_2A, calculate the percentage of each of the ionic species of thioglycolic acid present at pH 9.0. [3]

(v) Hence, calculate the volume of 0.100 mol dm^{-3} aqueous sodium hydroxide needed to form the solution in **(iv)** when added to 25.0 cm^3 of 0.100 mol dm^{-3} thioglycolic acid. [2]

(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

DEB^{2-} is produced from compound **A** which is a disubstituted benzene, $C_6H_4R_2$, where R− is the same substituent.

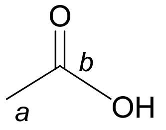
(i) Draw all the possible structures of $C_6H_4R_2$. [1]

(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

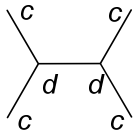
Suggest the functional group present in the substituent R− that is responsible for the effervescence. Hence, deduce a structure for R−. [1]

^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

For example, the ^{13}C NMR spectra for the ethanoic acid and 2,3-dimethylbutane would both show two distinct signals since each molecule has only two different carbon environments. This is shown in the diagram below where equivalent carbon environments are labelled with the same letter.



ethanoic acid



2,3-dimethylbutane

(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]

(iv) Compound **A** forms DEB^{2-} via intermediates **B**$^{2-}$ and **C**$^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

$$\underset{C_{12}H_6O_4}{\text{Compound } \mathbf{A}} \longrightarrow \underset{M_r = 212}{\mathbf{B}^{2-}} \longrightarrow \underset{M_r = 168}{\mathbf{C}^{2-}} \longrightarrow \underset{M_r = 124}{\text{DEB}^{2-}}$$

Determine the skeletal structures of **B**$^{2-}$, **C**$^{2-}$ and DEB^{2-}. [2]

(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **F** reacts with ethanol in the presence of a catalyst to form compound **G**, $C_6H_{10}O_4$.

Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

Both compounds, **G** and **H**, produce **E** on heating with dilute sulfuric acid.

Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chlorine dioxide, ClO_2, is a reddish-yellow gas that does not occur naturally in the environment. When added to aqueous hydroxide, chlorine dioxide undergoes the following reaction producing chlorate(III) and chlorate(V) ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

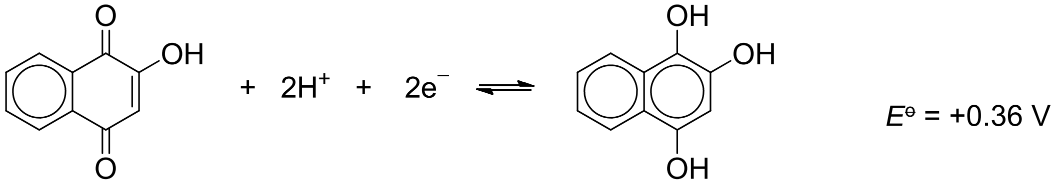
Unlike ClO_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(i) Write a balanced equation for the reaction of bromine dioxide with sodium hydroxide. Hence, state the type of reaction. [2]

(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

Lawsone is a dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can be readily reduced to a colourless compound **A**, 1,2,4-trihydroxynaphthalene. However, the hair dye containing lawsone is relatively resistant to the decolourisation by chlorine water in swimming pools.



$E^\ominus = +0.36$ V

lawsone

compound **A**,
1,2,4-trihydroxynaphthalene

(iii) With reference to the *Data Booklet*, explain why chlorine water cannot spontaneously decolourise lawsone. [2]

(iv) The Gibb's free energy change, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, through the following equation:

$$\Delta G^\ominus = -RT \ln K_c$$

where $\Delta G^\ominus$ is in J mol^{-1}.

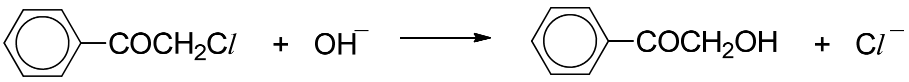
Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

(v) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory. [1]

(vi) When lawsone is reacted with Br_2(aq), compound **B** with molecular formula, $C_{10}H_5O_3Br$, is formed. **B** reacts with 3 mol of 2,4-DNPH. Reaction of **B** with NaOH(aq) gives **C**. Compound **C** reacts with HC*l* and ZnC*l*$_2$ to produce **D**. The reaction of **D** with methylamine gives **E** with molecular formula, $C_{11}H_9O_3N$, which further reacts with CH_3COCl to give a neutral compound **F**.

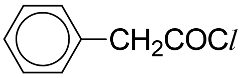
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]

(b) Chloroacetophenone was formerly the most widely used tear gas, under the codename *CN*. It was used in warfare and in riot control. Residues of *CN* can be destroyed by the hydrolysis of alkali.

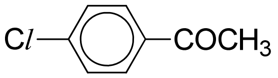


chloroacetophenone

G and **H** are isomers of chloroacetophenone.



G



H

(i) Arrange the isomers, chloroacetophenone, **G** and **H**, in increasing ease of hydrolysis. Explain your choice. [3]

(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

(iii) Suggest a suitable experimental technique for studying the rate of hydrolysis. [1]

(iv) Compound **H** reacts with alkaline aqueous iodine to give a yellow solid, CHI_3. Similar reaction occurs between compound **H** and alkaline aqueous chlorine.

Write a balanced equation for the reaction of compound **H** with alkaline aqueous chlorine. State the observation. [2]

[Total: 20]

5 **(a)** Copper can be extracted from a double salt, $CuFeS_2$ by reacting it with oxygen and silicon dioxide. In this reaction, copper, iron(II) silicate, $FeSiO_3$, and an oxide of sulfur are produced. The oxide of sulfur does not decolourise acidified potassium manganate(VII).

(i) Draw a dot-and-cross diagram for $CuFeS_2$. [1]

(ii) Write a balanced equation for the overall reaction. Deduce the reducing agent in the reaction. [2]

(iii) Copper(I) sulfide is one of the reaction intermediate. Write the full electronic configuration of copper(I). [1]

(iv) The crude copper obtained contains trace amount of silver and nickel. With relevant data from the *Data Booklet* and a labelled diagram, describe how the crude copper can be purified through electrolysis. [4]

(v) 5.0 g of crude copper containing 0.1 g of silver and 0.1 g of nickel is purified through electrolysis as in **(a)(iv)**. During electrolysis, 80% of the current is used to oxidise the metals. With reference to the *Data* Booklet, determine the time needed to purify the copper completely using a current of 2 A. [2]

(vi) A student accidentally added some iron(III) nitrate into a solution of copper(II) nitrate. You are provided with

- NH_3(aq), NaOH(aq), HNO_3(aq) and
- apparatus commonly found in a college laboratory.

Describe how the student could separate these two metal ions in the mixture. Give relevant equations and state the types of reactions that have occurred. [3]

(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

	Test	**W**	**X**	**Y**	**Z**
1	Rotate plane-polarised light	Yes	No	Yes	Yes
2	Add dilute NaOH at room temperature	Soluble	Soluble	Soluble	Insoluble
3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	No brick-red precipitate	No brick-red precipitate	No brick-red precipitate
6	Warm with Tollens' reagent	Grey ppt	No grey ppt	No grey ppt	Grey ppt
7	Warm with I_2(aq) and NaOH(aq)	No pale yellow precipitate	Pale yellow precipitate	No pale yellow precipitate	Pale yellow precipitate

(i) Use the information in the table above to suggest a skeletal formula for each of these four isomers. [4]

(ii) Write a balanced equation for the reaction between **W** and 2,4-DNPH. [1]

(iii) Explain why **W** is soluble in NaOH(aq) at room temperature. [2]

[Total: 20]

End of Paper

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/03

Paper 3 Free Response **17 September 2018**

Candidates answer on separate paper. **2 hours**

Additional Materials: Cover Page
Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
You must start the answer to each question on a fresh piece of writing paper.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** All the elements in the third period of the Periodic Table, sodium to sulfur, form chlorides by direct combination with chlorine. Aluminium chloride may be produced by passing a stream of chlorine over heated aluminium metal in a long hard–glass tube.

(i) With the aid of equations, explain the following observations when different amounts of water were added to solid aluminium chloride.

(I) When a limited amount of water was added, a white solid was formed together with steamy fumes.

(II) When excess water was added, a solution of pH 3 was obtained. [2]

For **(I)**: $AlCl_3$ reacts with a limited amount of water to give $Al(OH)_3(s)$ and $HCl(g)$:

$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$

For **(II)**:

$AlCl_3$ undergoes hydrolysis as Al^{3+} has high charge density / strong polarising power. Polarisation of H_2O molecules favours the loss of H^+, and hence, acidity of the solution increases (pH ≈ 3).

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

(ii) Both aluminium chloride and copper(I) complex solutions are colourless whereas a solution of copper(II) sulfate appears blue. Explain these observations. [3]

$AlCl_3$ solution is colourless because the energy gap between the n=2 and n=3 electronic shells is not within the visible light region. Hence, visible light is not absorbed.

Cu(I) complex is colourless because the 3d subshell is fully filled. Hence, no d-d /electronic transition can occur.

$CuSO_4$ solution appears blue because partially-filled 3d subshell is split into two different energy levels in the presence of ligands.

Electron from the lower energy level absorb a wavelength of light complementary to the observed colour and get promoted to the higher energy level. Thus, d-d transition can take place.

(iii) Briefly describe the process of anodisation of aluminium. Write ion-electron equations for the reactions occurring at the anode and the cathode. [2]

The aluminium is made the anode in the electrolysis of dilute sulfuric acid.

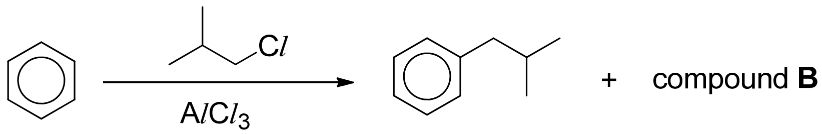
The oxygen released at the anode reacts with the aluminium surface to build up a thicker layer of aluminium oxide.

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) Compound **A** can be synthesised from benzene using aluminium chloride via a simple Friedel–Crafts alkylation as shown in **Reaction 1**. In addition, compound **B**, an isomer of compound **A** is also formed.

Reaction 1:

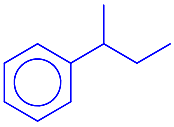


compound **A**

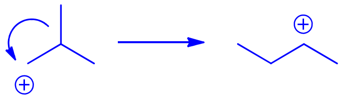
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

Draw the structure of compound **B**. Explain why the rearrangement of the carbocation is favoured. [2]

B:



A primary carbocation rearranges into a secondary carbocation that is more stable because more electron-donating alkyl groups help dispersed the positive charge and stabilised the carbocation:

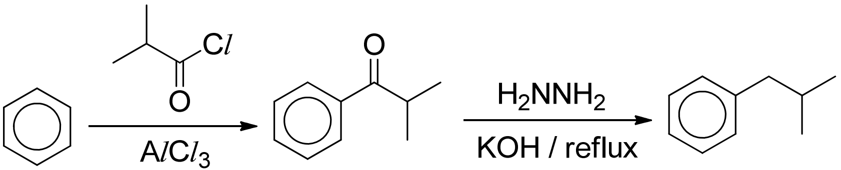


(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

The alkyl group that is bonded to the benzene ring exerts electron–donating inductive effect.
This activates the benzene ring, making it even more susceptible towards electrophilic attack / reactive with respect to electrophilic substitution, thus forming multi-substituted product.

(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

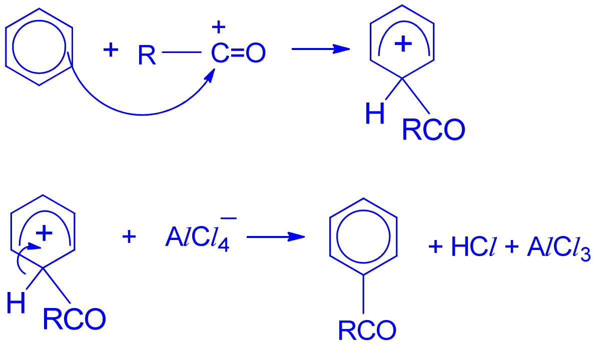
Reaction 2:



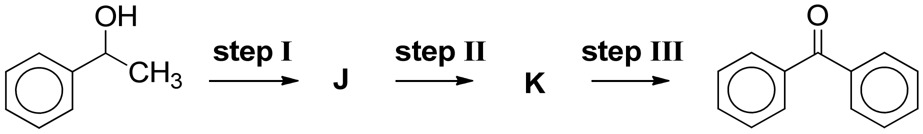
compound **C** compound **A**

step 1 **step 2**

(i) Draw the mechanism for **step 1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]
Mechanism: Electrophilic substitution
Let R be $(CH_3)_2CH–$
$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$



(ii) Hence, suggest reagents and conditions for **steps I** to **III** in the following synthesis of benzophenone from 1-hydroxyethylbenzene. Give the structural formulae of **J** and **K**.

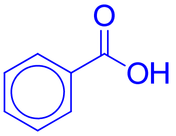


1-hydroxyethylbenzene

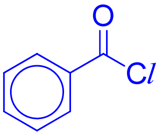
benzophenone

[4]

J:



K:



step I: $KMnO_4$, H_2SO_4, reflux
step II: PCl_5, room temperature OR PCl_3, reflux OR $SOCl_2$, reflux
step III: C_6H_6, anhydrous $AlCl_3$, room temperature

(d) A student wants to synthesise benzophenone using the reaction pathway illustrated in **(c)(ii)**. However, the solid sample of 1-hydroxyethylbenzene is contaminated with phenylamine. Briefly explain how you can separate 1-hydroxyethylbenzene from phenylamine via extraction. You are provided with

- ethanol, hexane, HCl(aq), NaOH(aq),
- separating funnel and
- apparatus commonly found in a college laboratory.

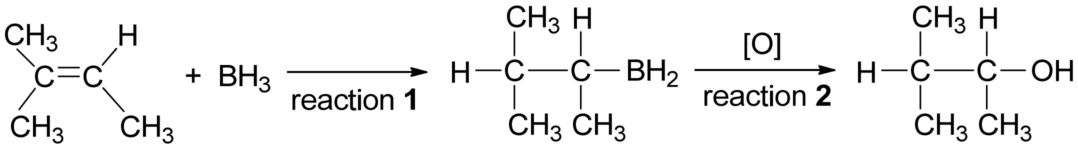
[3]

(i) Dissolve the solid sample in hexane.
(ii) Transfer the mixture to a separating funnel.
(iii) Add HCl(aq) to the mixture to convert phenylamine to the salt.
(iv) Shake the separating funnel and then drain off the bottom aqueous layer to get the organic layer.
(v) Evaporate the organic layer to obtain 1-hydroxyethylbenzene.

[Total: 20]

2 **(a)** Borane, BH_3, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

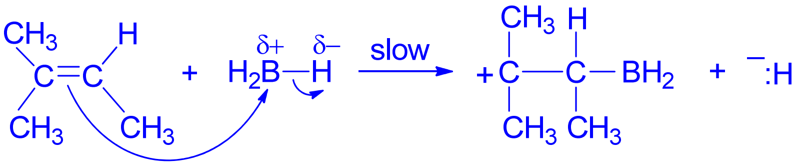
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



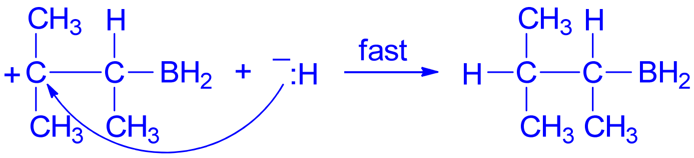
(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic addition

Step 1:



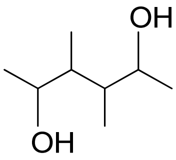
Step 2:



(ii) The product formed in reaction **1** contains a chiral centre. Explain whether the product formed rotates plane-polarised light. [2]

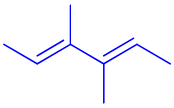
The product does not rotate plane-polarised light.
The alkene carbon atom is sp^2 hybridised (or trigonal planar).
Electrophile can attack from either the top or bottom plane of the C=C with equal probability. Hence, a racemic mixture is formed.

(iii) The diol **W** can be prepared by the same method as shown above.



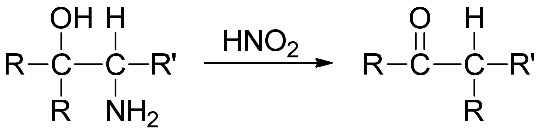
W

Draw the skeletal structure of the diene which could be used to prepare diol **W**. [1]



(b) A carbonyl compound, **Y**, $C_6H_{10}O$, can be synthesised from aminoalcohol, **X**, $C_6H_{13}ON$, in the presence of nitrous acid, HNO_2, via Tiffeneau-Demjanov Rearrangement.

The simplified illustration of the rearrangement is shown below.

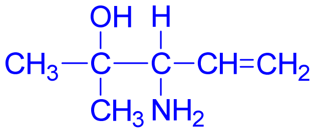


$$R-C(OH)(R)-CH(NH_2)-R' \xrightarrow{HNO_2} R-CO-CH(R)-R'$$

Y produces a yellow precipitate with iodine in alkaline solution. Treatment of **Y** with hot acidified solution of potassium manganate(VII) produces **Z,** $C_5H_8O_3$, along with a gas that forms a white precipitate in limewater. **Y** was also observed to decolourise bromine in tetrachloromethane readily.

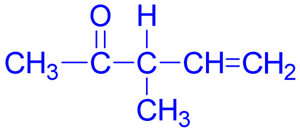
(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

X is



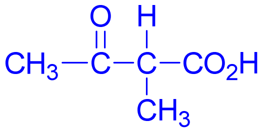
$$CH_3-C(OH)(CH_3)-CH(NH_2)-CH=CH_2$$

Y is



$$CH_3-CO-CH(CH_3)-CH=CH_2$$

Z is



$$CH_3-CO-CH(CH_3)-CO_2H$$

Y undergoes oxidative cleavage with iodine in alkaline solution to give yellow ppt., CHI_3. Y has CH_3CO- group.

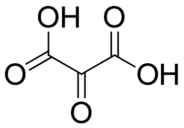
Y undergoes oxidative cleavage with hot acidified $KMnO_4(aq)$ to produce $CO_2(g)$ which forms white ppt. in limewater. Y is a terminal alkene (OR has $=CH_2$ group).

Y undergoes electrophilic addition with Br_2 in CCl_4. Y is an alkene.

(ii) With reference to the *Data Booklet*, identify an infra-red absorption range that will be shown by the functional group in **Y** but **not** in **X**. [1]

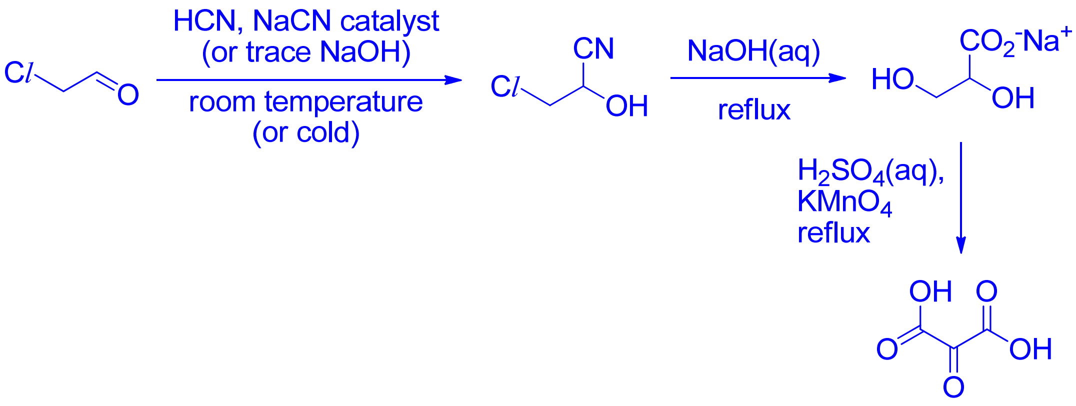
1670 – 1740 cm^{-1} due to ketone functional group.

(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, $ClCH_2CHO$.

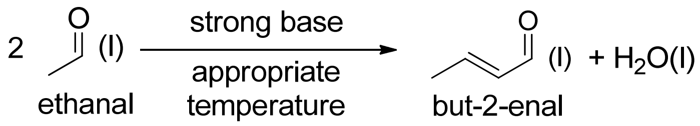


V

Give the reagents and conditions for each step. Draw the structural formulae of all the intermediates. [4]



(d) By either adjusting the reaction temperature or using a stronger base, ethanal can undergo Aldol Condensation reaction to form but-2-enal as shown below.



(i) With reference to the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

bonds broken	
one C=O	+740
two C–H	2(+410)
Total	+1560

bonds formed	
one C=C	+610
two O–H	2(+460)
Total	+1530

ΔH = +1560 – (+1530) = +30 kJ mol^{-1}

(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

Bond energies quoted from *Data Booklet* are average values derived from a full range of molecules that contain the particular bonds.
OR
The bond energies quoted are for gaseous molecules but the reactants and products are in liquid state. Hence, the enthalpy changes of vapourisation are not accounted for.

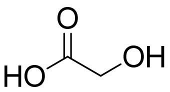
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

Test: Add $Br_2(aq)$ (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange $Br_2(aq)$ decolourise.
OR
Test: Add Br_2 in CCl_4 (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange-red Br_2 decolourise.

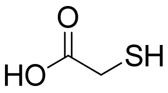
[Total: 20]

3 This question is about acids, bases and their derivatives.

(a) Glycolic acid and thioglycolic acid have very similar structures as shown below.



glycolic acid



thioglycolic acid

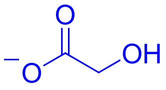
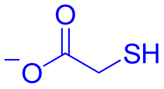
Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(i) Both oxygen and sulfur are Group 16 elements. Hence, suggest why the alcohol functional group of glycolic acid is a weaker acid than the –SH group of thioglycolic acid. [1]

The S–H bond is easier to break since S atom is bigger. Hence, less effective overlap of orbitals for the S–H bond.

(ii) Compare the first pK_a values of glycolic acid and thioglycolic acid. Explain its significance. [2]

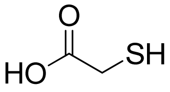
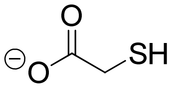
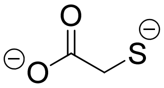
Glycolic acid is the stronger acid since it has a lower pK_a value.
O atom is more electronegative than S,

hence the anion formed,  is more stable than that of thioglycolic acid, . This is due to the stronger electron withdrawing effect of O atom, dispersing the negative charge.

(iii) Suggest the major species present in solutions of thioglycolic acid with the following pH values.

- pH 0
- pH 7
- pH 14

[2]

pH 0	pH 7	pH 14
		

(iv) Assuming thioglycolic acid to be H_2A, calculate the percentage of each of the ionic species of thioglycolic acid present at pH 9.0. [3]
Let the thioglycolic acid be H_2A. As pH 9 is after the 1st end-point, we shall use

$pK_a = 10.31$ for calculation.

$pK_a = pH - \log_{10}\frac{[A^{2-}]}{[HA^-]}$

$10.31 = 9 - \log_{10}\frac{[A^{2-}]}{[HA^-]}$

$\log_{10}\frac{[A^{2-}]}{[HA^-]} = -1.31$

$\frac{[A^{2-}]}{[HA^-]} = 0.0490$

Or $K_a = \frac{[A^{2-}][H^+]}{[HA^-]}$

$\frac{[A^{2-}]}{[HA^-]} = \frac{K_a}{[H^+]} = \frac{10^{-10.31}}{10^{-9}} = 0.0490$

$[A^{2-}] + [HA^-] = 100\%$

$0.049[HA^-] + [HA^-] = 100\%$

$\Rightarrow [A^{2-}] = 4.67\%$; $[HA^-] = 95.3\%$

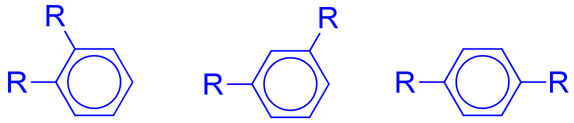
(v) Hence, calculate the volume of 0.100 mol dm^{-3} aqueous sodium hydroxide needed to form the solution in **(iv)** when added to 25.0 cm^3 of 0.100 mol dm^{-3} thioglycolic acid. [2]

$H_2A + NaOH \rightarrow HA^- + H_2O$
$HA^- + NaOH \rightarrow A^{2-} + H_2O$
Amount of H_2A used = $25/1000 \times 0.100 = 2.50 \times 10^{-3}$ mol
Amount of NaOH required
= amount of NaOH to form HA^- from H_2A + amount of NaOH to form 4.67% A^{2-}
= $2.50 \times 10^{-3} + (4.67\% \times 2.50 \times 10^{-3})$
= 2.62×10^{-3} mol
Volume of NaOH
= amount of NaOH / [NaOH]
= $2.62 \times 10^{-3} \div 0.100$
= 0.0262 dm^3 = 26.2 cm^3

(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

DEB^{2-} is produced from compound **A** which is a disubstituted benzene, $C_6H_4R_2$, where R− is the same substituent.

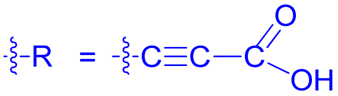
(i) Draw all the possible structures of $C_6H_4R_2$. [1]



(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

Suggest the functional group present in the substituent R− that is responsible for the effervescence. Hence, deduce a structure for R−. [1]

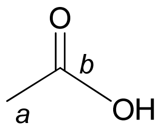
Carboxylic acid



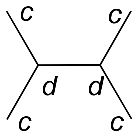
$-R = -C\equiv C-C(=O)OH$

^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

For example, the ^{13}C NMR spectra for the ethanoic acid and 2,3-dimethylbutane would both show two distinct signals since each molecule has only two different carbon environments. This is shown in the diagram below where equivalent carbon environments are labelled with the same letter.

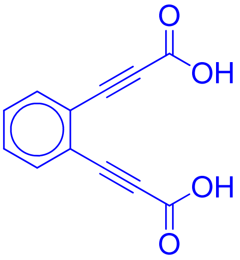


ethanoic acid



2,3-dimethylbutane

(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]

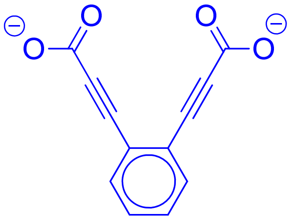


(iv) Compound **A** forms DEB^{2-} via intermediates **B**$^{2-}$ and **C**$^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

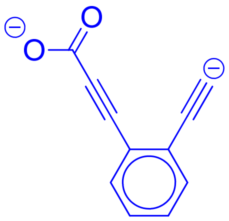
$$\text{Compound } \mathbf{A} \longrightarrow \mathbf{B}^{2-} \longrightarrow \mathbf{C}^{2-} \longrightarrow \text{DEB}^{2-}$$

$$C_{12}H_6O_4 \qquad M_r = 212 \qquad M_r = 168 \qquad M_r = 124$$

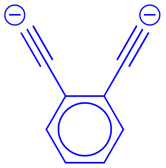
Determine the skeletal structures of **B**$^{2-}$, **C**$^{2-}$ and DEB^{2-}. [2]



B^{2-}



C^{2-}



DEB^{2-}

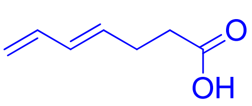
(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **F** reacts with ethanol in the presence of a catalyst to form compound **G**, $C_6H_{10}O_4$.

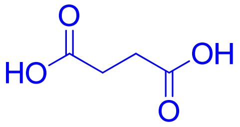
Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

Both compounds, **G** and **H**, produce **E** on heating with dilute sulfuric acid.

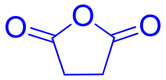
Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]



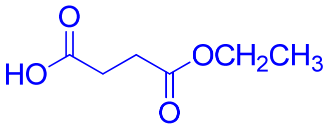
D



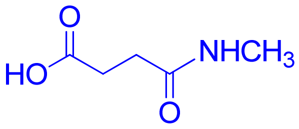
E



F



G



H

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chlorine dioxide, ClO_2, is a reddish-yellow gas that does not occur naturally in the environment. When added to aqueous hydroxide, chlorine dioxide undergoes the following reaction producing chlorate(III) and chlorate(V) ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Unlike ClO_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(i) Write a balanced equation for the reaction of bromine dioxide with sodium hydroxide. Hence, state the type of reaction. [2]

$6BrO_2 + 6NaOH \rightarrow NaBr + 5NaBrO_3 + 3H_2O$
Disproportionation.

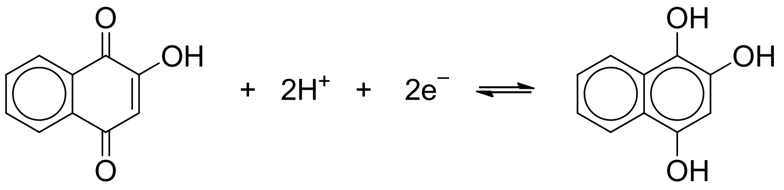
(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

Bromine element is a stronger reducing agent than chlorine, hence, it is more likely to be oxidised to a higher oxidation state.
OR

Bromine atom is bigger / less electronegative, hence, easier to lose electrons to form the +5 oxidation state.

Lawsone is a dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can be readily reduced to a colourless compound **A**, 1,2,4-trihydroxynaphthalene. However, the hair dye containing lawsone is relatively resistant to the decolourisation by chlorine water in swimming pools.



$E^\ominus = +0.36$ V

lawsone

compound **A**,
1,2,4-trihydroxynaphthalene

(iii) With reference to the *Data Booklet*, explain why chlorine water cannot spontaneously decolourise lawsone. [2]

$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$ $E^\ominus = +1.64$ V
If lawsone undergoes decolourisation, it is reduced while chlorine water is oxidised.
$E^\ominus_{cell} = E^\ominus_{Red} - E^\ominus_{Ox} = +0.36 - (+1.64) = -1.28$ V
Since $E^\ominus_{cell} < 0$, the reaction is thermodynamically non-spontaneous.

(iv) The Gibb's free energy change, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, through the following equation:

$$\Delta G^\ominus = -RT \ln K_c$$

where $\Delta G^\ominus$ is in J mol^{-1}.

Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

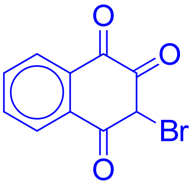
$\Delta G^\ominus = -nFE^\ominus_{cell} = -2 \times 96500 \times (-1.28) = 2.47 \times 10^5$ J mol^{-1}
$\Delta G^\ominus = -RT \ln K_c = -8.31 \times 298 \times \ln K_c = 2.47 \times 10^5$
$\Rightarrow K_c = 4.73 \times 10^{-44} << 1$ means position of equilibrium lies more to the left.

(v) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory. [1]

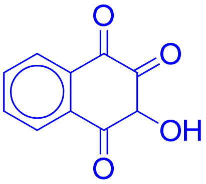
$NaBH_4$ (in ethanol) or $LiAlH_4$ (in dry ether)

(vi) When lawsone is reacted with Br_2(aq), compound **B** with molecular formula, $C_{10}H_5O_3Br$, is formed. **B** reacts with 3 mol of 2,4-DNPH. Reaction of **B** with NaOH(aq) gives **C**. Compound **C** reacts with HCl and $ZnCl_2$ to produce **D**. The reaction of **D** with methylamine gives **E** with molecular formula, $C_{11}H_9O_3N$, which further reacts with CH_3COCl to give a neutral compound **F**.

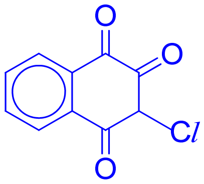
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]



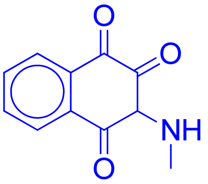
B



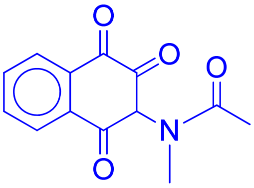
C



D

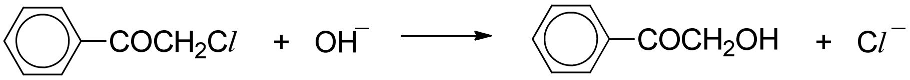


E



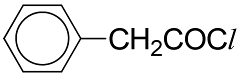
F

(b) Chloroacetophenone was formerly the most widely used tear gas, under the codename *CN*. It was used in warfare and in riot control. Residues of *CN* can be destroyed by the hydrolysis of alkali.

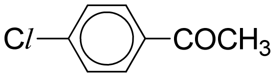


chloroacetophenone

G and **H** are isomers of chloroacetophenone.



G



H

(i) Arrange the isomers, chloroacetophenone, **G** and **H**, in increasing ease of hydrolysis. Explain your choice. [3]

Increasing ease of hydrolysis: H < chloroacetophenone < G

H: The partial double bond character due to the overlapping of the p-orbitals between the C*l* and C atoms of benzene makes the C−C*l* bond difficult to break.

G: The carbonyl carbon is highly electron-deficient due to the presence of electronegative O atom. Hence, more susceptible to nucleophilic attack by water molecule.

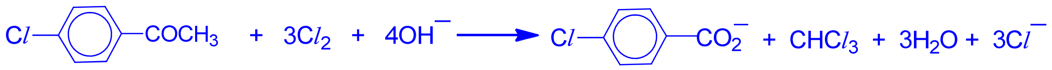
(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

The C−I bond is weaker than the C−C*l* bond because less effective overlap of orbitals due to bigger I atom.

(iii) Suggest a suitable experimental technique for studying the rate of hydrolysis. [1]

Monitor the concentration of OH^- by titration with acid at regular time intervals.
OR Monitor the change in pH using a pH probe at regular time intervals.

(iv) Compound **H** reacts with alkaline aqueous iodine to give a yellow solid, CHI_3. Similar reaction occurs between compound **H** and alkaline aqueous chlorine. Write a balanced equation for the reaction of compound **H** with alkaline aqueous chlorine. State the observation. [2]

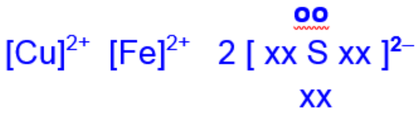


Pale greenish-yellow solution decolourised.

[Total: 20]

5 **(a)** Copper can be extracted from a double salt, $CuFeS_2$, by reacting it with oxygen and silicon dioxide. In this reaction, copper, iron(II) silicate, $FeSiO_3$, and an oxide of sulfur are produced. The oxide of sulfur does not decolourise acidified potassium manganate(VII).

(i) Draw a dot-and-cross diagram for $CuFeS_2$. [1]



$[Cu]^{2+}\ [Fe]^{2+}\ \ 2\,[\,\mathrm{xx}\,\overset{\mathrm{oo}}{\underset{\mathrm{xx}}{S}}\,\mathrm{xx}\,]^{2-}$

(ii) Write a balanced equation for the overall reaction. Deduce the reducing agent in the reaction. [2]

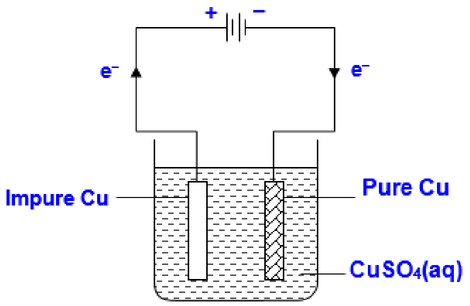
$CuFeS_2 + \frac{7}{2}O_2 + SiO_2 \rightarrow Cu + FeSiO_3 + 2SO_3$

S^{2-} or sulfide is the reducing agent as the oxidation number of S increases from –2 to +6

(iii) Copper(I) sulfide is one of the reaction intermediate. Write the full electronic configuration of copper(I). [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

(iv) The crude copper obtained contains trace amount of silver and nickel. With relevant data from the *Data Booklet* and a labelled diagram, describe how the crude copper can be purified through electrolysis. [4]



Set up an electrolytic cell with pure Cu connected to the negative terminal of the power source whereas the crude Cu to the positive end. Aqueous copper(II) sulfate is the electrolyte used.

At the anode, both Ni and Cu are oxidised due to their more negative/less positive $E^{\ominus}$ value than Ag.

Cu is oxidized to form Cu^{2+}.

Ag will not be oxidised because of a more positive $E^\ominus$ value. It will fall off.
$Ni^{2+} + 2e^- \rightleftharpoons Ni \quad -0.25\ V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad +0.34\ V$
$Ag^+ + e^- \rightleftharpoons Ag \quad +0.80\ V$

At the cathode, Cu^{2+} is reduced to Cu because the $E^\ominus$ value is more positive than that of Ni^{2+}.

(v) 5.0 g of crude copper containing 0.1 g of silver and 0.1 g of nickel is purified through electrolysis as in **(a)(iv)**. During electrolysis, 80% of the current is used to oxidise the metals. With reference to the *Data* Booklet, determine the time needed to purify the copper completely using a current of 2 A. [2]

Amount of Cu = 4.8/63.5 = 0.0756 mol
Amount of Ni = 0.1/58.7 = 0.00170 mol
Total amount of electrons needed = (0.0756 + 0.00170) x 2 = 0.1546 mol
Charge needed = 0.1546 x 96500 = 14918.9 C
Time = Q/I
$= \frac{14918.9}{2} \times \frac{100}{80}$ s
$= \frac{7456.45}{60} \times \frac{100}{80}$ min
= 155.3 min or 155 min

(vi) A student accidentally added some iron(III) nitrate into a solution of copper(II) nitrate. You are provided with

- NH_3(aq), NaOH(aq), HNO_3(aq) and
- apparatus commonly found in a college laboratory.

Describe how the student could separate these two metal ions in the mixture. Give relevant equations and state the types of reactions that have occurred. [3]

Add aqueous NH_3 to the mixture. Cu^{2+} undergoes precipitation to form $Cu(OH)_2$ when ionic product > K_{sp}. Then in excess NH_3(aq), ligand exchange reaction takes place with NH_3.
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$
Fe^{3+} will form insoluble $Fe(OH)_3$ through precipitation when ionic product > K_{sp}.
$Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$
Filter the mixture.

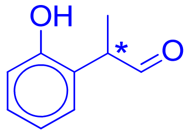
(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

	Test	W	X	Y	Z
1	Rotate plane-polarised light	Yes	No	Yes	Yes
2	Add dilute NaOH at room temperature	Soluble	Soluble	Soluble	Insoluble

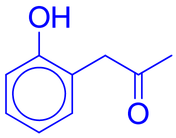
3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	No brick-red precipitate	No brick-red precipitate	No brick-red precipitate
6	Warm with Tollens' reagent	Grey ppt	No grey ppt	No grey ppt	Grey ppt
7	Warm with I_2(aq) and NaOH(aq)	No pale yellow precipitate	Pale yellow precipitate	No pale yellow precipitate	Pale yellow precipitate

(i) Use the information in the table above to suggest a skeletal formula for each of these four isomers. [4]

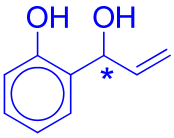
W



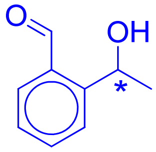
X



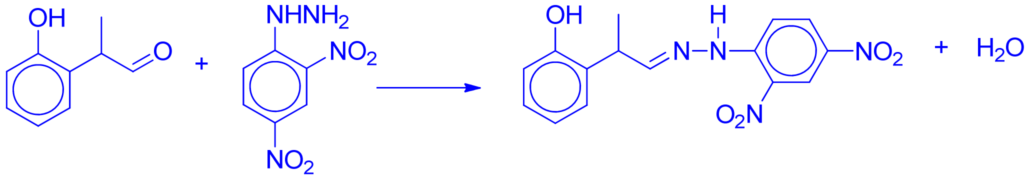
Y



Z



(ii) Write a balanced equation for the reaction between **W** and 2,4-DNPH. [1]



(iii) Explain why **W** is soluble in NaOH(aq) at room temperature. [2]

W contains phenol which undergo neutralization with NaOH to form ionic sodium phenoxide.

The ion-dipole interactions formed between the ions and water release sufficient energy to overcome the hydrogen bondings between water molecules and ionic bonds in sodium phenoxide.

[Total: 20]

End of Paper

VICTORIA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY 9729/04

Practical

30 August 2018

2 hours 30 minutes

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.
Periodic Table is printed on page 16.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **16** printed pages.

1 You are to determine the concentration, in g dm^{-3}, of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment involves two titrations.
In titration one, you will carry out a titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$.
In titration two, you will use the information provided to find the amount of ethanedioic acid, $H_2C_2O_4$.
Finally, you will use the values found in the two titrations to calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

FA 1 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FA 2 is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

Titration One

(a) 1. By using a burette, measure 42.50 cm^3 of **FA 1** into the 250 cm^3 graduated (volumetric) flask.
2. Record your burette readings and the volume of **FA 1** added to the flask in the space below.

[1]

3. Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA 4**.
4. Fill a second burette with **FA 3**.
5. Pipette 25.0 cm^3 of **FA 4** from the graduated flask into a conical flask.
6. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
7. Place the conical flask on a tripod and gauze and heat to about 65 °C.
8. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
9. Titrate the mixture in the conical flask with **FA 3** until a permanent pale pink colour is obtained. This is the end-point.
10. **If a brown colour appears during the titration**, reheat the flask to 65 °C. The brown colour should disappear and the titration can be completed as above. **If the brown colour does not disappear on reheating**, discard the solution and start the titration again.
11. Carry out as many titrations as you think necessary to obtain consistent results.
12. Record in an appropriate form below all of your burette readings and the volume of **FA 3** added in each titration.

[5]

(b) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

25.0 cm^3 of **FA 4** required ………………… cm^3 of **FA 3**. [1]

Titration Two

(c) When 25.0 cm^3 of **FA 4** used in **(a)** is titrated with 0.100 mol dm^{-3} sodium hydroxide using phenolphthalein as the indicator, 15.50 cm^3 of sodium hydroxide is needed for complete reaction.

(i) Write an equation for the reaction between sodium hydroxide and ethanedioic acid.

……………………………………………………………………………………………… [1]

(ii) Calculate the number of moles of sodium hydroxide required to react with 25.0 cm^3 of **FA 4**.

moles of NaOH = ………………… mol [1]

(iii) Hence, calculate the number of moles of ethanedioic acid in 25.0 cm^3 of **FA 4**.

moles of $H_2C_2O_4$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(d) **(i)** Use your answer from **(b)** to calculate the number of moles of potassium manganate(VII), **FA 3**, required to react with 25.0 cm^3 of **FA 4** in **Titration One**.

moles of $KMnO_4$ = ………………… mol [1]

(ii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Use your answer from **(d)(i)** to calculate the total number of moles of ethanedioate ions in 25.0 cm^3 of **FA 4**.

total moles of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(iii) Use your answers from **(c)(iii)** and **(d)(ii)** to calculate the number of moles of ethanedioate ions which came from the sodium ethanedioate in 25.0 cm^3 of **FA 4**.

moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(iv) Hence, calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

Concentration of sodium ethanedioate in **FA 1** = ………………… g dm^{-3} [2]

(e) Explain why the decolourisation of **FA 3** in **Titration One** is initially slow but becomes faster as the reaction proceeds.

…………………………………………………………………………………………………….

…………………………………………………………………………………………………….

…………………………………………………………………………………………………[1]

[Total: 16]

2 This question concerns the solubility of **FA 5**, potassium bromate(V), $KBrO_3$, in water.

The **solubility** of a substance in water is defined as:
the mass of substance that will dissolve in and just saturate 100 g of water at a particular temperature.
When a solution is saturated, the dissolved solid is in equilibrium with undissolved solid.
When a solution of potassium bromate(V) is cooled, it becomes saturated when crystals form in the solution.

You are to investigate how the solubility of **FA 5** in water varies with temperature.

You are provided with the following materials

- weighing bottle labelled **FA 5**, containing potassium bromate(V), $KBrO_3$, and
- deionised water.

Read through the instructions before starting any practical work.

(a) 1. Prepare a hot water bath by filling a 250 cm^3 beaker half full of water and heat it over the Bunsen burner until almost boiling. Turn off the Bunsen burner.
2. Weigh an empty boiling tube.
3. Add the contents of the weighing bottle labelled **FA 5** to the boiling tube.
4. Reweigh the boiling tube and its contents.
5. Record, in an appropriate form below, your weighings and the mass of **FA 5** used.

6. Use the 10 cm^3 measuring cylinder to transfer 8.0 cm^3 of deionised water to the weighed boiling tube containing **FA 5**.
7. Use the clamp as a holder for the boiling-tube. Take care not to break the tube by clamping it too tightly.
8. Warm the tube carefully in the water bath, while stirring the contents with a thermometer, until all the solid has dissolved. (Take care that you do not break the thermometer bulb or the tube while stirring.)
9. Remove the tube from the water bath and attach the clamp to a retort stand.
10. Let the tube cool and continue to stir gently with the thermometer.
11. Watch the solution carefully. Note and record (**on the next page**) the temperature at which you **first** notice crystals forming in the solution.
12. If you are uncertain about the temperature when crystals first form, warm the tube again for a few moments and repeat the cooling.
13. As soon as you have recorded the temperature, add a further 2.0 cm^3 of deionised water to the tube using the 10 cm^3 measuring cylinder.
14. Warm the tube in the water bath to re-dissolve the solid and cool as before.
15. Note and record (**on the next page**) the temperature at which crystals now form in the solution. This will be lower than the temperature obtained with 8.0 cm^3 of water.
16. Repeat the addition of 2.0 cm^3 of deionised water, the heating and the cooling, until you have **four** readings in total.

17. In an appropriate form in the space below, record the following.
    - the total volume of deionised water in the boiling-tube,
    - the temperature at which crystals first appeared for each solution,
    - the solubility (in grams of solid per 100 g of water) which can be calculated using the following formula

$$\text{solubility} = \frac{100}{\text{volume of water}} \times \text{mass of } \mathbf{FA\ 5} \text{ dissolved}$$

[6]

(b) On the grid, plot a graph of solubility against temperature and draw an appropriate line through the points. Do **not** start at zero on either axis. You will need to be able to find the solubility of **FA 5** at 55 °C.

[3]

(c) Use your solubility curve in **(b)** to answer the following.

(i) Explain if dissolving potassium bromate(V), $KBrO_3$, is an exothermic or endothermic process.

$$KBrO_3(s) \rightleftharpoons K^+(aq) + BrO_3^-(aq)$$

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…………………………………………………………………………………………………[1]

(ii) Calculate the solubility of potassium bromate(V), $KBrO_3$, at 55 °C in mol dm^{-3}.
[Given that the M_r of $KBrO_3$ is 167.0.]

[1]

(iii) Hence, calculate the K_{sp} of potassium bromate(V) at this temperature, giving the units.

[2]

(d) Student **A** claims that both the solubility and solubility product of potassium bromate(V) will decrease with the addition of some solid potassium nitrate at a particular temperature. Comment on this student's claim.

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…………………………………………………………………………………………………[1]

(e) A literature value for the solubility of potassium bromate(V) is 13.1 g per 100 g of water at 40 °C. Student **A** followed the instructions in part **(a)** and obtained a solubility value for $KBrO_3$ to be 15.0 g per 100 g of water at the same temperature. Calculate the magnitude of the percentage experimental error for student **A**'s measurement.

[1]

[Total:15]

3 Planning

FA 6 is a powdered mixture of mica and iron(III) oxide, Fe_2O_3, which is used as ingredients in mineral makeup such as eye shadow or blusher. Iron(III) oxide adds a red colour to makeup while mica gives makeup a light reflecting quality.

The reaction between Fe_2O_3, and ethanedioic acid, $H_2C_2O_4$, is exothermic as shown.

$$Fe_2O_3(s) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 3H_2O(l) \quad \Delta H < 0$$

In a thermometric titration, the end–point is reached when the maximum temperature change occurs. A thermometric titration between Fe_2O_3 and $H_2C_2O_4$ can be carried out to find out the percentage by mass of iron(III) oxide in **FA 6**. The temperature of the reaction mixture is monitored when a certain mass of **FA 6** is added into a fixed volume of aqueous $H_2C_2O_4$ solution. The experiment is then repeated using different masses of **FA 6**. You may assume mica remains unchanged in this experiment.

The data obtained is plotted and two best–fit graph lines are drawn. One line is drawn using data before the end–point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(a) Using the information given above, you are required to write a plan for a thermometric titration between **FA 6** and aqueous $H_2C_2O_4$ solution.

You are provided with

- 500 cm^3 of 1.00 mol dm^{-3} $H_2C_2O_4$,
- 30 g of solid **FA 6** containing approximately 90% by mass of Fe_2O_3,
- styrofoam cup,
- thermometer, and
- apparatus commonly found in a college laboratory.

In your plan you should include details of

- justification of specific quantities of reactants that you would use,
- the apparatus you would use and the procedure you would follow,
- a sketch of the graph you would expect to obtain, with the end–point clearly labelled, and
- how the data obtained from the graph would be used to calculate the actual percentage by mass of Fe_2O_3 in **FA 6**.

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…………………………………………………………………………………………[10]

(b) A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%. Is the student correct? Explain your answer.

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…………………………………………………………………………………………[2]

[Total: 12]

4 You are given samples of eight aqueous solutions.

FB 1	containing bromide ions, Br^-
FB 2	containing bromate(I) ions, BrO^-
FB 3	containing iron(III) ions, Fe^{3+}
FB 4	containing hydrogen peroxide, H_2O_2
FB 5	containing aqueous iodine, I_2
FB 6	containing iodide ions, I^-
FB 7	containing potassium manganate(VII), $KMnO_4$

You are also given hexane, sulfuric acid and starch solution.

You will perform a series of tests to investigate if any redox reaction has occurred.

You will make deductions about the relative oxidising powers of different substances.

For example, under appropriate conditions, chlorine water will oxidise iodide ions to iodine.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Deduction would be that chlorine is a stronger oxidising agent than iodine. This is represented by $Cl_2 > I_2$.

In another example, iodine will **not** oxidise bromide ions to bromine. So, the deduction would be that bromine is a stronger oxidising agent than iodine. This is represented by $Br_2 > I_2$.

(a) Perform the tests described in **Table 1**. Record your observations in the spaces provided. If there is no observable reaction, write **'no reaction'** in the observations column.

Your observations should allow you to deduce the relative oxidising powers of the substances involved.

State the relative oxidising power of the substances involved under the deductions column of **Table 1**. They should be written in the form e.g. $Cl_2 > I_2$.

[10]

Table 1

Tests		Observations	Deductions
1	Add 1 cm^3 of **FB 6** to a test–tube. Then add 8 drops of **FB 3**, followed by 5 drops of starch solution.		
2	Add 1 cm^3 of **FB 3** to a test–tube. Then, add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.		
3	Add 1 cm^3 of **FB 4** to a test–tube. Then add 8 drops of **FB 5**.		
4	Add 1 cm^3 of **FB 4** to a test–tube. Now add 1 cm^3 of dilute sulfuric acid. Then add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.		
5	Add 1 cm^3 of **FB 1** to a test–tube. Now add 4 drops of dilute sulfuric acid. Then add 1 cm^3 of **FB 2**.		
6	Add 1 cm^3 of **FB 4** to a test–tube. Then add 1 cm^3 of **FB 3**. Make observations for about 2 minutes before recording your results.		

Tests		Observations	Deductions
7	Add 1 cm^3 of **FB 1** in a test–tube followed by 1 cm^3 of dilute sulfuric acid. Then add 8 drops of **FB 7** and 1 cm^3 of hexane. Shake the mixture.		

(b) Using your answers in **Table 1**, arrange the following substances below in descending order of their oxidising power.

Br_2, BrO^-, Fe^{3+}, I_2, O_2

……..[1]

(c) What are the roles of **FB 3** in tests **1** and **6** respectively?

…...

………………………………………………………………………………………………[1]

[Total: 12]

End of paper

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

The Periodic Table of Elements

Key

atomic number
atomic symbol
name
relative atomic mass

Group

1	2											13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Apparatus and Chemicals for each candidate

Apparatus list

1. 2 × 50.00 cm^3 burette (to invert burette and put on retort stand)
2. 1 × 25.0 cm^3 pipette
3. 2 × 250 cm^3 conical flask
4. 2 x 150 cm^3 beaker
5. 1 × 250 cm^3 beaker
6. 1 × 250 cm^3 graduated flask
7. 1 × 10 cm^3 measuring cylinder
8. 1 × 50 cm^3 measuring cylinder
9. 1 × glass rod
10. Plastic bag: 6 × dropper, 1 × long wooden splint, 2 × paper towel, blue & red litmus papers, filter paper strips
11. Plastic bag: 5 test tubes
12. 1 × dry boiling tube (pack with 5 test tubes)
13. 1 × pipette filler
14. 1 × retort stand and burette clamp
15. 1 × clamp – to hold a boiling tube (to mount on retort stand)
16. 1 × white tile
17. 2 × filter funnel
18. 1 × Bunsen burner
19. 1 × wire gauge (heat proof mat)
20. 1 × tripod stand
21. 1 × lighter
22. 1 × alcohol thermometer (–10 ^{o}C to 110 ^{o}C at 1 ^{o}C)
23. 1 × wash bottle containing distilled water
24. 1 × test tube rack
25. 1 × test tube holder
26. 1 × visualiser per lab
27. electronic weighing balance (5 per lab)
28. synchronise all the clocks in the 8 labs

Chemical List

29. **FA 1** is 0.250 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$ (100 cm^3 in a vial labelled **FA 1**)
30. **FA 2** is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4 (100 cm^3 in a vial labelled **FA 2**)
31. **FA 3** is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$ (120 cm^3 in a vial labelled **FA 3**)
32. **FA 5** is solid potassium bromate(V), $KBrO_3$ (1.90–2.10 g in a weighing bottle labelled **FA 5**)
33. One rack of bench reagents (only for show, no need to prepare fresh solutions)
34. 1 red tub per student for 3 shifts containing **FB 1** to **FB 8**, sulfuric acid, hexane and starch

Label	Capacity per student in capped reagent bottle
FB 1	10 cm^3 of 0.1 mol dm^{-3} potassium bromide, KBr, made by dissolving about 11.9 g of KBr in 1 dm^3 of deionised water
FB 2	10 cm^3 of 10% aqueous potassium bromate(I), KBrO
FB 3	5 cm^3 of 0.2 mol dm^{-3} ammonium iron(III) sulfate, $NH_4Fe(SO_4)_2{\cdot}12H_2O$, made by dissolving about 96.4 g of $NH_4Fe(SO_4)_2{\cdot}12H_2O$ in 1 dm^3 of deionised water
FB 4	10 cm^3 of 20 volume hydrogen peroxide, H_2O_2 (containing 200 cm^3 of freshly opened 100 volume hydrogen peroxide, made up to 1 dm^3 with deionised water)
FB 5	5 cm^3 of 0.01 mol dm^{-3} aqueous iodine, I_2, made by dissolving about 2.5 g of iodine and about 8 g of potassium, KI, in 1 dm^3 of deionised water
FB 6	5 cm^3 of 0.1 mol dm^{-3} potassium iodide, KI, made by dissolving about 16.6 g of KI in 1 dm^3 of deionised water
FB 7	5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) (same solution as **FA 3**)
sulfuric acid	one labelled reagent bottle containing 2 mol dm^{-3} H_2SO_4 (same solution as **FA 2**, one full reagent bottle)
hexane	hexane (one full reagent bottle)
starch	starch (one full reagent bottle)

VICTORIA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY **9729/04**

Practical **30 August 2018**

2 hours 30 minutes

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.
Periodic Table is printed on page 16.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **16** printed pages.

1 You are to determine the concentration, in g dm^{-3}, of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment involves two titrations.
In titration one, you will carry out a titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$.
In titration two, you will use the information provided to find the amount of ethanedioic acid, $H_2C_2O_4$.
Finally, you will use the values found in the two titrations to calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

FA 1 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FA 2 is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

Titration One

(a) 1. By using a burette, measure between 42.50 cm^3 of **FA 1** into the 250 cm^3 graduated (volumetric) flask.
2. Record your burette readings and the volume of **FA 1** added to the flask in the space below.

Final burette reading / cm^3	42.50
Initial burette reading / cm^3	0.00
Volume of **FA 1** used / cm^3	42.50

[1]

3. Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA 4**.
4. Fill a second burette with **FA 3**.
5. Pipette 25.0 cm^3 of **FA 4** from the graduated flask into a conical flask.
6. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
7. Place the conical flask on a tripod and gauze and heat to about 65 °C.
8. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
9. Titrate the mixture in the conical flask with **FA 3** until a permanent pale pink colour is obtained. This is the end-point.
10. **If a brown colour appears during the titration**, reheat the flask to 65 °C. The brown colour should disappear and the titration can be completed as above. **If the brown colour does not disappear on reheating**, discard the solution and start the titration again.
11. Carry out as many titrations as you think necessary to obtain consistent results.
12. Record in an appropriate form all of your burette readings and the volume of **FA 3** added in each titration.

Final burette reading / cm^3	19.50	39.50
Initial burette reading / cm^3	0.00	20.00
Volume of **FA 3** used / cm^3	19.50	19.50

[5]

(b) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

Average volume of **FA 3** used
= (19.50 + 19.50) ÷ 2
= 19.50 cm^3

25.0 cm^3 of **FA 4** required ……19.50……… cm^3 of **FA 3**. [1]

Titration Two

(c) When 25.0 cm^3 of **FA 4** used in **(a)** is titrated with 0.100 mol dm^{-3} sodium hydroxide using phenolphthalein as the indicator, 15.50 cm^3 of sodium hydroxide is needed for complete reaction.

(i) Write an equation for the reaction between sodium hydroxide and ethanedioic acid.

$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$ …… [1]

(ii) Calculate the number of moles of sodium hydroxide required to react with 25.0 cm^3 of **FA 4**.

No. of moles of NaOH required
= $0.100 \times 15.50 \times 10^{-3}$
= 1.55×10^{-3} mol

moles of NaOH = …1.55×10^{-3}… mol [1]

(iii) Hence, calculate the number of moles of ethanedioic acid in 25.0 cm^3 of **FA 4**.

No. of moles of $H_2C_2O_4$ present in 25.0 cm^3
= ½ × no. of moles of NaOH required
= $\frac{1}{2} \times 1.55 \times 10^{-3}$
= 7.75×10^{-4} mol

moles of $H_2C_2O_4$ in 25.0 cm^3 of **FA 4** = …7.75×10^{-4}… mol [1]

(d) **(i)** Use your answer from **(b)** to calculate the number of moles of potassium manganate(VII), **FA 3**, required to react with 25.0 cm^3 of **FA 4** in **Titration One**.

No. of moles of $KMnO_4$ required
= $0.0200 \times 19.50 \times 10^{-3}$
= 3.90×10^{-4} mol

moles of $KMnO_4$ = …3.90×10^{-4}… mol [1]

(ii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Use your answer from **(d)(i)** to calculate the total number of moles of ethanedioate ions in 25.0 cm^3 of **FA 4**.

Total no. of moles of $C_2O_4^{2-}$ present in 25.0 cm^3
= 5/2 × no. of moles of MnO_4^- required
= $5/2 \times 3.90 \times 10^{-4}$
= 9.75×10^{-4} mol

total moles of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 4** = …9.75×10^{-4}… mol [1]

(iii) Use your answers from **(c)(iii)** and **(d)(ii)** to calculate the number of moles of ethanedioate ions which came from the sodium ethanedioate in 25.0 cm^3 of **FA 4**.

No. of moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3
$= (9.75 \times 10^{-4}) - (7.75 \times 10^{-4})$
$= 2.00 \times 10^{-4}$ mol

moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 4** = 2.00×10^{-4} …… mol [1]

(iv) Hence, calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

No. of moles of $Na_2C_2O_4$ in 250 cm^3 of solution of **FA 4**
$= 2.00 \times 10^{-4} \times \frac{250}{25.0}$
$= 2.00 \times 10^{-3}$ mol

Mass of $Na_2C_2O_4$ in 42.70 cm^3 of **FA 1**
$= 2.00 \times 10^{-3} \times (2\times23.0 + 2\times12.0 + 4\times16.0)$
$= 0.268$ g

Concentration, in g dm^{-3}, of $Na_2C_2O_4$ in **FA 1**
$= 0.268 \div \frac{42.50}{1000}$
$= 6.31$ g dm^{-3}

Concentration of sodium ethanedioate is 6.31 ……………… g dm^{-3} [2]

(e) Explain why the decolourisation of **FA 3** in **Titration One** is initially slow but becomes faster as the reaction proceeds.

Sufficient auto-catalyst, Mn^{2+}(aq) ions, will be formed to catalyse the reaction to occur faster.

…………………………………………………………………………………………… [1]

[Total: 16]

2 This question concerns the solubility of **FA 5**, potassium bromate(V), $KBrO_3$, in water.

> The **solubility** of a substance in water is defined as:
> the mass of substance that will dissolve in and just saturate 100 g of water at a particular temperature.
> When a solution is saturated, the dissolved solid is in equilibrium with undissolved solid.
> When a solution of potassium bromate(V) is cooled, it becomes saturated when crystals form in the solution.

You are to investigate how the solubility of **FA 5** in water varies with temperature.

You are provided with the following materials
- weighing bottle labelled **FA 5**, containing potassium bromate(V), $KBrO_3$, and
- deionised water.

Read through the instructions before starting any practical work.

(a) 1. Prepare a hot water bath by filling a 250 cm^3 beaker half full of water and heat it over the Bunsen burner until almost boiling. Turn off the Bunsen burner.
2. Weigh an empty boiling tube.
3. Add the contents of the weighing bottle labelled **FA 5** to the boiling tube.
4. Reweigh the boiling tube and its contents.

5. Record, in an appropriate form below, your weighings and the mass of **FA 5** used.

Mass of boiling tube + **FA 5** / g	32.360
Mass of boiling tube / g	30.299
Mass of **FA 5** used / g	2.061

6. Use the 10 cm^3 measuring cylinder to transfer 8.0 cm^3 of deionised water to the weighed boiling tube containing **FA 5**.

7. Use the clamp as a holder for the boiling-tube. Take care not to break the tube by clamping it too tightly.

8. Warm the tube carefully in the water bath, while stirring the contents with a thermometer, until all the solid has dissolved. (Take care that you do not break the thermometer bulb or the tube while stirring.)

9. Remove the tube from the water bath and attach the clamp to a retort stand.

10. Let the tube cool and continue to stir gently with the thermometer.
11. Watch the solution carefully. Note and record (**on the next page**) the temperature at which you **first** notice crystals forming in the solution.

12. If you are uncertain about the temperature when crystals first form, warm the tube again for a few moments and repeat the cooling.

13. As soon as you have recorded the temperature, add a further 2.0 cm^3 of deionised water to the tube using the 10 cm^3 measuring cylinder.

14. Warm the tube in the water bath to re-dissolve the solid and cool as before.

15. Note and record (**on the next page**) the temperature at which crystals now form in the solution. This will be lower than the temperature obtained with 8.0 cm^3 of water.

16. Repeat the addition of 2.0 cm^3 of deionised water, the heating and the cooling, until you have **four** readings in total.

17. In an appropriate form in the space below, record the following.

    - the total volume of deionised water in the boiling-tube

    - the temperature at which crystals first appeared for each solution

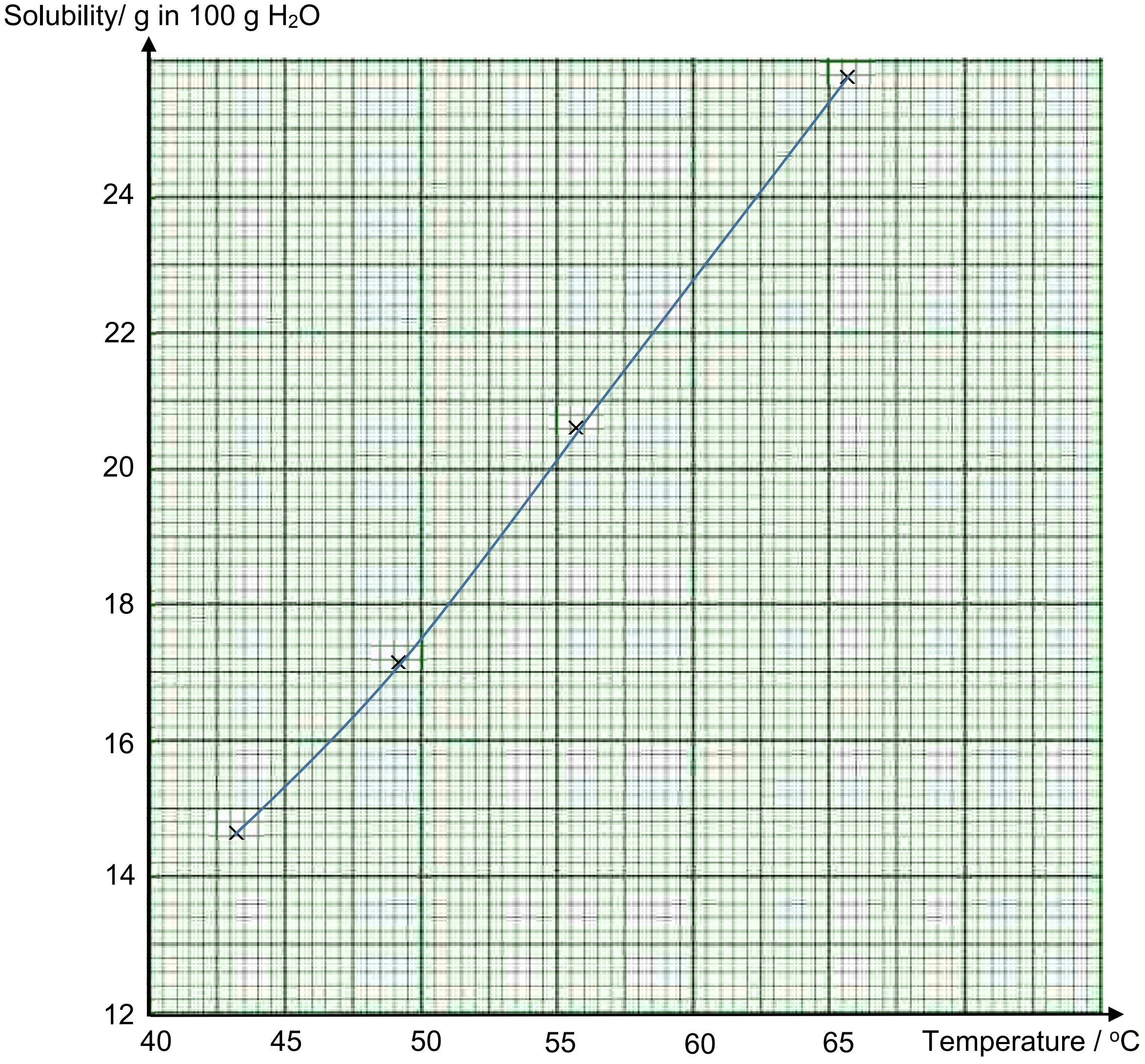
- the **solubility** (in grams of solid per 100 g of water) which can be calculated using the following formula

$$\text{solubility} = \frac{100}{\text{volume of water}} \times \text{mass of } \mathbf{FA\ 5} \text{ dissolved}$$

Volume of water/ cm^3	Temperature at first appearance of crystals/ °C	Solubility/ g per 100 g H_2O
8.0	65.5	25.8
10.0	55.5	20.6
12.0	49.0	17.2
14.0	43.0	14.7

[6]

(b) On the grid, plot a graph of solubility against temperature and draw an appropriate line through the points. Do **not** start at zero on either axis. You will need to be able to find the solubility of **FA 5** at 55 °C.



[3]

(c) Use your solubility curve in **(b)** to answer the following.

(i) Explain if dissolving potassium bromate(V), $KBrO_3$, is an exothermic or endothermic process.

$$KBrO_3(s) \rightleftharpoons K^+(aq) + BrO_3^-(aq)$$

The graph has a positive gradient. Hence, solubility of $KBrO_3$ increases with temperature. Dissolving $KBrO_3$ is an endothermic process.

[1]

(ii) Calculate the solubility of potassium bromate(V), $KBrO_3$, at 55 °C in mol dm^{-3}.
[Given that the M_r of $KBrO_3$ is 167.0.]

From the graph, solubility of $KBrO_3$ is 20.2 g per 100 g of H_2O.

Solubiity in mol dm^{-3} = $\frac{20.2}{167.0} \times \frac{1000}{100}$ = 1.21 mol dm^{-3}

[1]

(iii) Hence, calculate the K_{sp} of potassium bromate(V) at this temperature, giving the units.

$K_{sp} = [K^+][BrO_3^-] = (1.21)^2 = 1.46$ mol^2 dm^{-6} (ecf)

[2]

(d) Student **A** claims that both the solubility and solubility product of potassium bromate(V) will decrease with the addition of some solid potassium nitrate at a particular temperature. Comment on the student's claim.

On addition of potassium nitrate, concentration of K^+ increases and the position of equilibrium shift left. Solubility of $KBrO_3$ decreases.

However, solubility product is only dependent on temperature/independent of temperature and hence remains unchanged.

[1]

(e) A literature value for the solubility of potassium bromate(V) is 13.1 g per 100 g of water at 40 °C. Student **A** followed the instructions in **(a)** and obtained a solubility value for $KBrO_3$ to be 15.0 g per 100 g of water at the same temperature. Calculate the magnitude of the percentage experimental error for student **A**'s measurement.

Experimental error = $\left| \frac{13.1 - 15.0}{13.1} \right|$ x 100% = 14.5%

[1]

[Total:15]

3 Planning

FA 6 is a powdered mixture of mica and iron(III) oxide, Fe_2O_3, which is used as ingredients in mineral makeup such as eye shadow or blusher. Iron(III) oxide adds a red colour to makeup while mica gives makeup a light reflecting quality.

The reaction between Fe_2O_3, and ethanedioic acid, $H_2C_2O_4$, is exothermic as shown.

$$Fe_2O_3(s) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 3H_2O(l) \qquad \Delta H < 0$$

In a thermometric titration, the end–point is reached when the maximum temperature change occurs. A thermometric titration between Fe_2O_3 and $H_2C_2O_4$ can be carried out to find out the percentage by mass of iron(III) oxide in **FA 6**. The temperature of the reaction mixture is monitored when a certain mass of **FA 6** is added into a fixed volume of aqueous $H_2C_2O_4$ solution. The experiment is then repeated using different masses of **FA 6**. You may assume mica remains unchanged in this experiment.

The data obtained is plotted and two best–fit graph lines are drawn. One line is drawn using data before the end–point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(a) Using the information given above, you are required to write a plan for a thermometric titration between **FA 6** and aqueous $H_2C_2O_4$ solution.

You are provided with

- 500 cm^3 of 1.00 mol dm^{-3} of $H_2C_2O_4$,
- 30 g of solid **FA 6** containing approximately 90% by mass of Fe_2O_3,
- styrofoam cup,
- thermometer, and
- apparatus commonly found in a college laboratory

In your plan you should include details of

- justification of specific quantities of reactants that you would use,
- the apparatus you would use and the procedure you would follow,
- a sketch of the graph you would expect to obtain, with the end–point clearly labelled, and
- how the data obtained from the graph would be used to calculate the actual percentage by mass of Fe_2O_3 in **FA 6**

(i) Justification of quantities of reactants used for the experiments

Assume 50 cm^3 of 1.00 mol dm^{-3} $H_2C_2O_4$ is used.
Amount of $H_2C_2O_4$ used in 50 cm^3 of $H_2C_2O_4$ = (50/1000) x 1.00
= 0.0500 mol

Mass of Fe_2O_3 required to react completely with 50 cm^3 of $H_2C_2O_4$
= (0.05/3) x (55.8x2 + 16.0x3)
= 2.66 g

Approximate mass of FA 6 required to react with 50 cm^3 of $H_2C_2O_4$
= (2.66/90) x 100
= 2.96 g

Experiment	Volume of $H_2C_2O_4$/cm^3	Mass of FA 6 /g	ΔT / °C
1	50.0	1.000	
2	50.0	1.500	
3	50.0	2.000	
4	50.0	2.500	
5	50.0	3.000	
6	50.0	3.500	
7	50.0	4.000	
8	50.0	4.500	
9	50.0	5.000	

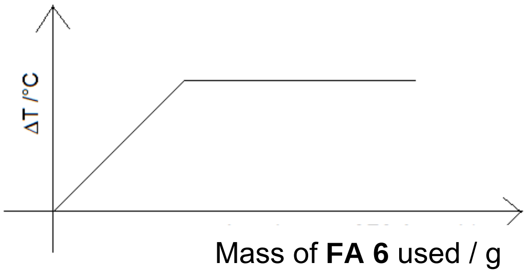
(ii) Procedure

1. Use a 50 cm^3 burette to introduce 50.00 cm^3 of 1 mol dm^{-3} of $H_2C_2O_4^-$ into a dry styrofoam cup.

2. Place the thermometer into the solution and record initial temperature of the solution.
3. Weigh accurately 1.000 g of FA 6 and put it into the Styrofoam cup.
4. Stir gently with the thermometer. Record the highest temperature rise.
5. Reweigh the emptied weighing bottle to get the actual mass of FA 6 that has been used.
6. Repeat steps 1 to 5 for experiment 2 to experiment 9.

(iii) Sketch of graph

1. Plot a graph of ∆T versus actual mass of FA 6 added.
2. Correct shape and indicate the intersection point will give us the mass of FA 6 needed to completely react with $H_2C_2O_4$. This is when end–point has been reached.



(iv) Calculations

Percentage mass of Fe_2O_3 in FA 6
= (2.66/Mass of FA 6 obtained from the graph) x 100%

[10]

(b) A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%. Is the student correct? Explain your answer.

Percentage error for burette = $\frac{2 \times 0.05}{25.0}$ x 100 = 0.40 %
No, the pipette is more accurate. This is because the percentage error of using the burette to measure the 25.0 cm^3 of acid is greater than the pipette.

[2]

[Total: 12]

4 You are given samples of eight aqueous solutions.

FB 1	containing bromide ions, Br^-
FB 2	containing bromate(I) ions, BrO^-
FB 3	containing iron(III) ions, Fe^{3+}
FB 4	containing hydrogen peroxide, H_2O_2
FB 5	containing aqueous iodine, I_2
FB 6	containing iodide ions, I^-
FB 7	containing potassium manganate(VII), $KMnO_4$

You are also given hexane, sulfuric acid and starch solution.

You will perform a series of tests to investigate if any redox reaction has occurred.

You will make deductions about the relative oxidising powers of different substances.

For example, under appropriate conditions, chlorine water will oxidise iodide ions to iodine.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Deduction would be that chlorine is a stronger oxidising agent than iodine. This is represented by $Cl_2 > I_2$.

In another example, iodine will **not** oxidise bromide ions to bromine. So, the deduction would be that bromine is a stronger oxidising agent than iodine. This is represented by $Br_2 > I_2$.

(a) Perform the tests described in **Table 1**. Record your observations in the spaces provided. If there is no observable reaction, write **'no reaction'** in the observations column.

Your observations should allow you to deduce the relative oxidising powers of the substances involved.

State the relative oxidising power of the substances involved under the deductions column of **Table 1**. They should be written in the form e.g. $Cl_2 > I_2$.

[10]

Table 1

Tests		Observations	Deductions
1	Add 1 cm^3 of **FB 6** to a test–tube. Then add 8 drops of **FB 3**, followed by 5 drops of starch solution.	• Solution turned brown. • Solution turned blue–black with starch.	• Fe^{3+} > I_2
2	Add 1 cm^3 of **FB 3** to a test–tube. Then, add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.	• No reaction.	• Br_2 > Fe^{3+}
3	Add 1 cm^3 of **FB 4** to a test–tube. Then add 8 drops of **FB 5**.	• No reaction.	• O_2 > I_2
4	Add 1 cm^3 of **FB 4** to a test–tube. Now add 1 cm^3 of dilute sulfuric acid. Then add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.	• Aqueous layer turned yellow/orange. • Organic layer turned orange/red/brown	• H_2O_2 > Br_2
5	Add 1 cm^3 of **FB 1** to a test–tube. Now add 4 drops of dilute sulfuric acid. Then add 1 cm^3 of **FB 2**.	• Solution turned orange/red/yellow.	• BrO^- > Br_2
6	Add 1 cm^3 of **FB 4** to a test–tube. Then add 1 cm^3 of **FB 3**. Make observations for about 2 minutes before recording your results.	• Solution turned brown. • Effervescence (or bubbles) observed. • O_2 gas • relighted a glowing splint. • Solution remained yellow/brown.	• Fe^{3+} > O_2

7	Add 1 cm^3 of **FB 1** in a test–tube followed by 1 cm^3 of dilute sulfuric acid. Then add 8 drops of **FB 7** and 1 cm^3 of hexane. Shake the mixture.	- Aqueous layer turned yellow/orange/red. - Organic layer turned orange/brown/red.	• $MnO_4^- > Br_2$

(b) Using your answers in **Table 1**, arrange the following substances below in descending order of their oxidising power.

Br_2, BrO^-, Fe^{3+}, I_2, O_2

$BrO^- > Br_2 > Fe^{3+} > O_2 > I_2$

[1]

(c) What are the roles of **FB 3** in tests **1** and **6** respectively?

In test 1, it is acting as an oxidising agent (as it is reduced) while in test 6, it is a catalyst.

[1]

[Total: 12]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

The Periodic Table of Elements

Group																	
1	2											13	14	15	16	17	18
				Key			1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0			atomic number atomic symbol name relative atomic mass								5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 T*l* thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 F*l* flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Apparatus and Chemicals for each candidate

Apparatus list

1. 2 × 50.00 cm^3 burette (to invert burette and put on retort stand)
2. 1 × 25.0 cm^3 pipette
3. 2 × 250 cm^3 conical flask
4. 2 x 150 cm^3 beaker
5. 1 × 250 cm^3 beaker
6. 1 × 250 cm^3 graduated flask
7. 1 × 10 cm^3 measuring cylinder
8. 1 × 50 cm^3 measuring cylinder
9. 1 × glass rod
10. Plastic bag: 6 × dropper, 1 × long wooden splint, 2 × paper towel, blue & red litmus papers, filter paper strips
11. Plastic bag: 5 test tubes
12. 1 × dry boiling tube (pack with 5 test tubes)
13. 1 × pipette filler
14. 1 × retort stand and burette clamp
15. 1 × clamp – to hold a boiling tube (to mount on retort stand)
16. 1 × white tile
17. 2 × filter funnel
18. 1 × Bunsen burner
19. 1 × wire gauge (heat proof mat)
20. 1 × tripod stand
21. 1 × lighter
22. 1 × alcohol thermometer (–10 °C to 110 °C at 1 °C)
23. 1 × wash bottle containing distilled water
24. 1 × test tube rack
25. 1 × test tube holder
26. 1 × visualiser per lab
27. electronic weighing balance (5 per lab)
28. synchronise all the clocks in the 8 labs

Chemical List

29. **FA 1** is 0.250 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$ (100 cm^3 in a vial labelled **FA 1**)
30. **FA 2** is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4 (100 cm^3 in a vial labelled **FA 2**)
31. **FA 3** is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$ (120 cm^3 in a vial labelled **FA 3**)
32. **FA 5** is solid potassium bromate(V), $KBrO_3$ (1.90–2.10 g in a weighing bottle labelled **FA 5**)
33. One rack of bench reagents (only for show, no need to prepare fresh solutions)
34. 1 red tub per student for 3 shifts containing **FB 1** to **FB 8**, sulfuric acid, hexane and starch

Label	Capacity per student in capped reagent bottle
FB 1	10 cm^3 of 0.1 mol dm^{-3} potassium bromide, KBr, made by dissolving about 11.9 g of KBr in 1 dm^3 of deionised water
FB 2	10 cm^3 of 10% aqueous potassium bromate(I), KBrO
FB 3	5 cm^3 of 0.2 mol dm^{-3} ammonium iron(III) sulfate, $NH_4Fe(SO_4)_2{\cdot}12H_2O$, made by dissolving about 96.4 g of $NH_4Fe(SO_4)_2{\cdot}12H_2O$ in 1 dm^3 of deionised water
FB 4	10 cm^3 of 20 volume hydrogen peroxide, H_2O_2 (containing 200 cm^3 of freshly opened 100 volume hydrogen peroxide, made up to 1 dm^3 with deionised water)
FB 5	5 cm^3 of 0.01 mol dm^{-3} aqueous iodine, I_2, made by dissolving about 2.5 g of iodine and about 8 g of potassium, KI, in 1 dm^3 of deionised water
FB 6	5 cm^3 of 0.1 mol dm^{-3} potassium iodide, KI, made by dissolving about 16.6 g of KI in 1 dm^3 of deionised water
FB 7	5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) (same solution as **FA 3**)
sulfuric acid	one labelled reagent bottle containing 2 mol dm^{-3} H_2SO_4 (same solution as **FA 2**, one full reagent bottle)
hexane	hexane (one full reagent bottle)
starch	starch (one full reagent bottle)

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME					
CLASS	6				
CENTRE NUMBER	S				

INDEX NUMBER				

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

20 September 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, class and index number on the Optical Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the one you consider correct and record your choice in **soft pencil** on the Optical Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **12** printed pages.

For each question there are four possible answers, **A, B, C** and **D**.

Choose the **one** you consider to be correct.

1 A mixture of argon and another gas is commonly used during welding. At s.t.p, the density of the gaseous mixture is 1.82 g dm^{-3}.

What is the identity of the other gas in the mixture?

[Density of argon = 1.78 g dm^{-3} at s.t.p.]

A neon

B nitrogen

C oxygen

D carbon dioxide

2 Sodium thiosulfate ($Na_2S_2O_3$) is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.

If 10 cm^3 of 0.20 mol dm^{-3} of sodium thiosulfate requires 192 cm^3 of chlorine for complete reaction at r.t.p., which of the following is a possible formula of the sulfur-containing product?

A S **B** SO_2 **C** HSO_4^- **D** H_2S

3 Which of the following ions would undergo the smallest deflection in an electric field?

A $^{16}O_2^+$ **B** $^{16}O^{18}O^+$ **C** $^{16}O^{18}O^{2+}$ **D** $^{18}O^{2+}$

4 The table below shows the fourth ionisation energies of five consecutive elements in the Periodic Table.

Element	V	W	X	Y	Z
Fourth ionisation energy / kJ mol^{-1}	10450	11710	4350	5030	4580

What is the formula of the bromide of V?

A VBr **B** VBr_2 **C** VBr_3 **D** VBr_5

5 Two identical bulbs at the same temperature contain ideal gases **P** and **Q** separately. The density of gas **P** is half that of gas **Q** while the molecular mass of gas **P** is twice that of gas **Q**.

What is the ratio of the pressure of gas **P** to that of gas **Q**?

A 1 : 1 **B** 1 : 2 **C** 1 : 4 **D** 2 : 1

6 The auto-ionisation of bromine trifluoride is represented by the equation:

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Which of the following statements is correct?

A BrF_3 is planar while BrF_4^- is non-planar.

B BrF_2^+ is linear while BrF_4^- is tetrahedral in shape.

C The F–Br–F bond angle in BrF_3 is smaller than that in BrF_2^+.

D There are more lone pairs of electrons around the Br atom in BrF_3 than that in BrF_2^+.

7 Dimerisation is described as a process in which two identical molecules combine to give a single product. Some examples include Al_2Cl_6, N_2O_4 and $(CH_3CO_2H)_2$.

Which of the following statements about the above dimers are correct?

1 Hydrogen bonds hold the CH_3CO_2H molecules together in the dimer.

2 All the nitrogen-oxygen bonds in N_2O_4 are of equal length.

3 The bond angle around each aluminium atom in Al_2Cl_6 is 109.5°.

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

8 Vaporisation is the process when a liquid is converted to a gas.

Given that the enthalpy change of vaporisation of water is +40.8 kJ mol^{-1}, what is the entropy change when 36.0 g of water boil to form water vapour?

A +109 J K^{-1}

B −109 J K^{-1}

C +219 J K^{-1}

D −219 J K^{-1}

9 At T °C and a total pressure of 6.00 atm, N_2O_4 is 60.0% dissociated into NO_2.

What is the K_p value at T °C?

A 3.0 **B** 5.4 **C** 13.5 **D** 21.6

10 H_2A is a weak acid which undergoes partial dissociation.

$$H_2A(aq) \rightleftharpoons 2H^+(aq) + A^{2-}(aq)$$

Given that the pH of 1.00 mol dm^{-3} H_2A(aq) solution is 2.3, what is the degree of dissociation of H_2A?

A 2.50×10^{-3} **B** 5.01×10^{-3} **C** 1.26×10^{-5} **D** 1.26×10^{-7}

11 The auto-ionisation of water is an endothermic process.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +6.5 \text{ kJ mol}^{-1}$$

Which of the following statements are correct?

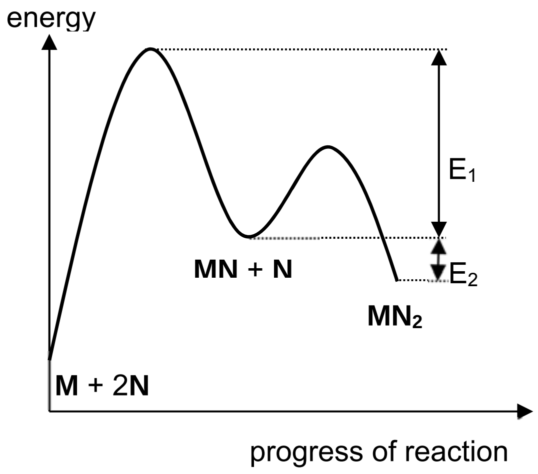
1 K_w increases as temperature increases.
2 pH of solution decreases as temperature increases.
3 Acidity of water increases as temperature increases.

A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

12 What is the pH of a saturated solution of aluminium hydroxide, $Al(OH)_3$, if its solubility product is 2.53×10^{-18} mol^4 dm^{-12}?

A 4.28 **B** 5.44 **C** 9.60 **D** 9.72

13 The energy profile diagram of the reversible reaction between **M** and **N** is shown below.



Which of the following statements are correct?

1 The activation energy of the reverse reaction is $E_1 + E_2$.

2 Rate equation of the reaction is rate = $k[\mathbf{M}][\mathbf{N}]^2$.

3 The equilibrium [$\mathbf{MN}_2$] increases as temperature increases.

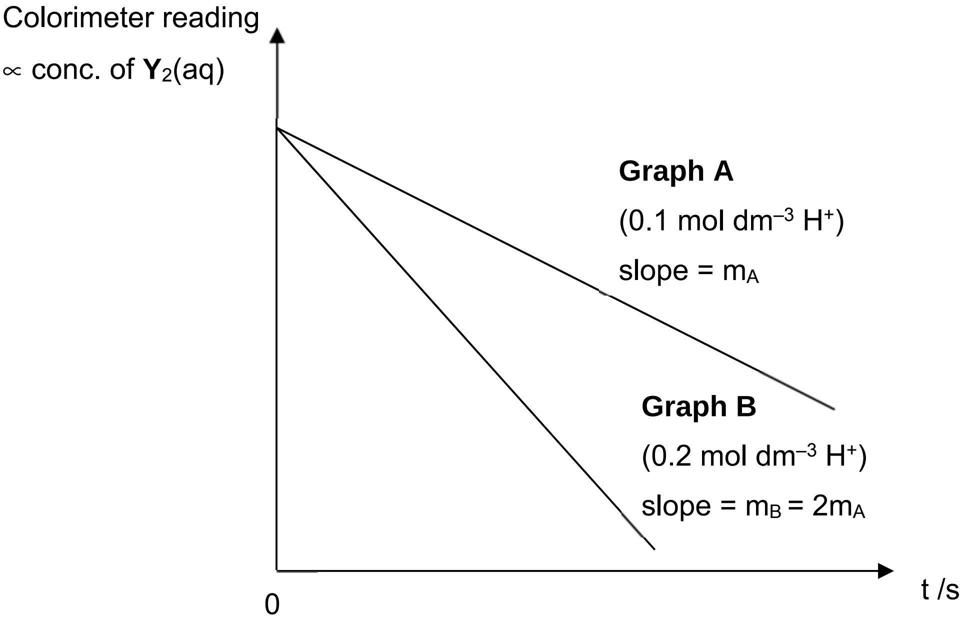
A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

14 The acid-catalysed reaction between **X** and **Y**$_2$ in aqueous solution has been investigated.

$$\mathbf{X} + \mathbf{Y}_2(aq) \xrightarrow{H^+} \mathbf{XY}(aq) + H\mathbf{Y}(aq)$$

It has been found that rate equation is rate = $k[\mathbf{X}][\mathbf{Y}_2]^m[H^+]^n$.

The change in concentration of **Y**$_2$ remaining for this reaction is measured by using a photoelectric colorimeter. **Graph A** is obtained when the concentration of hydrogen ions used is 0.1 mol dm^{-3}.



What is the overall order of reaction?

A 0 **B** 1 **C** 2 **D** 3

15 **W** and **X** are 2 different elements in Period 3. The following are some of their properties:

- The oxide of **W** is insoluble in water, but is soluble in both NaOH(aq) and HC*l*(aq).
- The chloride of **X** dissolves completely in water to give a colourless solution of pH = 2.

Which of the following is the likely identity of element **W** and **X**?

	W	**X**
A	A*l*	P
B	A*l*	Si
C	Mg	P
D	Mg	Si

16 **Y** and **Z** are two different elements from the same Group. The chlorides of both **Y** and **Z** have giant ionic lattice structure.

Which of the following statements is inconsistent with the other options?

A The first ionisation energy of **Y** is less endothermic compared to **Z**.

B The oxide of **Y** is less soluble in water compared to the oxide of **Z**.

C The magnitude of the lattice energy of chloride of **Y** is higher compared to the chloride of **Z**.

D The carbonate of **Y** decomposes at a lower temperature compared to the carbonate of **Z**.

17 Purification of copper involves placing the impure copper at the anode of an electrolytic cell of $CuSO_4$(aq) and running a current though the setup. Over time, pure copper will be deposited on the cathode.

In a particular setup, a copper sample with zinc and silver impurities was placed at the anode and a current of 6.00 A was passed through the circuit for 11 min. The cathode was then found to have an increase of mass of 1.12 g.

Which of the following statement is likely to be incorrect?

A Less time is needed if [$CuSO_4$] is increased.

B Anodic sludge containing silver would be formed.

C The maximum mass of copper that can be purified is 1.30 g.

D There would be Zn^{2+} ions found in the solution after the purification process.

18 *Use of the Data Booklet is relevant to this question.*

Patterns or designs can be etched on copper objects as a way to improve its aesthetics. Etching of copper objects are can be done chemically, where a solution of etching chemical is poured over copper surface to dissolve part of the copper.

Which of the following solution cannot be used as an etching chemical?

A Fe^{2+}(aq)

B Fe^{3+}(aq)

C Mn^{3+}(aq)

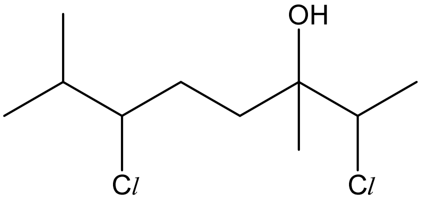
D acidified $Cr_2O_7^{2-}$(aq)

19 Which of the following galvanic cell information is incorrect?

You may assume that all ions stated are at 1.00 mol dm^{-3} and all measurements are made at standard conditions.

	Half-cell 1		Half-cell 2		$E^\ominus_{cell}$ / V
	Electrolyte	Electrode (Anode)	Electrolyte	Electrode (Cathode)	
A	H^+ Mn^{2+} MnO_4^-	Pt	Fe^{2+} Fe^{3+}	Pt	+0.75
B	Mn^{2+}	Mn	Fe^{2+} Fe^{3+}	Pt	+1.95
C	Mn^{2+}	Mn	Fe^{2+}	Fe	+0.74
D	Fe^{2+}	Fe	Mn^{2+} Mn^{3+}	Pt	+1.98

20 The following molecule is a derivative of linalool.



How many isomers may be formed when the molecule is heated under reflux with excess ethanolic potassium hydroxide?

A 2 **B** 4 **C** 6 **D** 8

21 Ethane reacts with chlorine gas in the presence of ultraviolet light to form a mixture via free radical substitution.

Which statement about this reaction is true?

A Homolytic fission occurs only in the initiation step.

B Bond formation occurs only in the termination step.

C Chloroethane is formed only in the propagation step.

D Small quantities of butane is formed only in the termination step.

22 Which of the following compounds are formed in the reaction between ethene and aqueous bromine in the present of sodium ethoxide ($CH_3CH_2O^-Na^+$)?

1 $BrCH_2CH_2OH$

2 $BrCH_2CH_2OCH_2CH_3$

3 $CH_3CH_2OCH_2CH_2OCH_2CH_3$

A 1 and 2 only **B** 2 and 3 only **C** 1 and 3 only **D** 1 only

23 Which of the following sequence of steps is expected to give the best yield for the synthesis of 3-bromo-4-methylphenylamine from benzene?

A alkylation, nitration, bromination, reduction

B alkylation, nitration, reduction, bromination

C bromination, alkylation, nitration, reduction

D nitration, alkylation, reduction, bromination

24 In which of the following pairs of compounds is the compound on the left more volatile than that on the right?

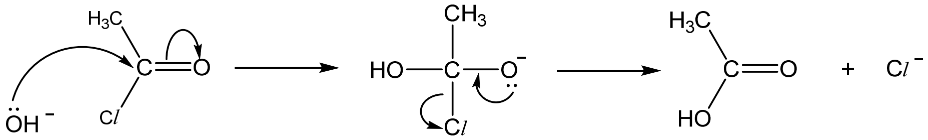
1 propylamine and propan-1-ol

2 pentan-2-one and pentan-2-ol

3 cyclohexylamine and aminoethanoic acid

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

25 The two-stage reaction given below shows a possible mechanism for the reaction between hydroxide ions and ethanoyl chloride.



Which of the following best describes the overall reaction mechanism?

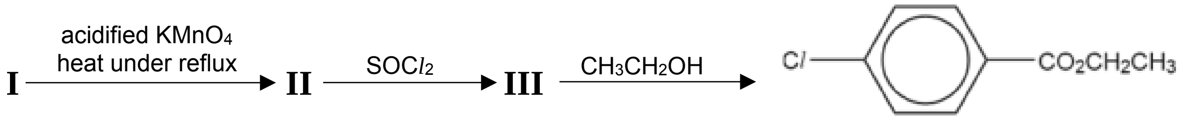
A electrophilic substitution

B electrophilic addition

C nucleophilic substitution

D nucleophilic addition

26 Consider the reaction scheme below:



Which of the following molecules is a possible identity of **I**?

A

B

C

D

27 A compound **X**, with molecular formula $C_9H_{10}O_2$, is heated under reflux with NaOH(aq) and the resulting mixture then cooled and acidified with H_2SO_4(aq). The final products include a compound that turns blue litmus solution red, and another which gives a violet colouration when tested with neutral $FeCl_3$(aq).

What is a possible identity of **X**?

A $C_6H_5OCOCH_2CH_3$

B $C_6H_5CH_2OCOCH_3$

C $C_6H_5COOCH_2CH_3$

D $C_6H_5CH_2COOCH_3$

28 Ascorbic acid, commonly known as vitamin C, is a water-soluble molecule that traps radicals formed in the aqueous environments of the cell and in the blood plasma.

Which of the following statements is correct?

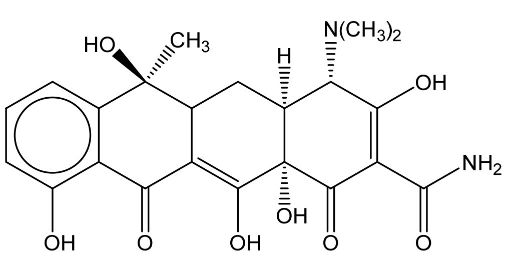
A Ascorbic acid molecule is planar.

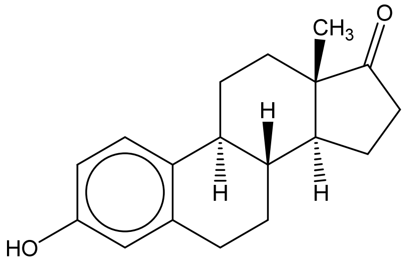
B Ascorbic acid can exhibit cis-trans isomerism.

C Ascorbic acid can react with hot hydrochloric acid.

D Ascorbic acid can react with 2,4-dinitrophenylhydrazine.

29 Which of the following procedures can be used to distinguish between the two molecules below?





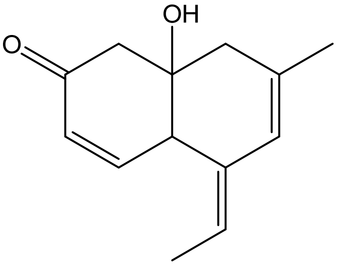
A Add 2,4-dinitrophenylhydrazine at room temperature.

B Add aqueous bromine at room temperature.

C Add silver(I) diammine solution and warm.

D Add dilute sodium hydroxide and warm.

30 Which of the following statements are true about molecule **Y** below?



1 1 mol of **Y** reacts with excess HBr(g) to yield a major product with 7 chiral centres.

2 1 mol of **Y** reacts with hot acidified $KMnO_4$(aq) to give a tribasic carboxylic acid as one of the products.

3 When heated, 1 mol of **Y** reacts with 4 mol of H_2(g) in the presence of Ni catalyst to yield a saturated compound.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

- End of Paper -

1)	D	**2)**	C	**3)**	B	**4)**	B	**5)**	C
6)	C	**7)**	D	**8)**	C	**9)**	C	**10)**	A
11)	A	**12)**	D	**13)**	B	**14)**	C	**15)**	A
16)	A	**17)**	A	**18)**	A	**19)**	A	**20)**	C
21)	D	**22)**	A	**23)**	A	**24)**	D	**25)**	C
26)	D	**27)**	A	**28)**	C	**29)**	D	**30)**	C

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME					
CLASS					
CENTRE NUMBER	S	3	0	4	4

INDEX NUMBER				

H2 CHEMISTRY
9729/02

Paper 2 Structured Questions

12 Sep 2018

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST.

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Write your name, class and index number in the spaces at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

PAPER 2	
QUESTION 1	**9**
QUESTION 2	**9**
QUESTION 3	**8**
QUESTION 4	**14**
QUESTION 5	**12**
QUESTION 6	**10**
QUESTION 7	**13**
Units	
s.f.	

PAPER 1	**PAPER 2**	**PAPER 3**	**TOTAL**	**PAPER 4**	**GRADE**
30	**75**	**80**	**185**	**55**	

This paper consists of **20** printed pages.

Answer **all** questions in the spaces provided.

1 Magnesium, aluminium**, W** and **X** are 4 different elements in the 3rd Period. The following are some of their properties:

The chloride of **W** dissolves in water to give a strongly acidic solution and the oxide of **W**.
The chloride of **X** reacts with ethanoic acid to form ethanoyl chloride as one of the products.

(a) Identify the elements, **W** and **X**, and write the balanced equations for the reactions described above.

W: …………………………

Chloride of **W** dissolved in water (equation):

………………………………………………………………………………………

X: …………………………

Chloride of **X** reacting with ethanoic acid (equation):

………………………………………………………………………………………

[2]

(b) Aluminium oxide is a white solid that is soluble in NaOH(aq) to give a colourless solution.

(i) Write a balanced equation, with state symbols, to describe the reaction of aluminium oxide with NaOH(aq).

……………………………………………………………………………………… **[1]**

(ii) Describe the observations made when HC*l*(aq) is carefully added to this colourless solution, until HC*l*(aq) is in excess.

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……………………………………………………………………………………… **[2]**

(c) State and explain how the decomposition temperature of $BaCO_3$ compares with that of $MgCO_3$.

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(d) Explain why the 1st ionisation energy of aluminium is of lower magnitude compared to that of magnesium.

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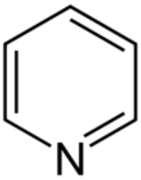
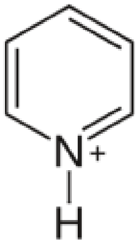
……………………………………………………………………………………….. **[1]**

[Total: 9]

2 Pyridine C_5H_5N is a weak alkali with a distinctive, unpleasant fish-like smell. Pyridine reacts readily with hydrochloric acid to form pyridinium chloride only. Pyridinium chloride is commercially available in a form of 98.0% purity by mass.



pyridine



pyridinium

Pyridinium chloride has a pK_a value of 5.25.

(a) Calculate the mass of 98.0% pyridinium chloride that must be added to 1.00 dm^3 of water to give a solution of pH 3.5.

(You may assume no change in volume of solution upon addition of the salt.)

[3]

(b) Calculate the pH of the reaction mixture when 5.00 cm^3 of 0.0125 mol dm^{-3} hydrochloric acid is added to 25.00 cm^3 of 0.100 mol dm^{-3} of pyridine.

[3]

(c) With the aid of **two** equations, explain how a solution of pyridinium chloride and pyridine can control pH.

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[Total: 9]

3 Nitrosoyl chloride, $\mathrm{NOC}l$, is a yellow gas that can be formed between nitryl chloride and nitric oxide in the following reversible reaction:

$$\mathrm{NO_2C}l\mathrm{(g)} + \mathrm{NO(g)} \rightleftharpoons \mathrm{NOC}l\mathrm{(g)} + \mathrm{NO_2(g)} \qquad \Delta H \text{ is negative}$$

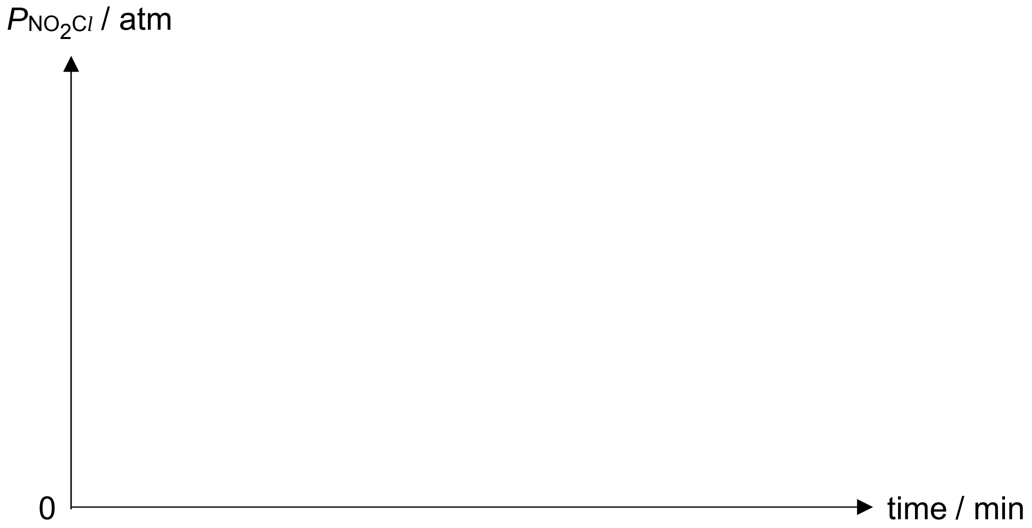
(a) A 3:1 molar ratio mixture of $\mathrm{NO_2C}l$(g) and NO(g), at a total initial pressure of 5 atm, was allowed to react in a closed vessel at 800 K. When equilibrium was reached at time $\boldsymbol{t_1}$, the partial pressure of $\mathrm{NO_2C}l$ was found to be 2.90 atm.

Calculate the value of the equilibrium constant, K_p, of the reaction at 800 K.

[2]

(b) At time $\boldsymbol{t_2}$, more $\mathrm{NO_2C}l$ gas was introduced into the vessel at 800 K, causing the partial pressure of $\mathrm{NO_2C}l$ to increase to 3.25 atm. The system was allowed to reach equilibrium before the temperature was increased to 1000 K at $\boldsymbol{t_3}$. A new equilibrium was established at $\boldsymbol{t_4}$.

In the pressure-time axes below, sketch the graph that would be observed from time = 0 to time = $\boldsymbol{t_4}$, clearly indicating the values of the partial pressure of $\mathrm{NO_2C}l$ at time = 0, $\boldsymbol{t_1}$ and $\boldsymbol{t_2}$.



[2]

(c) Given that nitrogen is the central atom, draw the dot-and-cross diagram for NOC*l*.

[1]

(d) NOC*l* reacts with $CH_3CH{=}CH_2$ to give a product as predicted by Markovnikov's rule. When the organic product is heated with NaOH(aq), followed by acidification and addition of $AgNO_3$(aq), a white precipitate is obtained.

Given that the oxidation state of chlorine in NOC*l* is +1, state and draw the mechanism for the reaction between NOC*l* and $CH_3CH{=}CH_2$.

[3]

[Total: 8]

4 **(a)** Sucrose, or table sugar, is the most common natural food sweetener. In acidic medium, sucrose is readily hydrolysed to a mixture of glucose and fructose. The reaction is also acid-catalysed.

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+(aq)} C_6H_{12}O_6 + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

A series of experiments was carried out at room temperature to investigate the kinetics of this reaction, using 0.850 mol dm^{-3} sucrose solution and 1.23 mol dm^{-3} hydrochloric acid.

Expt	Volume of sucrose / cm^3	Volume of HC*l* / cm^3	Volume of water / cm^3	Initial rate of reaction / mol dm^{-3} min^{-1}
1	20	30	0	1.77×10^{-3}
2	20	20	10	1.18×10^{-3}
3	10	30	10	8.85×10^{-4}
4	40	20	10	?

(i) Using the data given above, determine the order of reaction with respect to sucrose and HC*l*.

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(ii) Hence, write the rate equation and deduce the rate constant of the reaction, stating its units.

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(iii) Using your answer in **(a)(ii)**, calculate the initial rate of reaction for Experiment 4.

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………………………………………………………………………………….. **[2]**

(b) In bacteria, sucrose is broken down into glucose and fructose by the enzyme, invertase. Experiments were done to measure the rate of the enzyme-catalysed hydrolysis reaction for different concentrations of sucrose.

(i) Sketch a graph to show how the rate of this enzyme-catalysed hydrolysis reaction varies with the concentration of sucrose until sucrose is in large excess.

[1]

(ii) Explain the shape of the graph in **(b)(i)**. In your answer, make reference to the order of reaction with respect to sucrose.

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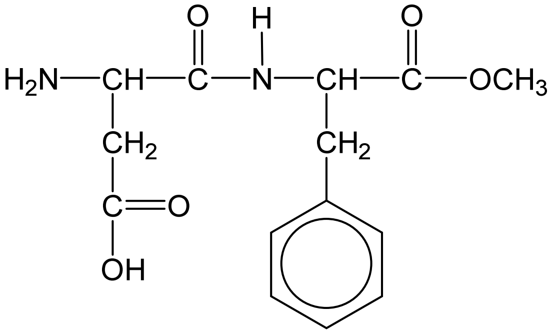
(c) Aspartame, an artificial sweetener, is 200 times sweeter than sucrose.

The structure of aspartame is as follows.



(i) Draw the structure in which aspartame exists in water.

[1]

(ii) Hence, explain why aspartame is soluble in water.

………………………………………………………………………………………...

………………………………………………………………………………………... **[1]**

(iii) Draw the structural formulae of all the organic products formed when aspartame is heated with aqueous NaOH.

Label any chiral carbon in each product with an asterisk.

[3]

[Total: 14]

5 Manganese exhibits the widest range of oxidation states among the 1st set of transition elements from titanium to copper.

In deaerated aqueous solution and in the presence of excess CN^- ions, pale pink $Mn^{2+}(aq)$ forms blue $[Mn(CN)_6]^{4-}$ ion. $[Mn(CN)_6]^{4-}$ ion reacts with 3% solution of hydrogen peroxide to form red $[Mn(CN)_6]^{3-}$ ion.

In the visible spectrum, red is the lowest energy light while violet is the highest energy light.

(a) Explain why transition elements exhibit variable oxidation states.

……………………………………………………………………………………………..

…………………………………………………………………………………………….. **[1]**

(b) Explain why there is a difference in the colour observed for $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_6]^{3-}$ ions.

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……………………………………………………………………………………………..

…………………………………………………………………………………………….. **[2]**

(c) Given that:

$$[Mn(CN)_6]^{3-} + e \rightleftharpoons [Mn(CN)_6]^{4-} \qquad E^\ominus = -0.24\ \text{V}$$

Use the *Data Booklet* to suggest why Mn(III) ion exhibits stronger oxidising power in aqueous solution than in concentrated cyanide solution in terms of

- $E^\ominus$ and
- effect of ligand exchange on $E^\ominus$.

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…………………………………………………………………………………………….. **[2]**

(d) The figure below gives the splitting diagram of the d-orbitals in the presence of an octahedral ligand field.

A transition metal complex can exist in a 'high spin' state or in a 'low spin' state.

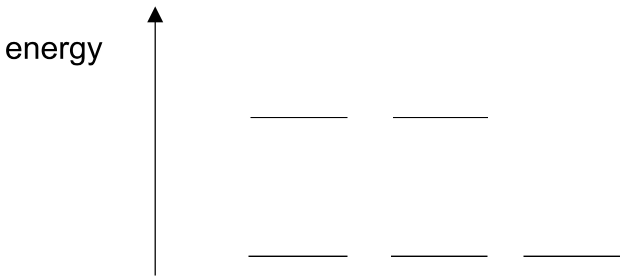
In a 'high spin' state, the electrons occupy all the d-orbtials singly, before starting to pair up in the lower energy d-orbitals.

In a 'low-spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Electrons usually prefer to occupy orbitals singly, rather than in pairs, to minimise coulombic repulsion, also known as the pairing energy.

In this question, only one of the cyanido-complexes of manganese is high-spin.

(i) Using this information, and compare the colour of the cyanido-complexes of manganese, deduce and draw the electronic configuration of the $[Mn(CN)_6]^{3-}$ on the splitting diagram.



[1]

(ii) Explain the spin-state of $[Mn(CN)_6]^{3-}$ in **(d)(i)** in terms of the energy gap between the d-orbitals in both manganese cyanido-complexes and pairing energy.

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………………………………………………………………………………… **[1]**

(e) Standard reduction potentials are often presented in the form of a potential diagram. The figure below gives the potential diagram of manganese under the condition of $[H^+] = 1\ \text{mol dm}^{-3}$.

$$\begin{tikzcd}
MnO_4^{\,-} \arrow[r, "+0.90\ V"] \arrow[rr, bend right, "+1.67\ V"'] & HMnO_4^{-} \arrow[r, "+2.10\ V"] & MnO_2
\end{tikzcd}$$

(i) Given that $HMnO_4^-$ undergoes disproportionation, construct a balanced equation for the reaction.

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… **[1]**

(ii) Calculate $\Delta G^\ominus$ for the reaction.

……………………………………………………………………………………

…………………………………………………………………………………… **[2]**

(f) It is necessary to carry out reactions involving Mn(II) in deaerated solution as Mn(II) may react with aerated solutions.

Consider the data given below and appropriate values from the *Data Booklet*, calculate the $E^\ominus_{\text{cell}}$ values for the oxidation of Mn(II) to Mn(III) in aerated solutions at pH = 0 and pH = 14.

Comment on what the signs of $E^\ominus_{\text{cell}}$ indicate about the stability of Mn(II) in acidic and alkaline aerated solutions.

$$Mn(OH)_3(s) + e^- \rightleftharpoons Mn(OH)_2(s) + OH^-(aq) \qquad E^\ominus = +0.18\ V$$

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… **[2]**

[Total: 12]

6 Anaerobic digestion is a natural form of waste-to-energy that uses the process of fermentation to break down organic matter in the absence of oxygen. Typically, 50 to 75% of biogas can be combusted, therefore it produces a deep blue flame and can be used as an energy source.

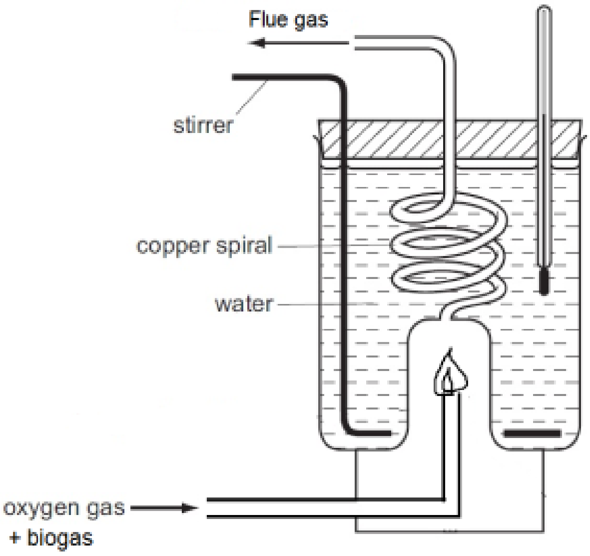
Biogas is primarily made up of methane, along with carbon dioxide. Depending on the type of biodegradable material involved, hydrogen sulphide (H_2S), hydrogen and nitrogen may be produced.

The composition of a sample of biogas by mass is given in the following table, along with the enthalpy change of combustion for each gas.

Biogas component	Percentage mass	ΔH_c / kJ mol^{-1}
methane	72.2	?
carbon dioxide	21.6	0.00
hydrogen sulfide	1.2	– 482
hydrogen	2.7	– 386
nitrogen	2.3	– 43.1

The total energy evolved from the combustion of biogas can be determined using a calorimeter as shown in Figure 6.1.

Figure 6.1



(a) **(i)** The cooled flue gas contains carbon dioxide, sulfur dioxide and nitrogen gas.

Two gases present in the sample of biogas do not react with oxygen. Identify the two gases and explain why they do not react.

Identity of gases: ……………………… and ………………………

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………... **[2]**

(ii) Write balanced equations to show the reaction for 1 mole of each component of biogas that reacted under standard conditions.

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………... **[2]**

(iii) An experiment was carried out to determine the fuel value of a sample of biogas using a calorimeter as shown in Figure 6.1. Fuel value is defined as the amount of energy generated by complete combustion of one gram of the fuel.

In this experiment, biogas was mixed with excess oxygen at room temperature and pressure before it was passed into the calorimeter.

Assuming that the efficiency of heat transferred to water is 100%, use the *Data Booklet* and the following information to determine the energy evolved. Hence determine the fuel value of biogas.

Volume of biogas used = 1.00 dm^3

Density of biogas is 6.44×10^{-4} g cm^{-3}

Volume of water heated = 200 cm^3

Density of water = 1.00 g cm^{-3}

Initial temperature of water = 29.6 °C

Maximum temperature of water reached = 64.7 °C

[2]

(iv) Use the information provided, calculate the amount of each gas that combusted. Hence, determine the enthalpy change of combustion of methane.

[2]

(c) To determine the fuel values of biogas, the apparatus in Figure 6.1 can simply be replaced with a beaker of water with lid and a thermometer.

Suggest how the design of the apparatus in Figure 6.1 improves the efficiency of heat transfer to the water.

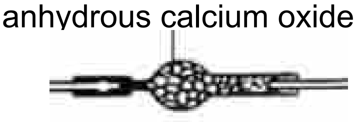
…………………………………………………………………………………………..

…………………………………………………………………………………………..

………………………………………………………………………………………….. **[1]**

(d) Cooled flue gas was passed through a tube containing anhydrous calcium oxide, as shown in Figure 6.2, before being discharged into the atmosphere.

Figure 6.2



Explain why it is important for the cooled flue gas to be passed through anhydrous calcium oxide.

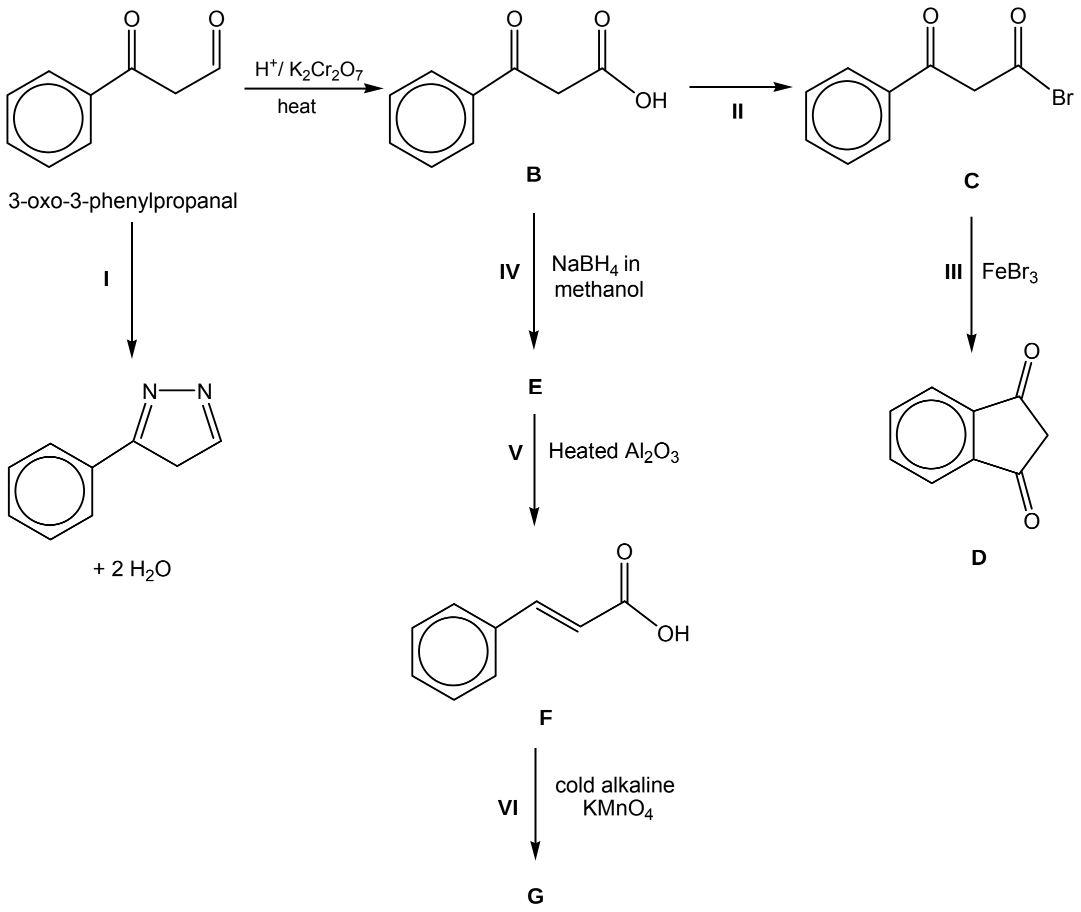
…………………………………………………………………………………………..

…………………………………………………………………………………………..

………………………………………………………………………………………….. **[1]**

[Total: 10]

7 **(a)** A student carried out a series of tests on 3-oxo-3-phenylpropanal.



(i) Suggest the reagents and conditions required for reactions **I** and **II**.

Reaction **I**: ……………………………………………………………….

Reaction **II**: ………………………………………………………………. **[2]**

(ii) Draw the structures of **E** and **G**.

E	**G**

[2]

(iii) Describe the mechanism for reaction **III**, and provide the name of the mechanism.

[3]

(b) Suggest simple laboratory tests to distinguish between compounds **B**, **C** and **F**. State the expected observations for each compound.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

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…………………………………………………………………………………….. **[4]**

(c) Describe what the student will observe when 3-oxo-3-phenylpropanal is warmed with Fehling's solution. Write an equation for this reaction.

[Total: 13]

- End of Paper -

MARK SCHEME

1	**(a)**	**W**: Si $SiCl_4 + 2H2O \rightarrow SiO_2 + 4HCl$ **X**: P $PCl_5 + CH_3COOH \rightarrow POCl_3 + CH_3COCl$ *OR* $3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$	**[4]**
	(b) (i)	$Al_2O_3(s) + 2NaOH(aq) \rightarrow 2Na[Al(OH)_4](aq) + H_2O(l)$ OR $Al_2O_3(s) + 2OH^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + H_2O(l)$	**[3]**
	(b) (ii)	On addition of HCl(aq), a white ppt is formed. Ppt would dissolve in excess HCl(aq) to give a colourless solution.	
	(c)	$BaCO_3$ has a higher thermal decomposition temperature. Ba^{2+} has a larger ionic radius compared to **Z**$^{2+}$/Mg^{2+}. Ba^{2+} hence has a lower charge density, and polarise the CO_3^{2-} anion to a lower extent (compared to **Z**$^{2+}$/Mg^{2+}), and the C–O bonds are weakened to a smaller extent, resulting in a higher thermal decomposition temperature.	
	(d)	The 3p electron to be removed from Al is at a higher energy level compared to the 3s electron to be removed from Mg, hence the p electron is less strongly attracted to the nucleus and require less energy to remove.	**[1]**
			[Total: 9]

2	**(a)**	For pH = 3.5 $[H^+] = 10^{-3.5} = 3.16$ x 10^{-4} moldm^{-3} Let the number of moles of C_5H_5NHCl be Y mol Since pK_a = 5.25 , $K_a = 10^{-5.25} = 5.62 \times 10^{-6}$ $(3.16 \times 10^{-4})^2 / Y - (3.16 \times 10^{-4}) = 5.62 \times 10^{-6}$ $Y = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}] + (3.16 \times 10^{-4})$ = 0.0181 mol ***Or*** $(3.16 \times 10^{-4})^2 / Y = 5.62 \times 10^{-6}$ $Y = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}]$ = 0.0178 mol Mass to be added = (0.0181 × (12.0 × 5 + 1.0 × 6 + 14.0 + 35.5)) ÷ 0.98 = 2.13 g (or 2.10 g)	**[3]**
	(b)	$[C_5H_5N] = [(0.100 \times 0.025) - (0.0125 \times 0.005)] / 0.03 = 0.0813$ mol dm^{-3} [pyridinium chloride] = $(0.0125 \times 0.005) / 0.03 = 2.08 \times 10^{-3}$ mol dm^{-3} pK_b =14 – pK_a = 8.75 pOH = pK_b + lg [salt]/[base] pOH = 8.75 + lg $(2.08 \times 10^{-3} / 0.0813)$ = 7.16 pH = 14 – 7.16 = 6.84	**[3]**
	(c)	On addition of a small amount of acid (H^+) to the buffer solution, nearly all the added H^+ ions are neutralised by the large amount of C_5H_5N. Hence $[H^+]$ does not increase appreciably and the pH is kept approximately constant. $C_5H_5N(aq) + H^+(aq) \rightarrow C_5H_5NH^+(aq)$ On addition of a small amount of base (OH^-) to the buffer solution, nearly all the added OH^- ions are neutralised by the large amount of $C_5H_5NH^+$. Hence $[OH^-]$ does not increase appreciably and the pH is kept approximately constant. $C_5H_5NH^+(aq) + OH^-(aq) \rightarrow C_5H_5NH(aq) + H_2O(l)$	**[3]**
			[Total: 9]

3 **(a)**

Initial P of NO(g) = $\frac{1}{4} \times 5 = 1.25$ atm

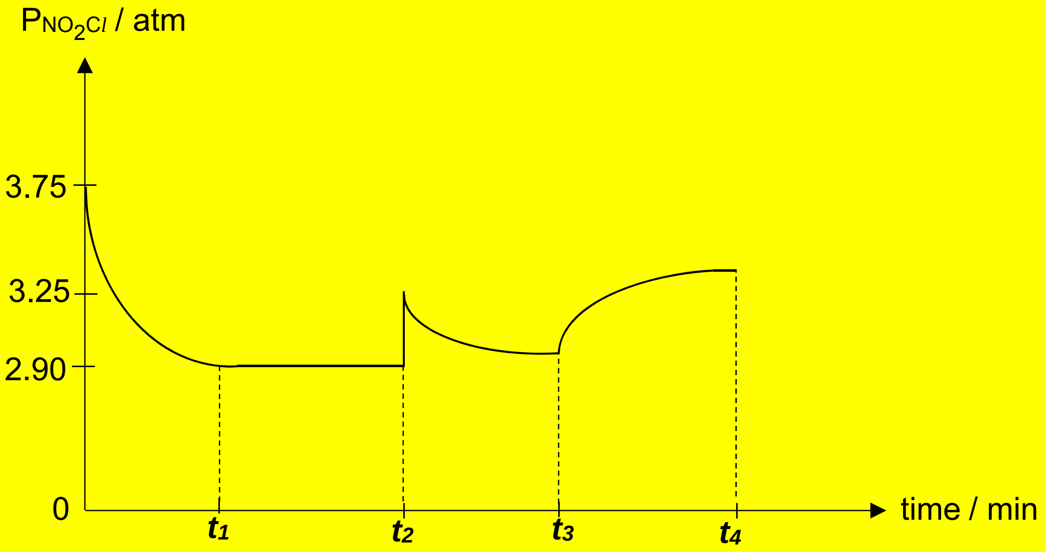
Initial P of NO_2Cl(g) = 5 – 1.25 = 3.75 atm

	NO_2Cl	+	NO	⇌	NOC*l*	+	NO_2
Initial P / atm	3.75		1.25		0		0
Δ in P / atm	–0.85		–0.85		+0.85		+0.85
Eqm P / atm	2.90		0.40		0.85		0.85

$K_p = \frac{(0.85)(0.85)}{(2.90)(0.40)}$ = <u>0.623</u> (no units)

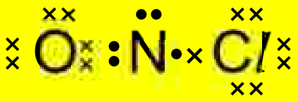
[2]

(b)



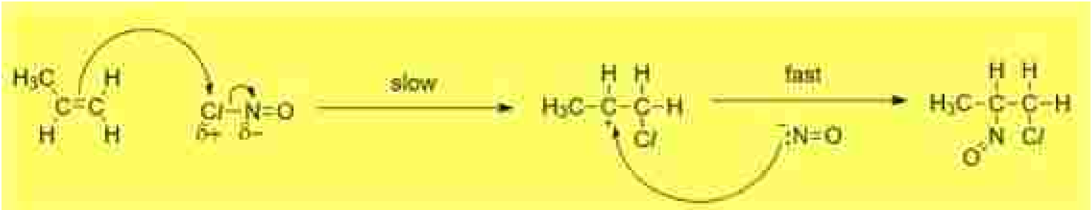
[2]

(c)



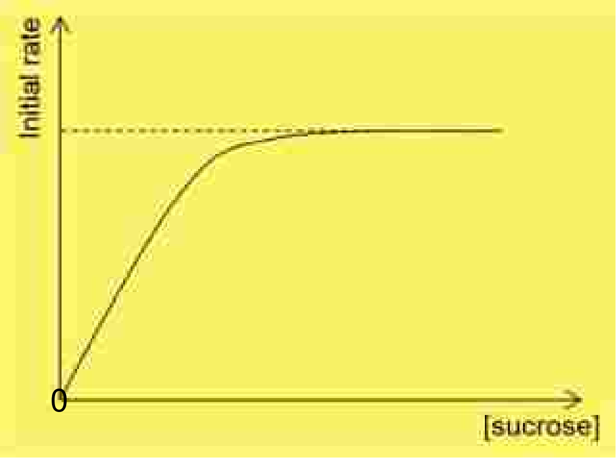
[1]

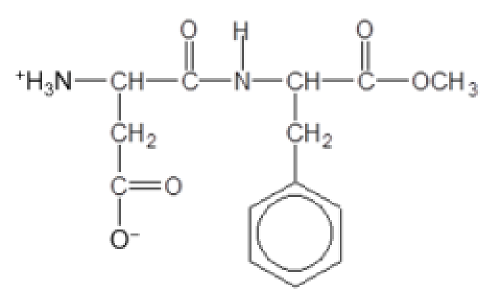
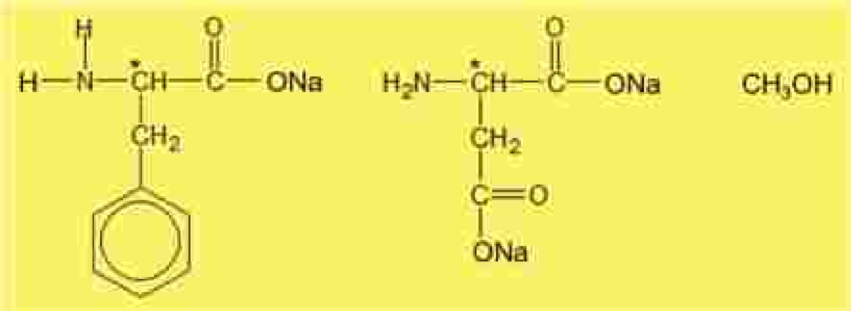
(d) Electrophilic addition

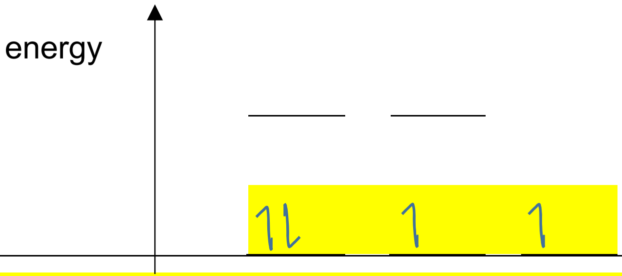


[3]

[Total: 8]

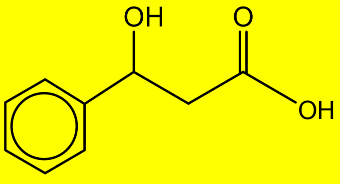
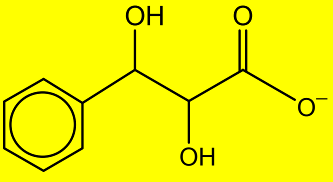
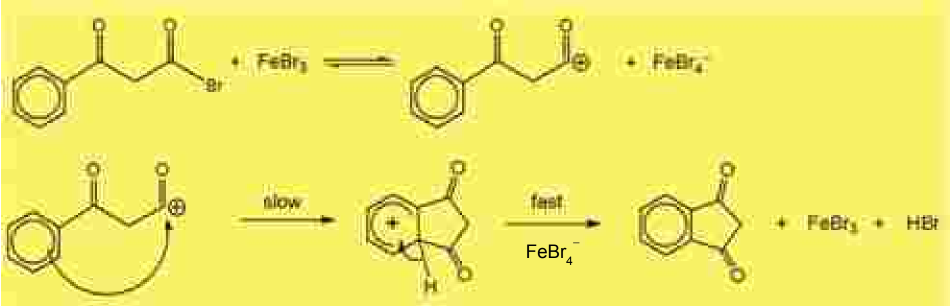
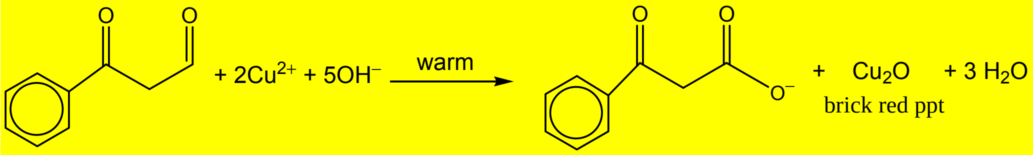
4	**(a)**	**(i)**	Comparing Experiments 1 and 2, When the volume/concentration of $\mathrm{HC}l$ increases to 1.5 times, rate increases to 1.5 times. Hence, reaction is first order with respect to $\mathrm{HC}l$. Comparing Experiments 1 and 3, When the volume/concentration of sucrose doubles, rate doubles. Hence, reaction is first order with respect to sucrose.	**[2]**
		(ii)	Rate = k [sucrose] [$\mathrm{HC}l$] From Experiment 1, $[\text{sucrose}] = 0.850 \times \frac{20}{50} = 0.340\ \text{mol dm}^{-3}$ $[\mathrm{HC}l] = 1.23 \times \frac{30}{50} = 0.738\ \text{mol dm}^{-3}$ $k = \frac{1.77 \times 10^{-3}}{(0.340)(0.738)} = 7.05 \times 10^{-3}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{min}^{-1}$	**[2]**
		(iii)	$[\text{sucrose}] = 0.850 \times \frac{40}{70} = 0.486\ \text{mol dm}^{-3}$ $[\mathrm{HC}l] = 1.23 \times \frac{20}{70} = 0.351\ \text{mol dm}^{-3}$ Both concentrations for Initial rate of reaction = $7.05 \times 10^{-3} \times 0.486 \times 0.351$ $= 1.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{min}^{-1}$	**[2]**
	(b)	**(i)**	 	**[1]**

		(ii)	When [sucrose] is low, reaction is first order with respect to sucrose due to the availability of active sites on the enzyme molecules for binding. When [sucrose] is high, all active sites on the enzyme molecules are occupied. The rate of reaction then is independent of [sucrose] and the reaction is zero order with respect to sucrose.	**[2]**
	(c)	**(i)**		**[1]**
		(ii)	The zwitterions of aspartame form ion-dipole interactions with water.	**[1]**
		(iii)		**[3]**
				[Total: 14]

5	**(a)**		Due to the similar energy/ close proximity of the 3d and 4s electrons in the transition elements, transtion element can form ions of approximately the similar stability by losing different number of electrons.	**[1]**
	(b)		In the presence of octahedral ligand field, the degenerate d-orbitals in the metal complex were spilt into two energy levels. The colour observed is due to the difference in energy levels, ΔE. The difference in electronic configuration due to different oxidation state affect ΔE. Light of different energies/ different wavelengths are absorbed for the promoion of electrons from the lower energy orbital to the vacant/partially filled higher energy orbital/ d-d transition, different complementary colour is observed.	**[2]**
	(c)		$E^{\ominus}(Mn^{3+}/Mn^{2+})$ is more positive than $E^{\ominus}([Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-})$, which shows that Mn^{3+} is more readily reduced, hence a weaker oxidising agent in cynaide solution than in water. More energy is required to add an electron to the negatively charged $[Mn(CN)_6]^{3-}$ due to repulsion.	**[2]**
	(d)	**(i)**	Figure 1.1  	**[1]**
		(ii)	Since $[Mn(CN)_6]^{3-}$ ions are red, the energy gap between the 2 sets of d-orbitals in $[Mn(CN)_6]^{3-}$ is bigger. This suggests that $[Mn(CN)_6]^{3-}$ is the low spin complex, as its energy gap, ΔE, is greater than the pairing energy/ Coulombic repulsion/ repulsion energy, electrons in $[Mn(CN)_6]^{3-}$ would pair up.	**[1]**
	(e)	**(i)**	[O] $HMnO_4^- \rightarrow MnO_4^- + H^+ + e$ [R] $3H^+ + 2e + HMnO_4^- \rightarrow MnO_2 + 2H_2O$ Overall equation: $3HMnO_4^- + H^+ \rightarrow MnO_2 + 2\,MnO_4^- + 2H_2O$	**[1]**
		(ii)	$E_{cell} = +2.10 - (+0.90) = +1.20$ V $\Delta G = -nFE_{cell} = -(2)(96500)(1.20) = -232$ kJ mol^{-1}	**[2]**
	(f)		In acidic condition, $O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23$ V $Mn^{3+} + e \rightleftharpoons Mn^{2+}$ $E^{\ominus} = +1.54$ V $E^{\ominus}_{cell} = +1.23 - (+1.54) = -0.31$ V	**[2]**

		In alkaline solution, $O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$ $E^{\ominus} = +0.40$ V $E^{\ominus}_{cell} = +0.40 - (+0.18) = +0.22$ V Since the $E^{\ominus}_{cell} > 0$ in alkaline environment and $E^{\ominus}_{cell} < 0$ in acidic environment, Mn(II) is more stable in acidic environment than in alkaline environment.	
			[Total: 12]

6	**(a)**	**(i)**	CO_2: Carbon in CO_2 has attained maximum oxidation state. N_2: N≡N is very strong resulting high activation energy.	**[2]**
		(ii)	Methane: $CH_4(g) + 2O_2\ (g) \rightarrow CO_2(g) + 2H_2O(l)$ Hydrogen sulfide: $H_2S\ (g) + 1\tfrac{1}{2}\ O_2\ (g) \rightarrow SO_2(g) + H_2O(l)$ Hydrogen: $H_2(g)\ + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O(l)$	**[2]**
		(iii)	Energy evolved = $200 \times 4.18 \times (64.7 - 29.6) = 29.34$ kJ mass of biogas used = $1000 \times 6.44 \times 10^{-4} = 0.644$ g Fuel value of biogas = $29.34 \div 0.644 = 45.6$ kJ g^{-1}	**[2]**
		(iv)	Amount of methane in 1 dm^3 biogas = $0.644 \times 0.722 \div (12.0 + 4.0)$ $= 0.0291$ mol Amount of H_2S in 1 dm^3 biogas = $0.644 \times 0.012 \div (2.0 + 32.1)$ $= 0.000227$ mol Amount of H_2 in 1 dm^3 biogas = $0.644 \times 0.027 \div 2.0$ $= 0.00869$ mol Energy evolved = 29.34 kJ $= (0.0291 \times \lvert\Delta H_c(CH_4)\rvert) + (0.000227 \times 482) + (0.00869 \times 386)$ $\Delta H_c(CH_4) = -\ 890$ kJ mol^{-1}	**[2]**
	(c)		• Longer time for hot flue gas to pass through spiral copper coil • Spiral copper coil increase the surface area for energy transfer • copper is a good conductor of heat • the combustion takes place inside the apparatus, not affected by draught.		**[1]**
	(d)		To **remove sulfur dioxide** gas as low concentration of this gas can also irritates the respiratory system.		**[1]**
			[Total: 10]	

7	**(a)**	**(i)**	Reaction **I**: $H_2N{-}NH_2$ Reaction **II**: PBr_3	**[2]**
		(ii)	**E:**  **G:** 	**[2]**
		(iii)	Electrophilic substitution 	**[3]**
	(b)	1) Test: Add Br_2(aq). Compound **F**: Orange Br_2(aq) decolourises. Compounds **B** and **C**: Br_2(aq) remains orange. 2) Test: Add $AgNO_3$(aq) Compound **B**: No ppt forms. Compound **C**: Cream ppt (AgBr) forms.		**[4]**
	(c)	Brick-red precipitate forms. 		**[2]**
				[Total: 13]

- End of Paper -

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CLASS	6 ☐
CENTRE NUMBER	S ☐☐☐☐
INDEX NUMBER	☐☐☐☐

H2 CHEMISTRY
9729/03

Paper 3 Free Response

18 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials:
Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **15** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** **(i)** Phosphorus reacts with

- F_2 to produce PF_5 as the only product.
- Cl_2 to give both PCl_5 and PCl_3.
- Br_2 and I_2 to give PBr_3 and PI_3 respectively.

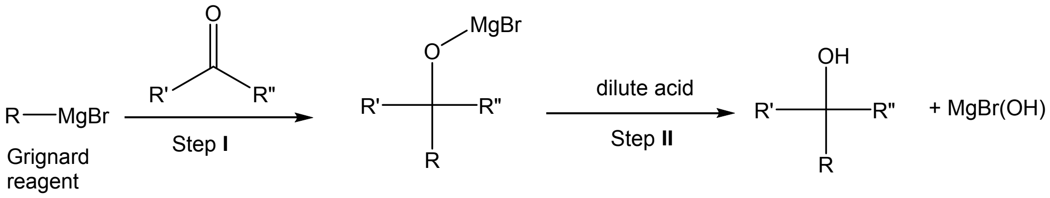
With reference to the *D*ata *B*ooklet, explain the difference in oxidation states of phosphorus in the phosphorus-containing compounds formed. **[3]**

(ii) The table below gives the pK_a values of the hydrogen halides.

hydrogen halide	pK_a
HF	3.17
HC*l*	–7
HBr	–9
HI	–10

Explain the trend in the pK_a values. **[2]**

(b) The following reaction scheme shows the formation of an alcohol via the Grignard reaction.



(i) Suggest the type of reaction undergone in Step **II**. **[1]**

(ii) Suggest the identities of a suitable carbonyl compound and Grignard reagent to form 1-methylcyclohexan-1-ol. **[2]**

(iii) The reaction between the carbonyl compound and the Grignard reagent suggested in **(b)(ii)** is a nucleophilic addition.

Propose the mechanism for this reaction, assuming that the Grignard reagent (R-MgBr) produces the $:R^-$, as the reacting species to form 1-methylcyclohexan-1-ol. **[3]**

(c) Calcium phosphate, $Ca_3(PO_4)_2$, is a sparingly soluble salt. ..

(i) Write the expression for the solubility product of calcium phosphate. **[1]**

(ii) Given that the solubility of calcium phosphate in water is 1.14×10^{-7} mol dm^{-3}, calculate the solubility product of calcium phosphate, stating its units. **[2]**

(iii) Calculate the solubility of calcium phosphate in the presence of 0.150 mol dm^{-3} of potassium phosphate. **[2]**

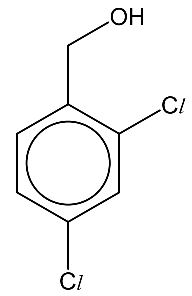
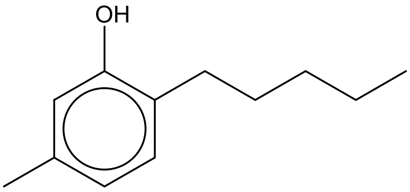
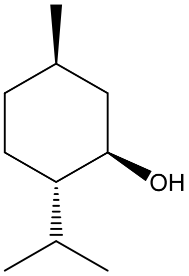
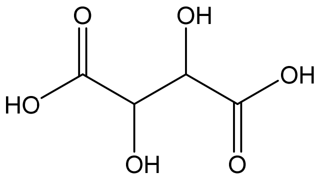
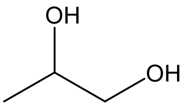
(iv) A saturated solution was prepared by dissolving two sparingly soluble salts, calcium phosphate and calcium sulfate, $CaSO_4$, in tap water. The tap water used was found to be contaminated with trace amounts of SO_4^{2-}.

Explain the impact of the contamination on the solubilities of calcium phosphate and calcium sulfate. **[2]**

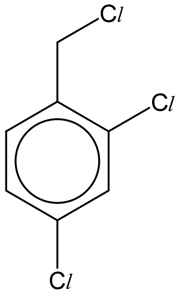
[Total: 18]

2 Strepsils® is a line of throat lozenges used to relieve discomfort caused by mouth and throat infections.

The table below shows the main active and non-active ingredients found in one lozenge.

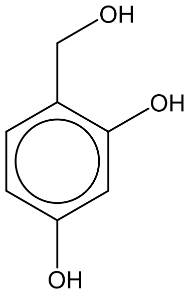
primary active ingredients	2,4-dichlorobenzyl alcohol	
	amylmetacresol	
non-active ingredients	(–)-menthol	
	tartaric acid	
	propylene glycol	

(a) 2,4-dichlorobenzyl alcohol can be prepared from 2,4-dichlorobenzyl chloride (shown below) via a one-step synthesis.



(i) State the reagent and condition for the reaction. **[1]**

(ii) Explain why the molecule below will not be obtained as a by-product.



[1]

(iii) A student carries out the synthesis using the reagent in **(a)(i)** that has been contaminated with sodium ethoxide.

Draw the structure of the possible by-product that may result. **[1]**

(iv) Describe a simple chemical test that can distinguish between 2,4-dichlorobenzyl alcohol and amylmetacresol.

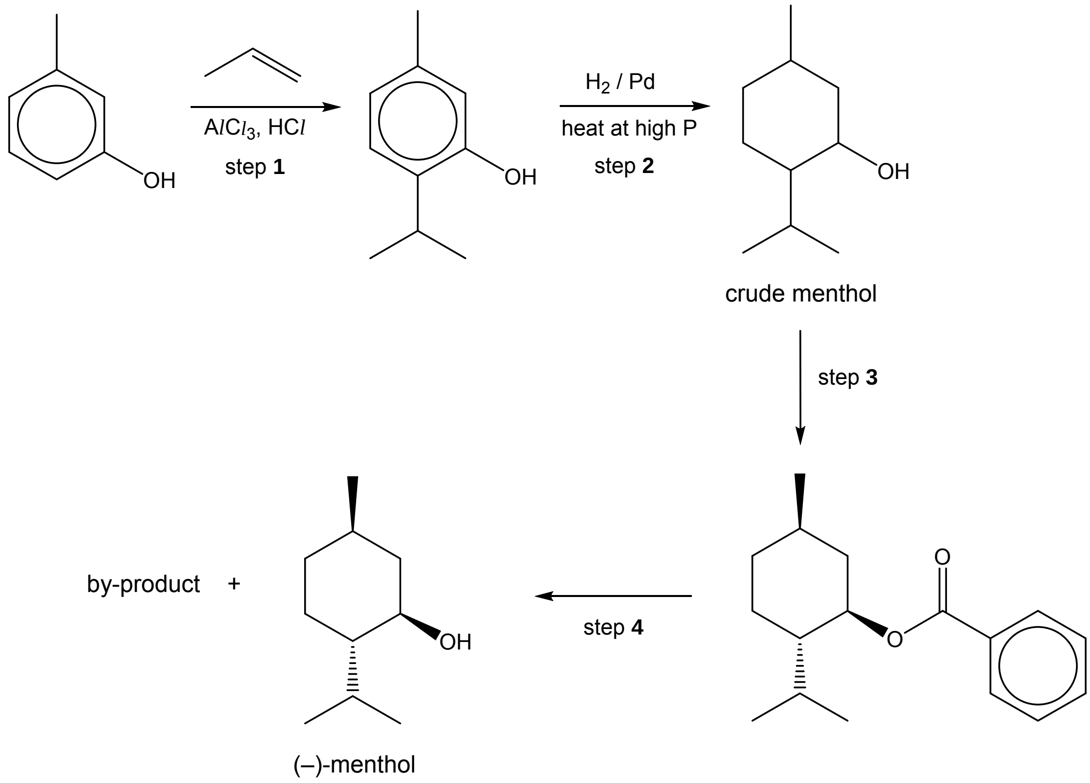
State the expected observations for each compound. **[2]**

(b) Arrange amylmetacresol, menthol and tartaric acid in increasing order of acidity.

Explain your answer.

You only need to consider the first acid dissociation of tartaric acid. **[3]**

(c) Menthol is produced commercially via the Haarmann-Reimer process. A modified version of the process is shown below.



(i) Suggest the types of reactions occurring in steps **1** and **2**. **[2]**

(ii) Given that crude menthol does not exhibit optical activity, determine the number of enantiomers crude menthol has.

Hence, calculate the proportion of each enantiomer formed. **[2]**

(iii) Draw the structure of the by-product formed. **[1]**

(d) **(i)** A 25.0 cm^3 solution of 0.0100 mol dm^{-3} tartaric acid in a conical flask is titrated with 0.0100 mol dm^{-3} NaOH(aq) from a burette.

Given that pK_{a1} = 2.89 and pK_{a2} = 4.40, and ignoring the auto-ionisation of water, determine the pH of the solution when the following volumes of NaOH(aq) are added:

- 0.00 cm^3
- 12.50 cm^3
- 50.00 cm^3 **[4]**

(ii) When the second equivalence point is reached, the solution is heated to dryness. The residue left is a white solid.

Explain, using structure and bonding, why the boiling point of the solid residue is higher than that of tartaric acid. **[2]**

(e) Propylene glycol can be produced from gaseous propene.

(i) State the reagent and condition required for propene to form propylene glycol. **[1]**

(ii) When propene is reacted with the reagent in **(e)(i)** under a different set of condition, an organic liquid and an inorganic gas are formed.

Draw the displayed formula of the organic liquid. **[1]**

(iii) The inorganic gas is collected in an evacuated glass bulb at 30 °C. It is found that the mass of the 500 cm^3 glass bulb increased by 0.36 g.

Identify the inorganic gas and determine the pressure of the gas collected. **[2]**

[Total:23]

3 Transition elements and their compounds have found many applications in industries as both homogeneous and heterogeneous catalysts.

For example, nickel is used as a catalyst for hydrogenation of alkenes and vanadium pentoxide (V_2O_5) is used in the manufacture of sulfuric acid.

(a) Explain what is meant by the term *heterogeneous catalyst*. **[2]**

(b) The following table list the colours of various vanadium ions in aqueous solution:

ion	oxidation state	colour
V^{2+}	+2	violet
V^{3+}	+3	green
VO^{2+}	+4	blue
VO_3^-	+5	yellow

When a sample of yellow VO_3^- solution is mixed with an excess of zinc powder, the solution undergo a series of colour changes over time.

Using relevant $E^\ominus$ values from the *Data Booklet*, account for all the observed colour changes. There is no need to write any balanced chemical equation. **[3]**

(c) A similar process as **(b)** was carried out as follows:

100 cm^3 of 0.0500 mol dm^{-3} of $NaVO_3$ is reacted completely with zinc powder. The final colour of the solution is blue-green.

25.0 cm^3 of this blue-green solution requires 20.63 cm^3 of 0.0200 mol dm^{-3} of $KMnO_4$ for complete reaction under acidic conditions.

(i) There are 2 different vanadium containing ions in this blue-green solution, of which one of them is VO^{2+}.

State the identity of the other ion. **[1]**

(ii) Write a balanced chemical equation between VO^{2+} and MnO_4^- under acidic conditions. **[1]**

(iii) Calculate the amount of $KMnO_4$ that has undergone reaction. **[1]**

(iv) Given that:

- 5 mol of the ion identified in **(c)(i)** reacts exactly with 2 mol of $KMnO_4$
- x mol of VO^{2+} is present in 25.0 cm^3 of the blue-green solution

Show that the total amount of $KMnO_4$ reacted = $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x$.

Hence, calculate the mass of zinc powder added to the original mixture. **[4]**

(d) Vanadium pentoxide can be used as a catalyst in a reaction known as oxidative esterification. In this reaction, an aldehyde can react with an alcohol or phenol to form an ester:

$$R_1{-}CHO + HO{-}R_2 \rightarrow R_1{-}COO{-}R_2 + 2[H]$$

Compound **A**, $C_8H_8O_2$ undergoes oxidative esterification in the presence of V_2O_5 catalyst to form a neutral compound **B**, $C_8H_6O_2$. On heating **B** under reflux with NaOH(aq), the sodium salt of compound **C**, $C_8H_8O_3$, was formed. Compounds **A**, **B** and **C** reacts with $LiAlH_4$ in dry ether to form compound **D**, $C_8H_{10}O_2$, while compounds **A**, **C** and **D** are able to decolourise aqueous bromine.

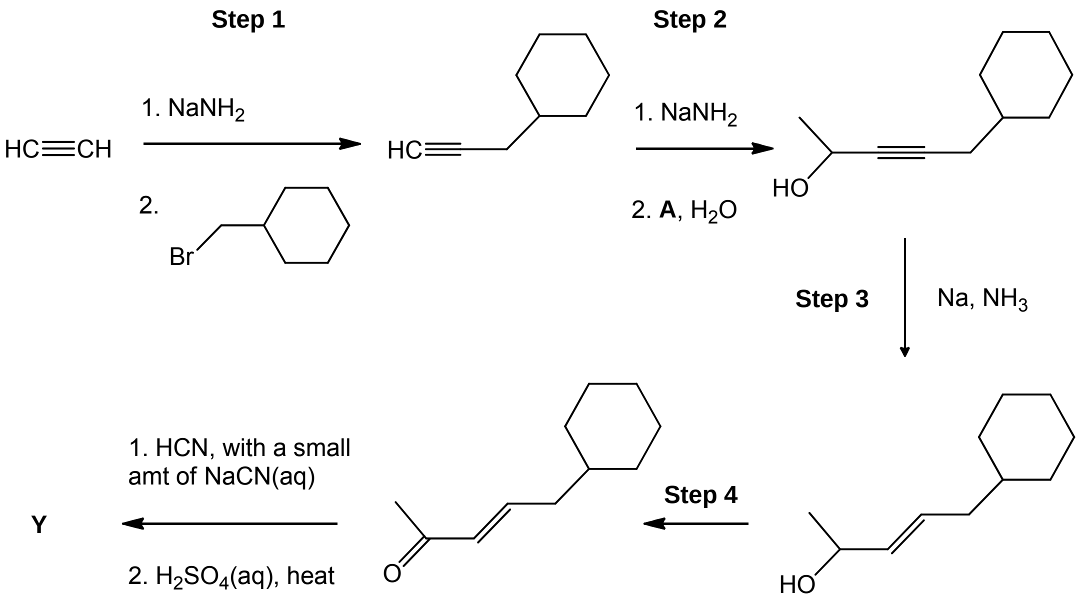
Draw the structures of **A**, **B**, **C** and **D**, and explain your reasoning. **[7]**

[Total: 19]

Section B

Answer **one** question from this section.

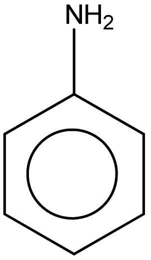
4 **(a)** Compound **Y** can be obtained from ethyne using the following synthesis pathway:



(i) Given that HC≡C⁻ is formed, state the role of $NaNH_2$ in Step **1**. **[1]**

(ii) Name and outline the mechanism for the reaction in Step **1** Part **2**. Show relevant lone pairs and dipoles, using curly arrows to indicate the movement of electron pairs. **[3]**

(iii)



phenylamine

Suggest why phenylamine is unable to carry out the role of sodium amide, $NaNH_2$, in Step **1**. **[1]**

(iv) Suggest the reagent **A** in Step **2**, and reagents and conditions for Step **4**. **[2]**

(v) Draw the structure of Compound **Y**.

Explain why HCN reacts with C=O but not with C=C in the same compound. **[3]**

(b) Sodium borohydride, $NaBH_4$, is another inorganic sodium compound that is often used in organic synthesis. It is also used to make the prototypes of direct borohydride fuel cell. Aqueous sodium borohydride undergoes catalytic decomposition to produce the hydrogen needed for the fuel cell.

$$NaBH_4(s) + 2H_2O(l) \rightarrow NaBO_2(s) + 4H_2(g) \qquad \Delta H^{\ominus} = -210 \text{ kJ mol}^{-1}$$

Boron is similar to carbon in its ability to form stable covalently bonded molecular network.

(i) What do you understand by the term *lattice energy*? **[1]**

(ii) With the aid of an energy cycle, use the following data and appropriate data from the *Data Booklet* to calculate the lattice energy of sodium borohydride.

enthalpy change of formation of $H_2O(g)$	−241 kJ mol^{-1}
standard enthalpy change of atomisation of Na	+107 kJ mol^{-1}
standard enthalpy change of formation of $BH_4^-(g)$	−78.2 kJ mol^{-1}
standard enthalpy change of vapourisation of $H_2O(l)$	+40.8 kJ mol^{-1}
standard enthalpy change of formation of $NaBO_2(s)$	−1059 kJ mol^{-1}

[5]

(c) A breathalyzer does not directly measure blood alcohol content or concentration, which involves the analysis of blood sample. It measures the blood alcohol content by measuring the amount of alcohol in the exhaled breath instead.

Ethanol is a volatile compound. In lungs, the ethanol dissolved in blood can change its state from liquid to gaseous and it is exhaled with air. When a user breathes into the breathlyzer, the ethanol in the exhaled air is passed through a solution of potassium dichromate. The ethanol is oxidised to ethanoic acid.

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

The direct oxidation of ethanol by potassium dichromate is carried out in an electrochemical cell and the current generated can be used to estimate the alcohol content of blood.

(i) When a user breathes into the breathlyzer which contains potassium dichromate, a current of 0.12 A is recorded for 1 min.

Determine the mass of ethanol per breath. **[3]**

(ii) A partition ratio of "2100:1" is used to estimate the blood alcohol content in blood from the amount of alcohol in a breath. This partition ratio implies that 2100 cm^3 of breath contains the same amount of ethanol as 1 cm^3 of blood.

Given that the volume of exhaled air in **(c)(i)** is 65 cm^3, calculate the amount of ethanol per cm^3 of blood. **[1]**

[Total: 20]

5 **(a)** Most plants do not thrive in highly acid or highly alkaline soil, though a few have adapted to such extremes. Soil pH may be adjusted using suitable chemicals.

Describe, with the aid of balanced equations, the actions of acid and/or base on the oxides of magnesium and phosphorus, if any.

Hence, suggest why oxides of phosphorus should not be used to adjust soil pH. **[3]**

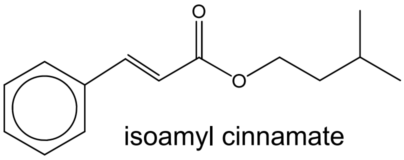
(b) RVCM®Calmag is a solid fertiliser containing calcium nitrate and magnesium nitrate in a fixed mole ratio of 2:1.

Two equal masses of fertiliser samples were heated at 575 K and 949 K respectively until there is no more change to their masses. For both samples, brown fumes were observed and a gas that rekindled a glowing splint was evolved.

(i) Write a balanced equation to represent any one reaction that occurred. **[1]**

(ii) The loss in mass for **sample 1** heated at 949 K is three times that of **sample 2** heated at 575 K. Account for this observation. **[3]**

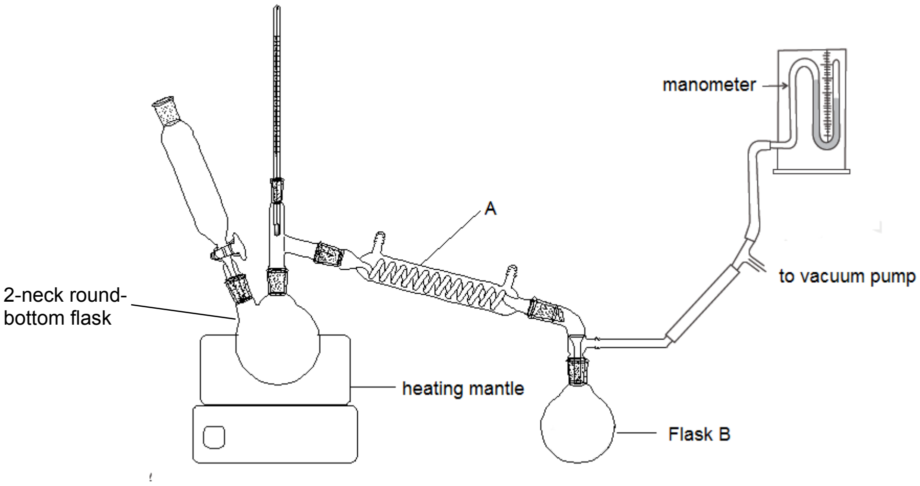
(c) Isoamyl cinnamate extracted from several types of trees from the genus *Cinnamomum* has a balsamic odour, reminiscent of cinnamon with an amber note.



isoamyl cinnamate

Isoamyl cinnamate can be oxidised to give different products depending on the choice of oxidising agents and the reaction conditions. A pure sample of isoamyl cinnamate was heated with acidified potassium dichromate using the apparatus setup as shown in **Figure 5.1**.

Figure 5.1



(i) State the function of the apparatus **A**. **[1]**

(ii) Name and write balanced equations for two major reactions that occur in the 2-neck round-bottom flask.

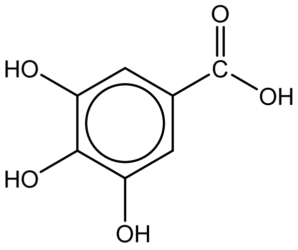
You may use [O] or [H] to balance the equations. **[2]**

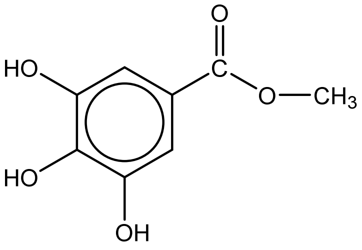
(iii) Identify the first organic compound that is likely to be collected in flask **B**. **[1]**

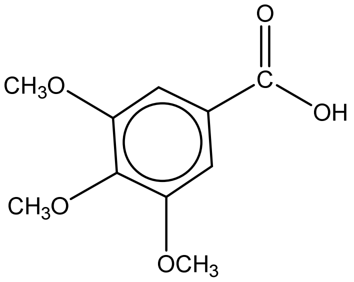
(iv) Draw the skeletal structures of all the organic products formed if acidified potassium manganate(VII) is used instead of acidified potassium dichromate. **[2]**

(d) Pu'erh (Chinese: 普洱）is a variety of fermented tea produced in Yunnan province, China. Black Pu'erh tea is known to contain more gallic acid than green Pu'erh tea. Gallic acid and its derivatives have been reported to elicit antioxidant, anti-cancer and anti-diabetic activities.

The structures of gallic acid and its derivatives are given below:


gallic acid


methyl gallate


3,4,5-trimethylgallic acid

(i) Gallic acid can dissolve in water and diethyl ether. The partition coefficient for the separation of gallic acid in the two immiscible phases is given below:

$$K_{partition} = \frac{[gallic\ acid]_{aqueous}}{[gallic\ acid]_{diethyl\ ether}}$$

In an experiment, 1.00 g sample of pure gallic acid was dissolved in 100 cm^3 of water. This aqueous solution of gallic acid and 50.0 cm^3 of diethyl ether were placed in a separatory funnel which is shaken to mix well. The mixture was then allowed to stand for 30 minutes before the two immiscible layers were separated.

It was found that 20.0 cm^3 of the aqueous layer required 20.25 cm^3 of 0.180 mol dm^{-3} sodium hydroxide for complete neutralisation.

Calculate the amount of gallic acid in each layer, and hence the partition coefficient. **[3]**

(ii) A sample containing both gallic acid and 3,4,5-trimethylgallic acid are dissolved in 50 cm^3 of diethyl ether.

Describe and explain how would you modify the solvent extraction method in **d(i)** such that mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer. **[2]**

(iii) Suggest a chemical test to distinguish methyl gallate from gallic acid. **[2]**

[Total: 20]

- End of Paper -

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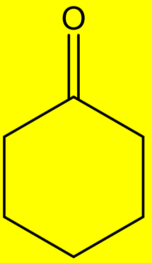
Section A

<table>
<tr><td>1</td><td>(a)</td><td>(i)</td><td>

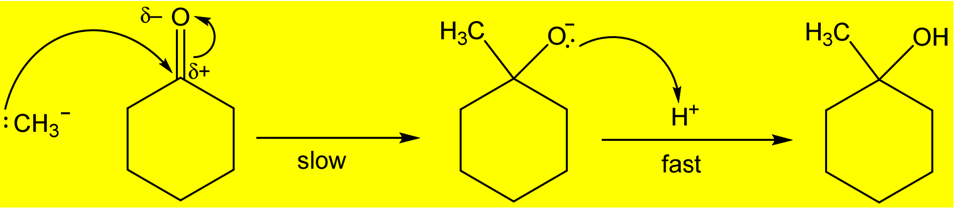
<table>
<tr><th>Element</th><th>$E^\ominus$ / V</th></tr>
<tr><td>$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$</td><td>+2.87</td></tr>
<tr><td>$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$</td><td>+1.36</td></tr>
<tr><td>$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-$</td><td>+1.07</td></tr>
<tr><td>$\frac{1}{2} I_2 + e^- \rightleftharpoons I^-$</td><td>+0.54</td></tr>
</table>

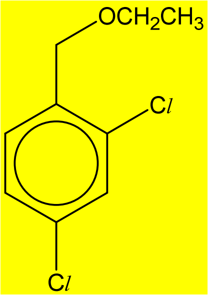
The order of oxidising strength of the halogens, as observed from the $E^\ominus$ values above, decreases down the Group.

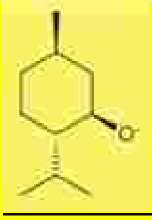
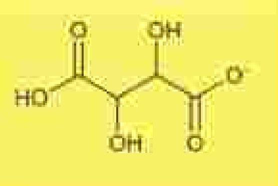
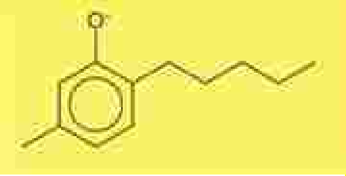
Due to the strong oxidising power of F_2, the oxidation number of Phosphorus +5 in PF_5, +5 and +3 in PCl_5 and PCl_3, +3 in PBr_3 and PI_3 respectively.</td><td>[3]</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>The smaller the pK_a, the stronger the acid, indicating HI is the strongest acid, followed by HBr, HCl and HF. Down the group from F to Cl to Br to I, atomic radius increases, effectiveness of orbital overlap between H and X decreases. The H–X bond becomes increasingly weaker, making it easier to lose the H^+.</td><td>[2]</td></tr>
<tr><td></td><td>(b)</td><td>(i)</td><td>(Acidic) hydrolysis</td><td>[1]</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>

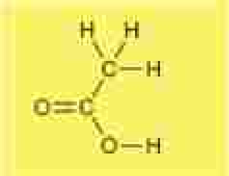


and CH_3MgBr</td><td>[2]</td></tr>
</table>

		(iii)		**[3]**
	(c)	**(i)**	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$	**[1]**
		(ii)	$[Ca^{2+}] = 1.14 \times 10^{-7} \times 3 = 3.42 \times 10^{-7}$ mol dm^{-3} $[PO_4^{3-}] = 1.14 \times 10^{-7} \times 2 = 2.28 \times 10^{-7}$ mol dm^{-3} $K_{sp} = (3.42 \times 10^{-7})^3(2.28 \times 10^{-7})^2 = 2.08 \times 10^{-33}$ mol^5 dm^{-15}	**[2]**
		(iii)	Let the solubility of calcium phosphate in the presence of potassium phosphate be y. $2.08 \times 10^{-33} = (3y)^3(0.15 + y)^2$ Assume that y is small such that $0.15 + y \approx 0.15$ $2.08 \times 10^{-33} = (3y)^3(0.15)^2$ $y = 1.51 \times 10^{-11}$ mol dm^{-3}	**[2]**
		(iv)	An increase in $[SO_4^{2-}]$ causes the equilibrium position of $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$ to shift left, decreasing the solubility of $CaSO_4$. Since the solubility of $CaSO_4$ is lowered, there will be less Ca^{2+} from dissolution of $CaSO_4$. Equilibrium position of $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$ shifts right, increasing the solubility of $Ca_3(PO_4)_2$.	**[2]**
			[Total: 18]	

2	**(a)**	**(i)**	NaOH(aq), heat under reflux	**[1]**
		(ii)	The C–Cl bond has a partial double bond character as the lone pair of electrons in the p orbital of the Cl atom can delocalise into the π electron cloud of the benzene ring. This strengthens the C–Cl bond, making it more difficult to break.	**[1]**
		(iii)		**[1]**
		(iv)	Add PCl_5 / $SOCl_2$ 2,4-dichlorobenzyl alcohol: white fumes (of HCl) observed amylmetacresol: no white fumes observed or Add Br_2(aq) 2,4-dichlorobenzyl alcohol: Br_2(aq) remains orange amylmetacresol: orange Br_2(aq) decolourises or Add neutral $FeCl_3$ 2,4-dichlorobenzyl alcohol: no violet complex formed amylmetacresol: violet complex formed	**[2]**

	(b)		Menthol < amylmetacresol < tartaric acid Menthol is the weakest acid.  is the least stable anion as the electron-donating alkyl group intensifies the negative charge on the oxygen atom in the anion. Amylmetacresol is more acidic than menthol as the  anion is more stable. The negative charge on the oxygen atom can be delocalised into the benzene ring. Tartaric acid is the most acidic as the  anion is the most stable. The negative charge on the oxygen atom is delocalised over the COO^- group, and the delocalisation is more effective than that in the  anion.	**[3]**
	(c)	**(i)**	Step 1: electrophilic substitution / electrophilic addition Step 2: reduction (Note: for step 1, the catalyst aids in the formation of $CH_3CHCH_3^+$ electrophile)	**[2]**
		(ii)	8 enantiomers Proportion = 0.125 / 12.5%/ 1/8	**[2]**

		(iii)	(Accept: benzoate salt)	**[1]**
	(d)	**(i)**	When 0.00 cm^3 of NaOH is added, solution contains only tartaric acid. $[H^+] = \sqrt{(0.0100)(10^{-2.89})} = 3.59 \times 10^{-3}$ mol dm^{-3} pH = $-\lg(3.59 \times 10^{-3}) = 2.45$ When 12.50 cm^3 of NaOH is added, solution contains equal concentration of unreacted tartaric acid and tartrate mono-anion, giving rise to a buffer at its maximum buffering capacity. Hence, pH = pK_{a1} = 2.89. When 50.00 cm^3 of NaOH is added, solution only contains tartrate di-anion which undergoes hydrolysis to form OH$^-$. [Tartrate di-anion] = $(\frac{25.00}{1000} \times 0.0100) \div \frac{75.00}{1000} = 0.00333$ mol dm^{-3} $[OH^-] = \sqrt{(0.00333)(\frac{1.00\times10^{-14}}{10^{-4.40}})} = 9.15 \times 10^{-7}$ mol dm^{-3} pOH = $-\lg(9.15 \times 10^{-7}) = 6.04$ pH = 14 – 6.04 = 7.96	**[4]**
		(ii)	The solid has a giant ionic lattice structure while tartaric acid has a simple covalent structure. More energy is needed to overcome the stronger electrostatic attraction between the cations and anions than the weak hydrogen bonds between tartaric acid molecules.	**[2]**
	(e)	**(i)**	Cold dilute acidified / alkaline KMnO$_4$(aq)	**[1]**
		(ii)		**[1]**

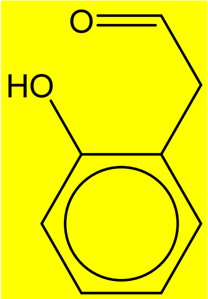
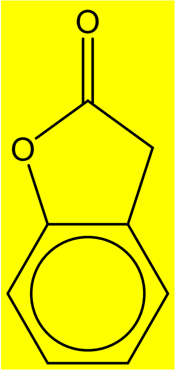
		(iii)	The gas is CO_2. $pV = nRT$ $p(500 \times 10^{-6}) = (\frac{0.36}{44.0})(8.31)(30 + 273)$ $p = \underline{4.12 \times 10^4\ \text{Pa}}$	**[2]**
			[Total: 23]	

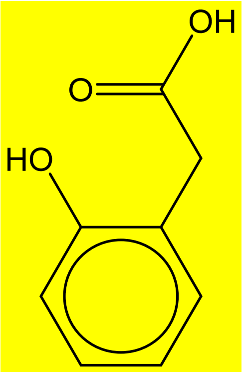
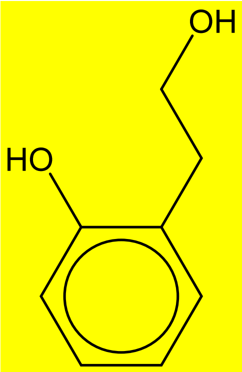
3	**(a)**		It is a substance that is at a different phase as the reactants, and it speeds up the rate of the reaction by providing an alternative reaction pathway with a lower activation energy.	**[2]**

	(b)		Zn/Zn^{2+} half-cell $E^\ominus = -0.76$ V
			VO_3^-/VO^{2+} half-cell $E^\ominus = +1.00$ V
			VO^{2+}/V^{3+} half-cell $E^\ominus = +0.34$ V
			V^{3+}/V^{2+} half-cell $E^\ominus = -0.26$
			$(VO_3^-/VO^{2+}//Zn/Zn^{2+})$ $E^\ominus_{cell} = +1.76$ V
			Zn is able to reduce VO_3^- to VO^{2+}/ reduction of VO_3^- to $VO^{2+}$by Zn is spontaneous.
			$(VO^{2+}/V^{3+}//Zn/Zn^{2+})$ $E^\ominus_{cell} = +1.10$ V
			Zn is able to reduce VO^{2+} to V^{3+}/ reduction of VO^{2+} to V^{3+} by Zn is spontaneous.
			$(V^{3+}/V^{2+}//Zn/Zn^{2+})$ $E^\ominus_{cell} = +0.50$ V
			Zn is able to reduce V^{3+} to V^{2+}/ reduction of V^{3+} to V^{2+} by Zn is spontaneous.
			Hence, the solution changes from yellow to blue to green to violet.
				[3]

	(c)	**(i)**	$V^{3+}(aq)$	**[1]**
		(ii)	$5VO^{2+} + MnO_4^- + 6H_2O \rightarrow 5VO_3^- + Mn^{2+} + 12H^+$ **OR** $5VO^{2+} + MnO_4^- + H_2O \rightarrow 5VO_2^+ + Mn^{2+} + 2H^+$	**[1]**
		(iii)	$n_{KMnO_4} = \frac{20.63}{1000} \times 0.02 = 0.000413\ mol$	**[1]**

		(iv)	$n_{V^{3+}} + n_{VO^{2+}} = \frac{25}{1000} \times 0.05 = 0.00125$ mol $n_{V^{3+}} = 0.00125 - x$ n_{KMnO_4} reacted with $VO^{2+} = \frac{1}{5}x$ n_{KMnO_4} reacted with $V^{3+} = \frac{2}{5}(0.00125 - x)$ $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x = 0.000413$ $0.0025 - 2x + x = 0.002063$ $x = 0.000437$ mol In 100 cm^3 of solution: $n_{V^{3+}} = 4(0.00125 - 0.000437) = 0.003252$ mol $n_{VO^{2+}} = 4x = 0.001748$ mol $m_{Zn} = 0.5[(65.4)(0.001748) + (65.4)(2)(0.003252)]$ $= 0.270$ g	**[4]**
	(d)	C:H ratio of **A**, **B**, **C** and **D** ≈ 1:1 - Contains a benzene ring Compound **A** undergo oxidative esterification: - **A** has an aldehyde group / phenol / alcohol group. - **B** has an ester group (also accept **B** being ester due to neutral nature) Compound **B** undergo (alkaline) hydrolysis to form the sodium salt of C - B is a cyclic ester - **C** has a carboxylic acid and alcohol / phenol group. **A**, **B** and **C** undergo reduction to form **D** - **D** contains 2 –OH group, of which one is a primary alcohol. **A**, **B** and **D** can undergo electrophilic substitution with $Br_2(aq)$ - **A**, **B** and **D** contains a phenol		**[7]**

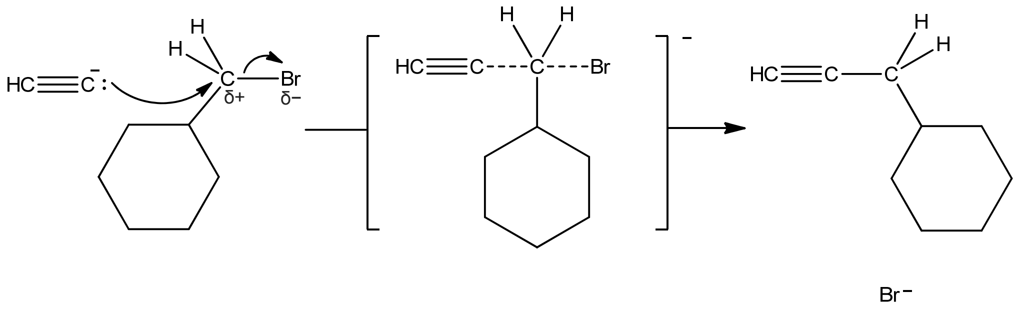
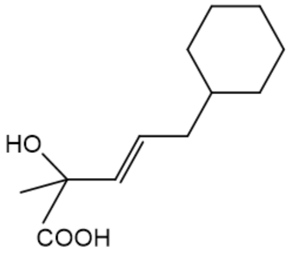
	
A	**B**

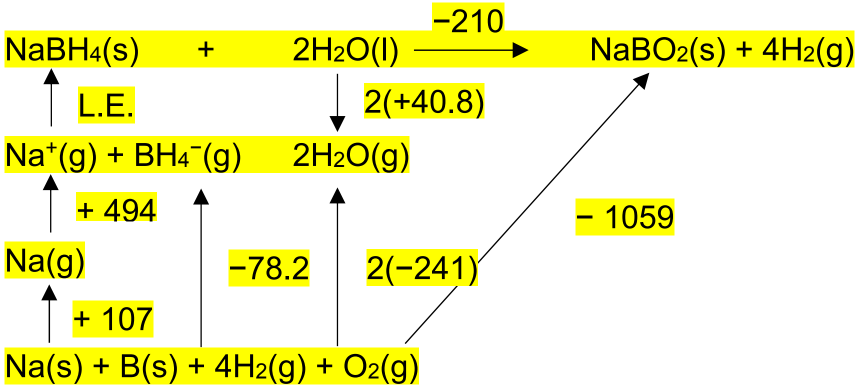
	
C	**D**

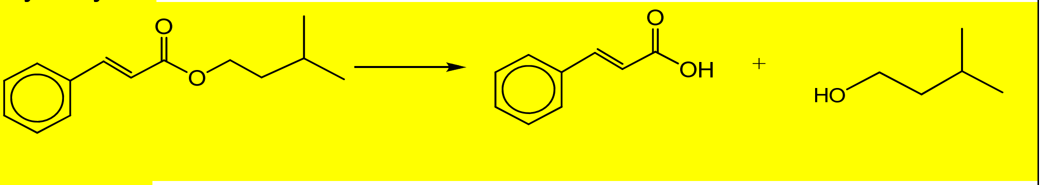
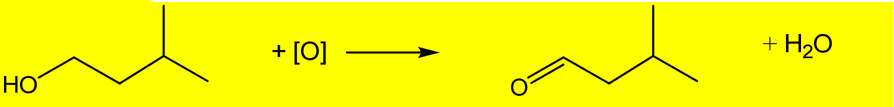
[Total: 20]

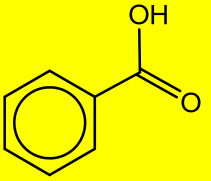
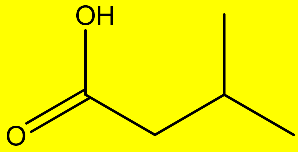
Section B

Answer **one** question from this section.

4	**(a)**	**(i)**	Base	**[1]**
		(ii)	S_N2 nucleophilic substitution 	**[3]**
		(iii)	Phenylamine is a weaker base. The lone pairs of electrons on the $-NH_2$ group is delocalised into the benzene ring, this makes the lone pair less available for protonation.	**[1]**
		(iv)	Step 2: ethanal Step 4: Acidified $K_2Cr_2O_7$, heat (under reflux)	**[2]**
		(v)	 The C=C is electron rich hence C=C does not attract CN^- nucleophiles. The carbonyl C in C=O is electron-deficient (or electrophilic) as it is bonded to highly electronegative O atom, attracting CN^- nucleophiles.	**[3]**
	(b)	**(i)**	Lattice energy is the enthalpy change when one mole of the solid ionic compound is formed from its constituent gaseous ions under standard conditions.	**[1]**

		(ii)	 By Hess' Law, $-\text{L.E.} - (+494) - (+107) - (-78.2) - 2(-241) + 2(+40.8) - 1059 = -210$ L.E. = − 808 kJ mol^{-1}	**[5]**
	(c)	**(i)**	$Q = It = nF$ $n = \frac{It}{F} = \frac{0.12 \times 60}{96500} = 7.4611 \times 10^{-5}\ mol$ $n_{ethanol} = \frac{1}{4} \times 7.4611 \times 10^{-5} = 1.87 \times 10^{-5}\ mol$ Mass of alcohol per breath = $1.87 \times 10^{-5} \times 46.0 = 8.58 \times 10^{-4}\ g$	**[3]**
		(ii)	Amount of ethanol per cm^3 of blood = $\frac{2100}{65} \times 1.87 \times 10^{-5}$ $= 6.04 \times 10^{-4}\ mol$	**[1]**
			[Total: 20]	

5	**(a)**	MgO(s) <u>reacts with acid</u> to form neutral salt and water. $MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$ $P_4O_6(s)$ (or $P_4O_{10}(s)$) <u>react violently/vigorously with alkali</u> to form salt and water. $P_4O_{10}(s) + 12OH^-(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(l)$ $P_4O_6(s) + 8OH^-(aq) \rightarrow 4HPO_3^{2-}(aq) + 2H_2O(l)$ $P_4O_6(s)$ (or $P_4O_{10}(s)$) reactions with alkali is too exothermic (could burn the roots of the plant), OR produces conjugate base which makes the soil alkaline.		**[3]**
	(b)	**(i)**	$Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + ½O_2(g)$ $Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + ½O_2(g)$	**[1]**
		(ii)	$Mg(NO_3)_2$ decomposed at 575 K but not $Ca(NO_3)_2$. Both $Mg(NO_3)_2$ and $Ca(NO_3)_2$ decomposed at 949 K. Mg^{2+} has a <u>smaller ionic radius</u> than Ca^{2+} while their ionic charges are the same. <u>Charge density of Mg^{2+} is higher</u> and hence has higher polarising power than Ca^{2+}. Mg^{2+} is able to <u>polarise / distort the electron cloud of NO_3^{2-} and weaken the covalent bonds in NO_3^{2-} to larger extent.</u> Since the mole ratio of $Mg(NO_3)_2$ and $Ca(NO_3)_2$ in the samples is 2:1, Sample at 575 K lost x g from $Mg(NO_3)_2$ Sample at 949 K lost x g from $Mg(NO_3)_2$ and $2x$ g from $Ca(NO_3)_2$ ($3x$ g in total).	**[3]**
	(c)	**(i)**	To <u>condense the product</u> formed so that it can be collected.	**[1]**
		(ii)	Hydrolysis:  Oxidation: 	**[2]**
		(iii)	3-methylbutanal (lowest b.p. compared to the isoamyl cinnamate, cinnamic acid and 3-methylbutanol, deduce using chem bonding knowledge)	**[1]**

		(iv)	 	**[2]**
	(d)	**(i)**	Total amount of gallic acid (GA) = $\frac{1.00}{170}$ = 0.005882 mol GA ≡ 4NaOH Amount of GA in 100 cm^3 aqueous layer = $\frac{20.25}{1000} \times 0.180 \times \frac{1}{4} \times 5$ = 4.556 × 10^{-3} mol Amount of GA in 50 cm^3 organic layer = 0.005882 – 4.556 × 10^{-3} = 1.326 × 10^{-3} mol $K_{partition} = \frac{\left(\frac{4.556 \times 10^{-3}}{0.100}\right)}{\left(\frac{1.326 \times 10^{-3}}{0.050}\right)} = 1.72$	**[3]**
		(ii)	Add (100 cm^3 of / an excess of) aqueous NaOH and the (50 cm^3 of) diethyl ether containing both gallic acid and 3,4,5-trimethylgallic acid to a separatory funnel. Shake the two layers to ensure all the gallic acid are neutralised by NaOH. Vent the separatory funnel periodically to prevent pressure build up. Salt of gallic acid much more soluble in aqueous layer than diethyl ether layer as it can form more ion-dipole interaction with water molecules. Thus, mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer. **modification:** use of aqueous NaOH to neutralise the gallic acid and its derivatives **explanation:** explain why mainly 3,4,5-trimethoxygallic acid is left in diethyl ether layer gallic acid forms anion with more charge (+4) than anion from 3,4,5-trimethoxygallic acid, therefore more ion-dipole interaction bulky 3,4,5-trimethoxybenzyl group hinders the formation of ion-dipole, thus anion from 3,4,5-trimethoxygallic acid form significant pd-pd with diethyl ether	**[2]**
		(iii)	Test: Add acidified KMnO$_4$, heat. Bubble gaseous product into limewater. For methyl gallate, purple KMnO$_4$ is decolourised and a colourless, odourless gas evolved gives white ppt in limewater. For gallic acid, KMnO$_4$ remained purple.	**[2]**
				[Total: 20]

RIVER VALLEY HIGH SCHOOL

YEAR 6 PRACTICAL EXAMINATION II

H2 CHEMISTRY 9729

23 AUGUST 2018

2 HOURS 30 MINUTES

NAME ______________________________

CLASS 6 (   )

INDEX NO. ______________________________

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a 2B pencil for any diagrams or graph.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer ***all*** *questions in the spaces provided on the Question Paper.*

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Shift
Laboratory

For Examiner's Use	
3 s.f.	
Units	
Total	55

This Question Paper consists of **22** printed pages and **0** blank page.

Answer **all** the questions in the spaces provided.

1 To investigate the kinetics of the reaction between iron(III) ions and iodide ions

You will investigate the rate of oxidation of iodide by iron(III) ions in **reaction 2**. The chemical changes in this experiment can be presented by the following equations:

Reaction 1: $Fe^{3+}(aq) + S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)]^{+}(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

The reaction is started by mixing acidic solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch.

The iodine, I_2, produced in **reaction 2** reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ in **reaction 3**.

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be determined by finding the time for the blue-black colour to appear.

FA 1 is 0.030 mol dm^{-3} iron(III) chloride, $FeCl_3$.

FA 2 is 0.060 mol dm^{-3} potassium iodide, KI.

FA 3 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

starch indicator

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 4.

You will need to include volume of **FA 1**, volume of water, reaction time and calculated rate of reaction for each of the five experiments. Record all calculated values to 3 significant figures.

(a) Method

Experiment 1

1. Use the measuring cylinders to place the following in a 100 cm^3 beaker.
   - 10 cm^3 of **FA 2**
   - 20 cm^3 of **FA 3**
   - 10 cm^3 of starch indicator
2. Using a measuring cylinder, transfer 20 cm^3 of **FA 1** rapidly into the same 100 cm^3 beaker. Start the stopwatch during this addition.
3. Stir the mixture and place the beaker on a white tile.
4. The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this blue-black colour appears. Record the time to the nearest 0.1 second.
5. Wash the beaker thoroughly with water and carefully dry the beaker.

Experiment 2

6. Repeat step **1** in **Experiment 1**.
7. Using a measuring cylinder, add 12 cm^3 of **FA 1**, and make up the volume to 20 cm^3 using deionised water. Transfer the solution rapidly into the same 100 cm^3 beaker. Start the stopwatch during this addition.
8. Stir the mixture and place the beaker on the white tile.
9. Stop timing when a blue-black colour appears.
10. Wash the beaker thoroughly with water and carefully dry the beaker.

Experiments 3−5

Carry out three further experiments to investigate the effect of changing the concentration of Fe^{3+}(aq) by altering the volume of aqueous $FeCl_3$, **FA 1**, used.

You should use a volume of **FA 1** that is at least 12 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

(b) Show, by means of calculation, that the change in the concentration of Fe^{3+}, $\Delta[Fe^{3+}]$, which occurred when the blue-black colour appeared was 2.00×10^{-3} mol dm^{-3}.

1	

(c) Results

The rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{\Delta[\mathrm{Fe^{3+}}]}{\text{reaction time}} \times 10^6$$

Calculate the rate of reaction for each experiment and complete your table.

For Examiner's Use

2	
3	
4	
5	

(d) **(i)** Plot the rate (y-axis) against the volume of **FA 1** (x-axis) on the grid. Draw a line of best fit through the points.

Your chosen scales should allow you to extrapolate this line to volume of **FA 1** = 0 cm^3.

You should also identify any points you consider anomalous by drawing a circle around it.

6	
7	
8	

For Examiner's Use

(ii) Explain why the volume of **FA 1** in each experiment can be used as [Fe^{3+}].

9

(iii) Deduce the order of reaction with respect to Fe^{3+}. Use evidence from your graph to support your deduction.

10

(e) **(i)** Use your graph to calculate the time that the reaction would have taken if 4.0 cm^3 of **FA 1** had been used. Show your working clearly.

time = ...

11

(ii) Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions if 4.0 cm^3 of **FA 1** had been used.

initial [Fe^{3+}] = ...

initial [I^-] = ...

12

(e) **(iii)** Given that the reaction is second order with respect to iodide, calculate the rate constant.

rate constant = ...

13	

(f) The complex $[Fe(S_2O_3)]^+$ formed in **reaction 1** is purple.

Consider the colour change observed when **FA 1** was added to the solution prepared in **Step 1** before the blue-black colour appeared. Suggest an explanation for the colour change in terms of the chemistry involved.

14	
15	

[Total: 15]

2 Determining the percentage purity of calcium carbonate

In this question, you will determine the percentage purity of an industrial grade calcium carbonate, $CaCO_3$, by two different methods.

(a) Method 1

The percentage purity of calcium carbonate can be determined by measuring the change in mass when the sample of calcium carbonate reacts with hydrochloric acid.

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

FA 4 is industrial grade calcium carbonate, $CaCO_3$.

FA 5 is 2.00 mol dm^{-3} dilute hydrochloric acid.

You do not need to carry out **Method 1**.

Procedure:

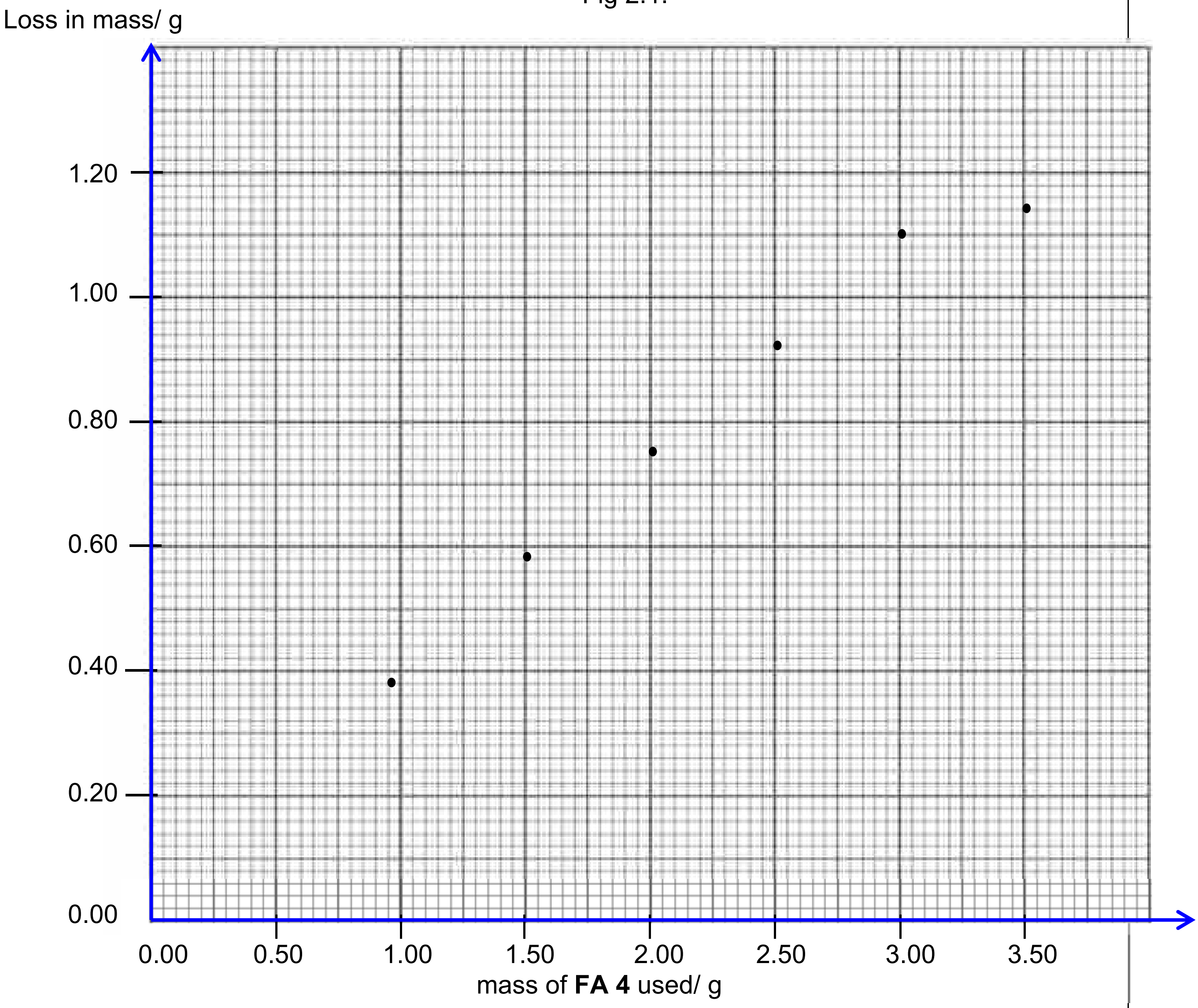
1. Weigh accurately about 2.0 g of **FA 4** in a small weighing bottle.
2. Measure about 25 cm^3 of **FA 5** in a small conical flask.
3. Add **FA 4** to **FA 5** and swirl the mixture continuously until no more bubbles is observed.
4. Reweigh the weighing bottle with its residual **FA 4**.
5. Reweigh the conical flask and its content.

A student performed a series of experiments by repeating the above procedure with different masses of **FA 4**.

The results from her series of experiment are plotted on the grid in Fig 2.1.

Identify the anomalous data point by drawing a circle around it. Draw the most appropriate best-fit line taking into account all of the plotted points, except for the anomaly. Extrapolate (extend) this line to the mass of **FA 4** used = 0.00 g.

Fig 2.1.



16	

Calculations

(b) **(i)** Determine the gradient of this line, showing clearly how you did this.

Hence, determine the mass of carbon dioxide evolved for per gram of **FA 4** used.

mass of carbon dioxide evolved =............................

17	
18	

(ii) Using your answer in **b(i)**, calculate a value for the percentage purity of the sample of industrial grade calcium carbonate, **FA 4**.

[A_r: Ca, 40.1; C, 12.0; O,16.0]

percentage purity of **FA 4** = ...

19	

(c) **Method 2**

You will determine the amount of hydrochloric acid remaining in flask **X** after the reaction with another sample of industrial grade calcium carbonate. You will do this by titration with sodium hydroxide of known concentration.

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

FA 6 is 0.140 mol dm^{-3} sodium hydroxide, NaOH.

Thymolphthalein indicator

Procedure:

1. Pipette 25.0 cm^3 of **FA 5** into flask **X**.
2. Weigh accurately about 0.6 g of **FA 4** in a weighing bottle.
3. Add the **FA 4** into flask **X**.
4. Reweigh the weighing bottle with its residual **FA 4**.
5. Swirl the mixture until no more bubbles are observed.
6. Transfer **all** the contents of flask **X** and the washings into a 250 cm^3 volumetric flask.
7. Add deionised water up to the mark, stopper the volumetric flask and mix the contents thoroughly. Label this solution **FA 7**.
8. Fill the burette with **FA 6**.
9. Wash and rinse the pipette then use it to transfer 25.0 cm^3 of **FA 7** into a conical flask.
10. Add about 5 drops of thymolphthalein indicator.
11. Titrate **FA 7** with **FA 6**.
12. Repeat the titration as many times as you think necessary to obtain consistent results.
13. Record in the space below, all of your mass readings, burette readings and the volume of **FA 6** added.

For Examiner's Use

Results

20	
21	
22	
23	
24	
25	

Supervisor expected titre
Student expected titre
Difference

(d) From your accurate titration results, obtain a suitable value for the volume of **FA 6** to be used in your calculations. Show clearly how you obtained this value.

For Examiner's Use

Volume of **FA 6** used = ………………

26	

Calculations

(e) **(i)** Calculate the number of moles of sodium hydroxide, NaOH, present in volume of **FA 6** calculated in **(d)**.

amount of NaOH = ...

27	

(ii) Calculate the number of moles of hydrochloric acid remaining in flask **X** after the reaction with **FA 4** has completed.

amount of HC*l* remaining in flask **X** = ...

28	

(iii) Calculate the number of moles of hydrochloric acid that reacted with the **FA 4** used.

amount of HC*l* reacted = ...

29	

(iv) Calculate the mass of $CaCO_3$ in the sample of **FA 4** used, and hence the percentage purity of the industrial grade $CaCO_3$.

[A_r: Ca, 40.1; C, 12.0; O,16.0]

For Examiner's Use

30	

percentage purity of the industrial grade $CaCO_3$ = ...

(f) The two different methods were used to find the percentage purity of industrial grade calcium carbonate.

It is found that the samples of **FA 4** used contain calcium oxide which reacts with dilute hydrochloric acid.

How would this affect the percentage purity calculated for each method? Explain your answers.

Method 1:

Method 2:

31	
32	

(g) Explain why sulfuric acid cannot be used in both methods.

33	

(h) **Planning**

Unlike the acid-base titration in **Part (c)** that uses acid-base indicator to mark the end-point, thermometric titration uses heat evolved or temperature change of solution. In thermometric titration, the titre value can be determined from the graph of energy evolved against volume of titrant (solution from the burette) added.

Since neutralisation reaction is exothermic, thermometric titration can be used to determine the amount of excess hydrochloric acid in flask **X** from **Part (c)**.

(i) Given that the concentration of undiluted excess hydrochloric acid in flask **X** is about 1.7 mol dm^{-3}, and the desired titre is around 24 cm^{3}, calculate the concentration of sodium hydroxide required for the thermometric titration.

Concentration of NaOH = ...

34

(ii) You are to plan a thermometric titration to determine the concentration of hydrochloric acid. The results obtained should allow the titre value to be determined graphically.

You may assume that you are provided with

- 50 cm^{3} of hydrochloric acid, HC*l*, of concentration around 1.7 mol dm^{-3}
- standard solution of sodium hydroxide solution, NaOH, of the same concentration calculated in **(h)(i)**
- apparatus commonly found in a school or college laboratory

In your plan you should include the following:

- a diagram of the apparatus set-up that may be used
- the procedure that you would follow and the measurements you would take
- the precautions and measures that you would take to minimise heat loss to the surroundings

For Examiner's Use

For
Examiner's
Use

35	
36	
37	
38	
39	
40	

(h) **(iii)** Your procedure in **(h)(ii)** should allow the graph of total energy evolved against volume of titrant to be plotted. Briefly describe how you would use the results obtained to determine the total energy evolved from the start of the experiment for each data point.

41	

For Examiner's Use

(h) **(iv)** Sketch, on the axes in Fig. 2.2, the graph you would expect to obtain and show how you would use this graph to determine the titre value.

Explain the shape of your graph.

Fig. 2.2

Explanation:

42	
43	

(v) Sketch, on the same axes in Fig. 2.2, the graph you would expect to obtain if aqueous ammonia of the same concentration as aqueous NaOH is used as the titrant instead.

Label this graph clearly as **Graph B**.

Explain the shape of **Graph B**.

44	
45	

[Total: 30]

3 Inorganic qualitative analysis

In this experiment you are to explore the chemistry of some compounds of an unknown transition element **W**. You are provided with 4 samples, **FA 8**, **FA 9**, **FA 10** and **FA 11**.

FA 8	is a solid sample of a common dioxide of the unknown transition element **W**.
FA 9	is a dilute sulfuric acid, H_2SO_4.
FA 10	is a solid sample of sodium ethanedioate, $Na_2C_2O_4$.
FA 11	is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

Carry out the following experiments. Carefully record your observations. Test for any gases produced.

	Test	Observations
(a)(i)	Transfer all of the solid sample of **FA 10** into a 100 cm^3 beaker. Add 25 cm^3 of **FA 9** to this beaker. Gently heat the beaker until the temperature of the mixture reaches about 60°C. Stir the mixture carefully. Place the beaker on the white tile. Add 2-3 spatulas of **FA 8** to the mixture, stir the mixture carefully with a thermometer and observe any changes in the temperature of the mixture. Filter the mixture into a boiling tube when you think the reaction is complete. Leave the filtrate to stand. The filtrate contains compound **X**. Retain this filtrate for use in **(a)(ii)**.	

46	
47	

(a) **(ii)** You are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of aqueous ammonia, to separate portions of the filtrate from **(a)(i)** and **FA 11**.

In the space below, record the details of the tests performed and the observations made in a suitable table.

48	
49	
50	

(b) Explain how you determined when the reaction is completed in **4(a)(i)**. You should support your answer by referring to your observations.

....

....

51	

(c) **(i)** Consider your observations in **(a)(ii)**.

Identify the transition metal ion formed in **(a)(i)**. Justify your choice by making reference to your observations in **(a)(ii)**.

ion present is ……………………………………

justification ……………………………………

……………………………………

……………………………………

For Examiner's Use

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(ii) In **(a)(i)**, the reaction between **FA 8** and **FA 10** occurs under acidic conditions.

Write a balanced equation for this reaction.

……………………………………

53

(iii) State the role of **FA 8** in the reaction and support your answer by referring to your observations.

……………………………………

……………………………………

……………………………………

54

(d) Deduce the nature of reaction, other than the type of reaction identified in **(c)**, occurring in **(a)(i)**.

Justify by referring to your observations.

……………………………………

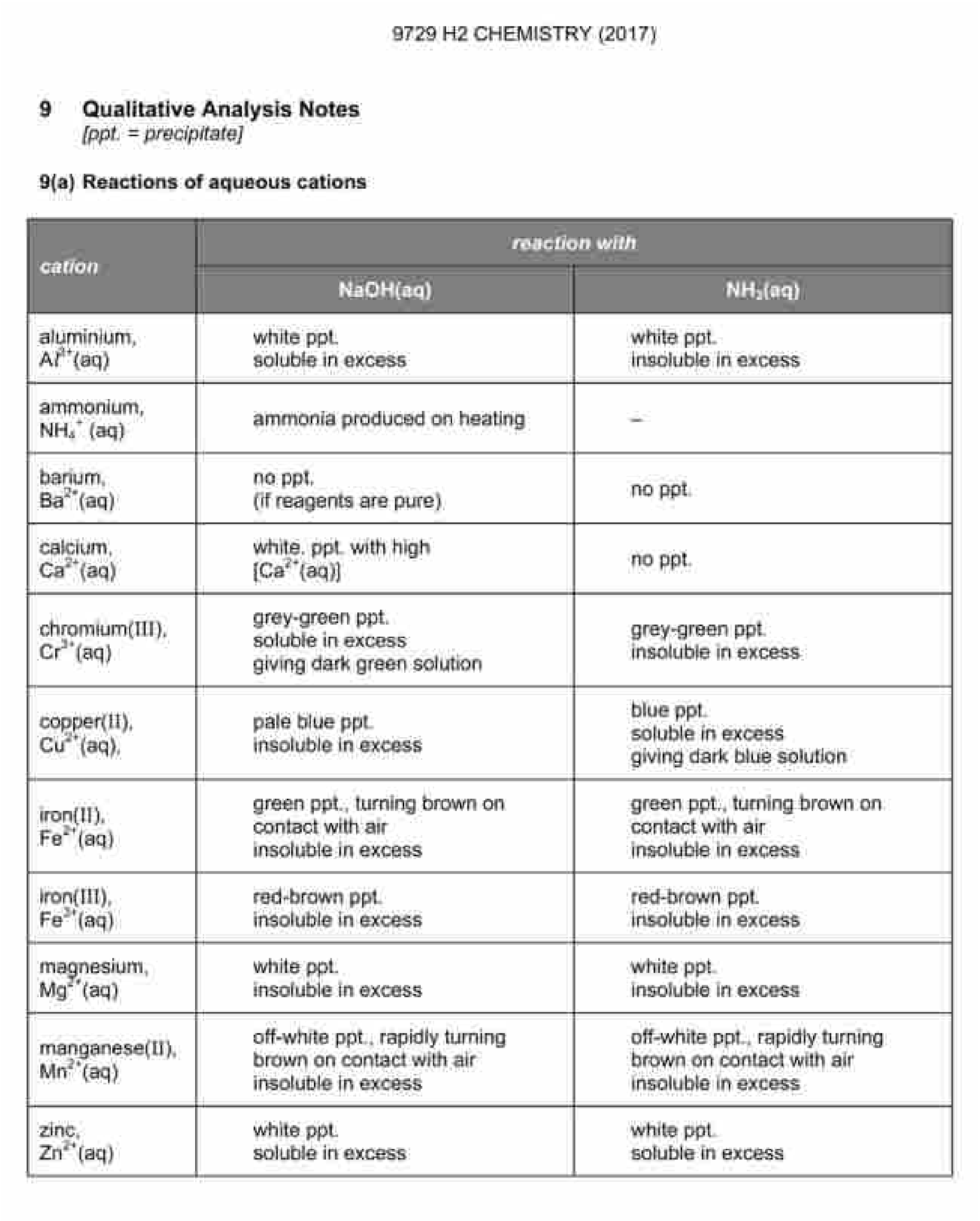
……………………………………

……………………………………

55

[Total: 10]

END OF PAPER



9729 H2 CHEMISTRY (2017)

9 Qualitative Analysis Notes

[ppt. = precipitate]

9(a) Reactions of aqueous cations

cation	*reaction with*	
	$NaOH(aq)$	$NH_3(aq)$
aluminium, $Al^{3+}(aq)$	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, $Ba^{2+}(aq)$	no ppt. (if reagents are pure)	no ppt.
calcium, $Ca^{2+}(aq)$	white. ppt. with high $[Ca^{2+}(aq)]$	no ppt.
chromium(III), $Cr^{3+}(aq)$	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), $Cu^{2+}(aq)$,	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), $Fe^{2+}(aq)$	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), $Fe^{3+}(aq)$	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, $Mg^{2+}(aq)$	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), $Mn^{2+}(aq)$	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, $Zn^{2+}(aq)$	white ppt. soluble in excess	white ppt. soluble in excess

9(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

9(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

9(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

RIVER VALLEY HIGH SCHOOL
YEAR 6 PRACTICAL EXAMINATION II
H2 CHEMISTRY 9729
23 AUGUST 2018

2 HOURS 30 MINUTES

NAME ____________________

CLASS 6 (   )

INDEX NO. ____________________

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a 2B pencil for any diagrams or graph.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer ***all*** *questions in the spaces provided on the Question Paper.*

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Shift
Laboratory

For Examiner's Use	
3 s.f.	
Units	
Total	55

This Question Paper consists of **14** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 To investigate the kinetics of the reaction between iron(III) ions and iodide ions

You will investigate rate of oxidation of iodide by iron(III) ions in **reaction 2**. The chemical changes in this experiment can be presented by the following equations:

Reaction 1: $Fe^{3+}(aq) + S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)]^{+}(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

The reaction is started by mixing acidic solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch. The iodine, I_2, produced in **reaction 2** reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ in **reaction 3**.

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be determined by finding the time for the blue-black colour to appear.

FA 1 is 0.030 mol dm^{-3} iron(III) chloride, $FeCl_3$.

FA 2 is 0.060 mol dm^{-3} potassium iodide, KI.

FA 3 is 0.0060 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

starch indicator

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 4.

You will need to include volume of **FA 1**, volume of water, reaction time and calculated rate of reaction for each of the five experiments. Record all calculated values to 3 significant figures.

(a) Method

Experiment 1

1. Use the measuring cylinders to place the following in a 100 cm^3 beaker.
    - 10 cm^3 of **FA 2**
    - 20 cm^3 of **FA 3**
    - 10 cm^3 of starch indicator
2. Using a measuring cylinder, transfer 20 cm^3 of **FA 1** rapidly into the same 100 cm^3 beaker. Start the stopwatch during this addition.
3. Stir the mixture and place the beaker on a white tile.
4. The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this blue-black colour appears. Record the time to the nearest 0.1 second.
5. Wash the beaker thoroughly with water and carefully dry the beaker.

Experiment 2

6. Repeat step **1** in **Experiment 1**.
7. Using a measuring cylinder, add 12 cm^3 of **FA 1**, and make up the volume to 20 cm^3 using deionised water. Transfer the solution rapidly into the same 100 cm^3 beaker. Start the stopwatch during this addition.
8. Stir the mixture and place the beaker on the white tile.
9. Stop timing when a blue-black colour appears.
10. Wash the beaker thoroughly with water and carefully dry the beaker.

Experiments 3−5

Carry out three further experiments to investigate the effect of changing the concentration of Fe^{3+}(aq) by altering the volume of aqueous $FeCl_3$, **FA 1**, used.

You should use a volume of **FA 1** that is at least 12 cm^3 and the total volume of the reaction mixture must always be 60 cm^3.

(b) Show, by means of calculation, that the change in the concentration of Fe^{3+}, $\Delta[Fe^{3+}]$, which occurred when the blue-black colour appeared was 2.00×10^{-3} mol dm^{-3}.

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$\text{Amount of } S_2O_3{}^{2-} = \frac{20}{1000} \times 0.006 = 1.20 \times 10^{-4}$ mol

$\Delta[Fe^{3+}] = \frac{1.20\times10^{-4}}{\frac{60}{1000}} = 2.00 \times 10^{-3}$ mol dm^{-3}

1	

(c) Results

The rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{\Delta[\text{Fe}^{3+}]}{\text{reaction time}} \times 10^6$$

Calculate the rate of reaction for each experiment and complete your table.

Expt	V_{FA1}/ cm^3	V_{H_2O} /cm^3	Reaction time, ***t*** /s	Rate/ mol dm^{-3} s^{-1}
1	20.00	0.00	12.9	155
2	12.00	8.00	28.8	69.4
3	14.00	6.00	20.7	96.6
4	16.00	4.00	17.3	115
5	18.00	2.00	14.7	136

2	
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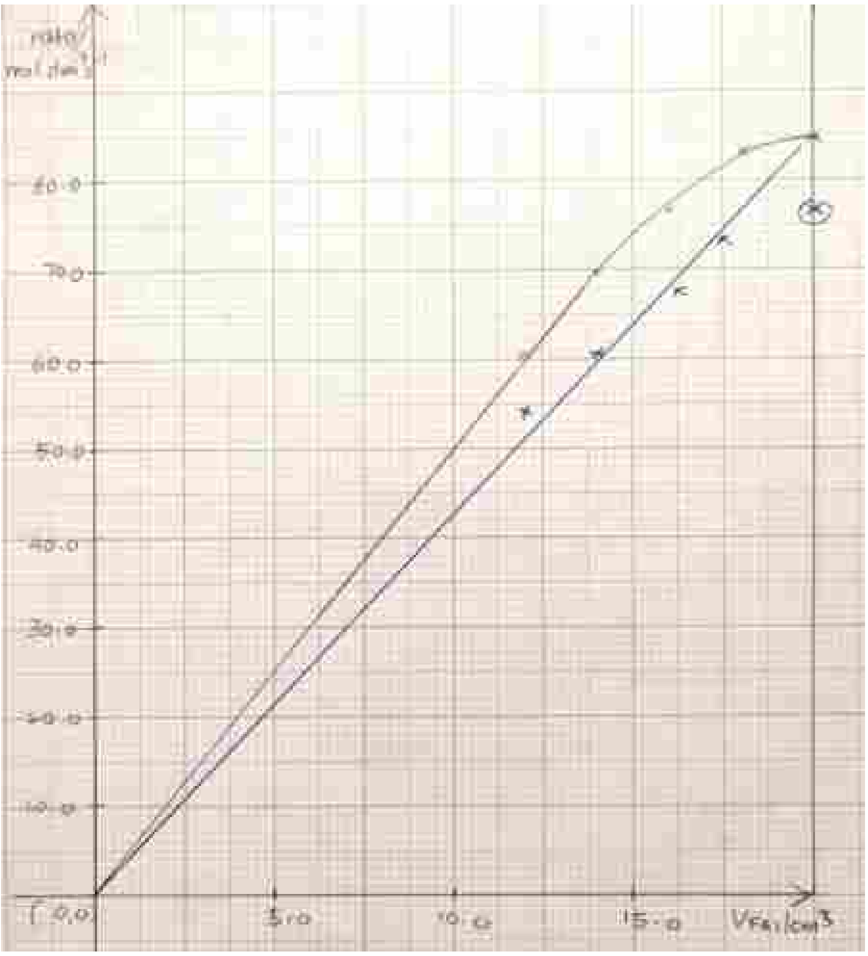
(d) (i) Plot the rate (y-axis) against the volume of **FA 1** (x-axis) on the grid. Draw a line of best fit through the points.

Your chosen scales should allow you to extrapolate this line to volume of **FA 1** = 0 cm^3.

You should also identify any points you consider anomalous by drawing a circle around it.



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(ii) Explain why the volume of **FA 1** in each experiment can be used as the [Fe^{3+}].

Since total volume is kept constant by adding deionised water, volume of **FA 1** used is proportional to [Fe^{3+}].

9	

(iii) Deduce the order of reaction with respect to Fe^{3+}. Use evidence from your graph to support your deduction.

✓ Observe from the graph, any one of the following:
- the rate increase by xxx for every additional xxx cm³ of **FA 1** used
- when volume of **FA 1** double, rate double (or other multiples)
- the graph is linear/gradient is a constant, showing that rate ∝ volume/ concentration of **FA 1** / state that it is a graph of rate against [Fe^{3+}]

✓ Therefore, the reaction is first order with respect to Fe^{3+}.

10	

(e) **(i)** Use your graph to calculate the time that the reaction would have taken if 4.0 cm^3 of **FA 1** had been used. Show your working clearly.

If 4.0 cm^3 of **FA 1** is used, rate = xxx mol dm^{-3} s^{-1}
Time = $\Delta[Fe^{3+}] \times 10^6$/ rate = xxx s (to 3 sf or nearest seconds).

time = ...

11	

(ii) Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions if 4.0 cm^3 of **FA 1** had been used.

$[Fe^{3+}] = \frac{0.030\times4.0}{60.0}$ = 0.00200 mol dm^{-3}

$[I^-] = \frac{0.060\times10.0}{60.0}$ = 0.0100 mol dm^{-3}

initial $[Fe^{3+}]$ = ...

initial $[I^-]$ = ...

12	

(iii) Given that the reaction is second order with respect to iodide, calculate the rate constant.

rate = $k[Fe^{3+}][I^-]^2$

$k = \frac{rate}{[Fe^{3+}][I^-]^2}$ = xxx mol^{-2} dm^6 s^{-1}

rate constant = ...

13	

(f) The complex $[Fe(S_2O_3)]^+$ formed in **reaction 1** is purple.

Consider the colour change observed when **FA 1** was added to the solution prepared in **Step 1** before the blue-black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved.

The brown solution is due to a mixture of purple complex $[Fe(S_2O_3)]^+$ and orange-brown Fe^{3+}(aq).

Since the I_2 formed reacted immediately with thiosulfate, $[S_2O_3^{2-}(aq)]$ decreased, and the position of equilibrium in (1) shifts left.

Thus, concentration of $[Fe(S_2O_3)]^+$decreased. Hence, the colour of the solution gradually fades/ until the solution became pale yellow due to Fe^{3+}.

14	
15	

[Total: 15]

2 Determining the percentage purity of calcium carbonate.

In this question, you will determine the percentage purity of an industrial grade calcium carbonate, $CaCO_3$, by two different methods.

(a) Method 1

The percentage purity of calcium carbonate can be determined by measuring the change in mass when the sample of calcium carbonate reacts with hydrochloric acid.

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

FA 4 is industrial grade calcium carbonate, $CaCO_3$.

FA 5 is 2.00 mol dm^{-3} dilute hydrochloric acid.

You do not need to carry out **Method 1**.

Procedure:

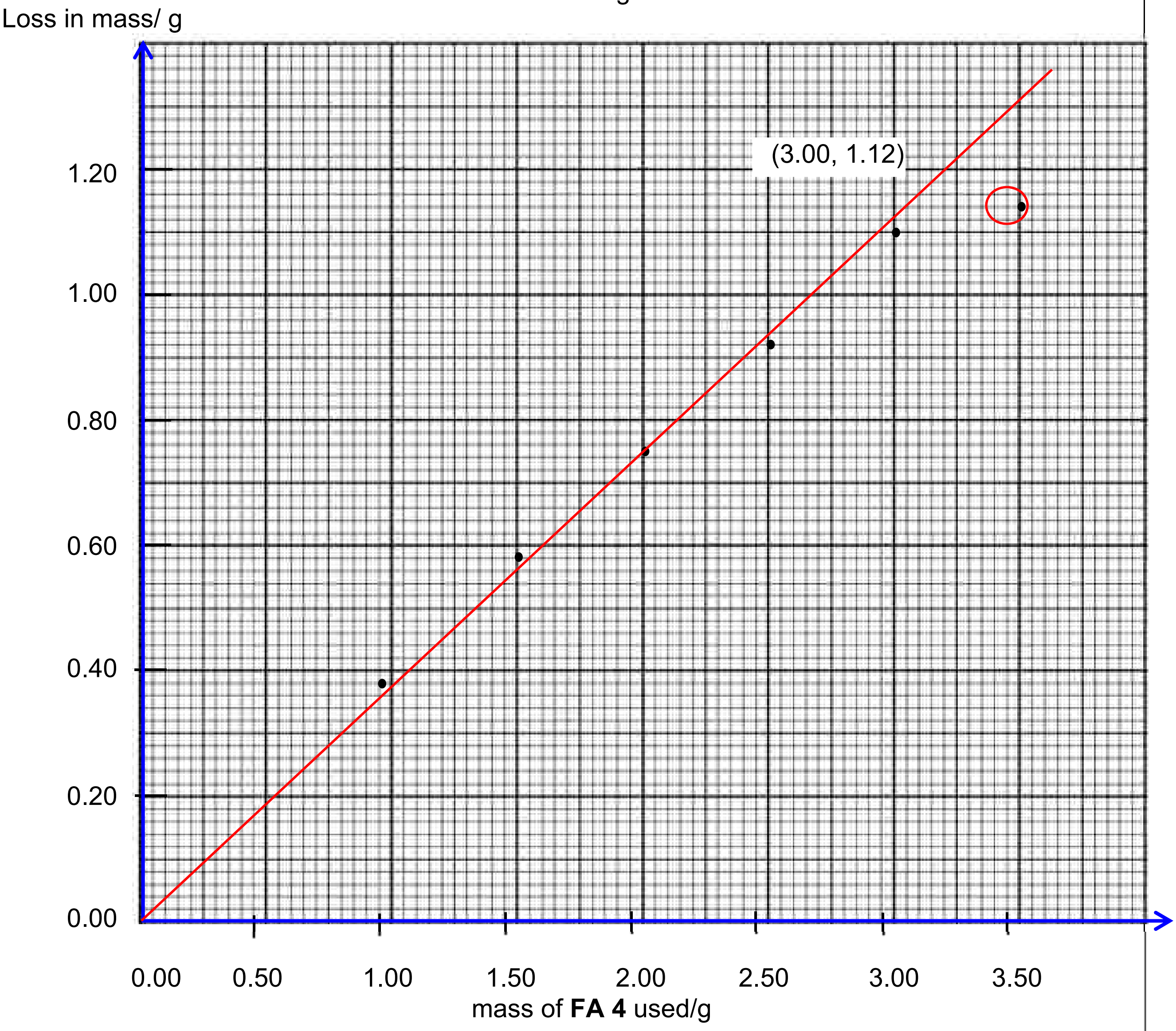
1. Weigh accurately about 2.0 g of **FA 4** in a small weighing bottle.
2. Weigh accurately about 25 cm^3 of **FA 5** in a small conical flask.
3. Add **FA 4** to **FA 5** and swirl the mixture continuously until no more bubbles is observed.
4. Reweigh the weighing bottle with its residual **FA 4**.
5. Reweigh the conical flask and its content.

A student performed a series of experiments by repeating the above procedure with different masses of **FA 4**.

The results from her series of experiment are plotted on the grid in Fig 2.1.

Identify the anomalous data point by drawing a circle around it. Draw the most appropriate best-fit line taking into account all of the plotted points, except for the anomaly. Extrapolate (extend) this line to the mass of **FA 4** used = 0.00 g.

Fig 2.1.



16	

Calculations

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(b) **(i)** Determine the gradient of this line, showing clearly how you did this.

Hence, determine the mass of carbon dioxide evolved per gram of **FA 4** used.

gradient = $\frac{1.12-0.00}{3.00-0.00}$ =0.3733

mass lost = mass of carbon dioxide evolved

= 0.3733 g per gram of **FA 4** used

mass of carbon dioxide evolved = 0.3733 g ....

17	
18	

(ii) Using your answer in **b(i)**, calculate a value for the percentage purity of the sample of industrial grade calcium carbonate, **FA 4**.

[A_r: Ca, 40.1; C, 12.0; O,16.0]

For every gram of **FA 4** used:

Amount of CO_2 evolved = $\frac{0.3733}{44}$ = 0.008484 mol

= amount of $CaCO_3$

Mass of $CaCO_3$ = 0.008484 × 100.1 = 0.8492

percentage purity of **FA 4** = $\frac{0.8492}{1.00} \times 100\%$ = 84.9 %

percentage purity of **FA 4** = ...

19	

(c) **Method 2**

You will determine the amount of hydrochloric acid remaining in flask **X** after the reaction with another sample of industrial grade calcium carbonate. You will do this by titration with sodium hydroxide of known concentration.

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

FA 6 is 0.140 mol dm^{-3} sodium hydroxide, NaOH.

Thymolphthalein indicator

Procedure:

1. Pipette 25.0 cm^3 of **FA 5** into flask **X**.
2. Weigh accurately about 0.6 g of **FA 4** in a dry weighing bottle.
3. Add the **FA 4** into flask **X**.
4. Reweigh the weighing bottle with its residual **FA 4**.
5. Swirl the mixture until no more bubbles are observed.
6. Transfer **all** the contents of flask **X** and the washings into a 250 cm^3 volumetric flask.
7. Add deionised water up to the mark, stopper the volumetric flask and mix the contents thoroughly. Label this solution **FA 7**.

8. Fill the burette with **FA 6**.
9. Wash and rinse the pipette then use it to transfer 25.0 cm^3 of **FA 7** into a conical flask.
10. Add about 5 drops of thymolphthalein indicator.
11. Titrate **FA 7** with **FA 6**.
12. Repeat the titration as many times as you think necessary to obtain consistent results.
13. Record in the space below, all of your mass readings, burette readings and the volume of **FA 6** added.

Results

Mass of weighing bottle and **FA 4**/ g	4.433
Mass of weighing bottle and residual **FA 4**/g Or Mass of weighing bottle and residue/g	3.823
Mass of **FA 4** used/ g	0.610

Titration number	1	2
Final burette reading /cm^3	29.30	29.30
Initial burette reading /cm^3	0.00	0.00
Volume of **FA 6** (used) /cm^3	29.30	29.25

20	
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25	

Supervisor expected titre
28.53
Student expected titre
Difference

(d) From your accurate titration results, obtain a suitable value for the volume of **FA 6** to be used in your calculations. Show clearly how you obtained this value.

$$\frac{29.30 + 29.25}{2} = 29.28\ cm^3$$

Volume of **FA 6** used = ………………

26	

For Examiner's Use

Calculations

(e) **(i)** Calculate the number of moles of sodium hydroxide, NaOH, present in volume of **FA 6** calculated in **(d)**.

amount of NaOH in titre = $\frac{titre}{1000} \times 0.140$ = _________ mol

amount of NaOH = ...

27

(ii) Calculate the number of moles of hydrochloric acid remaining in flask **X** after the reaction with **FA 4** has completed.

amount of NaOH in titre = amount of HC*l* in 25.0cm^3 **FA 7**

amount of HC*l* remaining in flask **X**

= amount of HC*l* in 250 cm^3 of **FA 7**

= $\frac{titre}{1000} \times 0.140 \times \frac{250}{25.0}$

amount of HC*l* remaining in flask **X** = ...

28

(iii) Calculate the number of moles of hydrochloric acid that reacted with the **FA 4** used.

Total amount of HC*l* used = 2.00 × 0.0250 = 0.0500 mol

Amount of HC*l* reacted = 0.0500 – ($\frac{titre}{1000} \times 0.140 \times \frac{250}{25.0}$)

amount of HC*l* reacted = ...

29

(vi) Calculate the mass of $CaCO_3$ in the sample of **FA 4** used, and hence the percentage purity of the industrial grade $CaCO_3$.

[Ar: Ca, 40.1; C, 12.0; O,16.0]

Mass of $CaCO_3$ in the sample = $\frac{n_{HCl\,reacted}}{2} \times 100.1$

Percentage purity = $\frac{mass\ of\ CaCO_3 in\ the\ sample}{mass\ of\ sample\ used} \times 100\%$

percentage purity of the industrial grade $CaCO_3$ = ...

30

(f) The two different methods were used to find the percentage purity of industrial grade calcium carbonate.

It is found that the samples of **FA 4** used contain calcium oxide which reacts with dilute hydrochloric acid.

How would this affect the percentage purity calculated for each method? Explain your answers.

Method 1: Percentage purity of **FA 4** calculated is not affected.

Reaction of calcium oxide with hydrochloric acid does not result in loss in mass/ does not produce any gases.

Method 2: Percentage purity of **FA 4** calculated is higher than expected.

Less HC*l* is left after reaction with sample. Based on the lower titre obtained/ less NaOH is needed to react with the remaining HC*l* , a greater amount of $CaCO_3$ is calculated to be present.

31	
32	

(g) Explain why sulfuric acid cannot be used in both methods.

The insoluble $CaSO_4$/ salt formed coats the calcium carbonate particles, which results in incomplete reaction/ owtte.

33	

(h) Planning

Unlike the acid-base titration in **Part (c)** that uses acid-base indicator to determine the end-point, thermometric titration uses heat evolved or temperature change of solution to determine the end-point of the reaction. In thermometric titration, the titre value can be determined from the graph of energy evolved against volume of titrant (solution from the burette) added.

Since a neutralisation reaction is exothermic, thermometric titration can be used to determine the amount of excess hydrochloric acid in flask **X** from **Part (c)**.

(i) Given that the concentration of undiluted excess hydrochloric acid in flask **X** is about 1.7 mol dm^{-3}, and the desired titre is around 24 cm^3, calculate the concentration of sodium hydroxide required for the thermometric titration.

[NaOH] = $\frac{0.025\times1.7}{0.024}$ = 1.77 mol dm^{-3}

34	

(ii) You are to plan a thermometric titration to determine the concentration of hydrochloric acid. The experimental results obtained should allow the titre value to be determined graphically.

You may assume that you are provided with

- 50 cm^3 of hydrochloric acid, HC*l*, of concentration around 1.7 mol dm^{-3}
- standard solution of sodium hydroxide solution, NaOH, of the same concentration calculated in **(h)(i)**
- apparatus commonly found in a school or college laboratory

In your plan you should include the following:

- a diagram of the apparatus set-up that may be used
- the procedure that you would follow and the measurement you would take
- the precautions and measures that you would take to minimise heat loss to the surroundings

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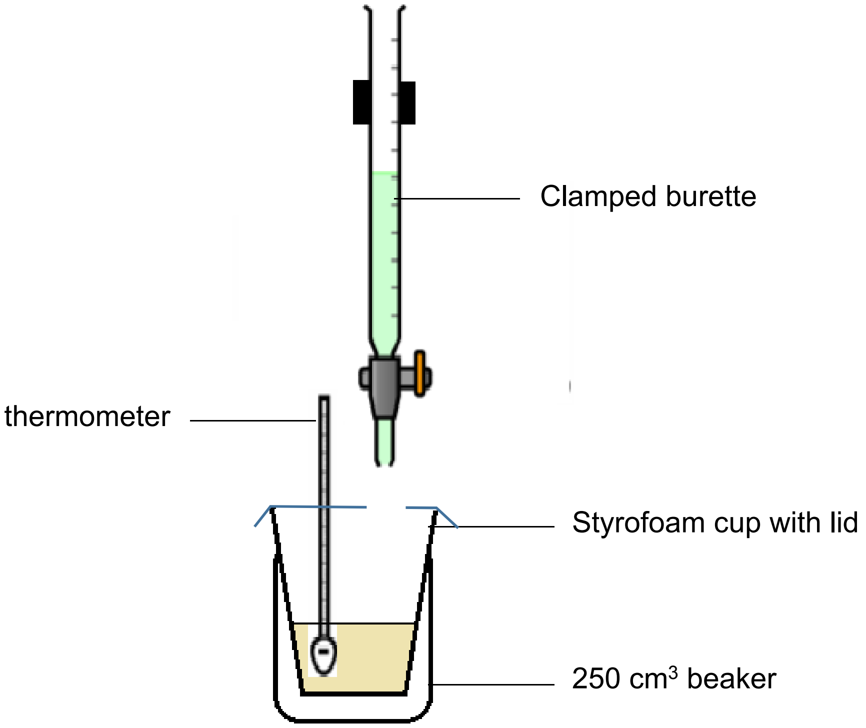


Procedure

1. Set up the apparatus as shown in the diagram and fill the burette with 1.77 mol dm^{-3} aqueous NaOH.
2. Using a burette/pipette, transfer 25.0 cm^3 of the HC*l* solution into the styrofoam cup, and measure its initial temperature.
3. Using the burette, add 5.00 cm^3 of NaOH solution to the HC*l* solution in the cup. Stir by swirling the cup/ stir using the thermometer and measure the highest temperature reached.
4. Immediately add another 5.00 cm^3 of the NaOH solution, stir, and again measure the highest temperature.
5. Repeat step 4 until the total volume of NaOH added is 45.00 cm^3.

Precaution: This experiment should be carried out in a draught-free room with the fans switched off.

(iii) Your procedure in **(h)(ii)** should allow the graph of total energy evolved against volume of titrant to be plotted. Briefly describe how you would use the results obtained to determine the total energy evolved since the start of the experiment for each data point.

Energy evolved = $mc\Delta T$

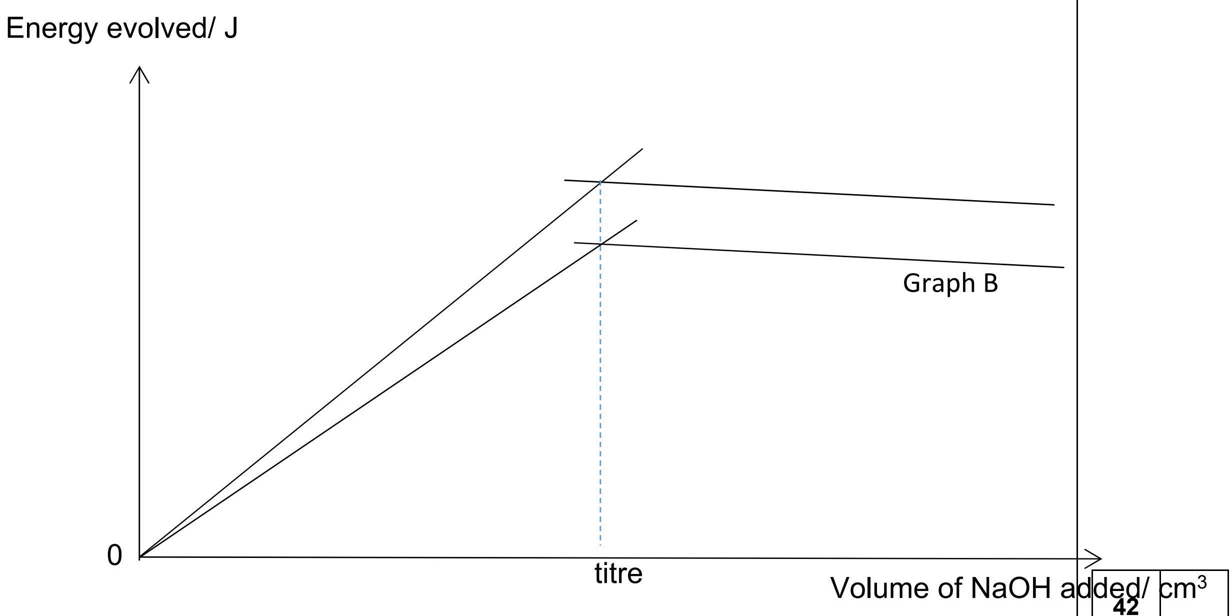
Where m = (Volume of HC*l* + total volume of NaOH added/ total volume of reaction mixture) × density , c = specific heat capacity of the solution/ 4.18 $Jg^{-1}K^{-1}$, ΔT = highest temperature – initial temperature of HC*l* in step x.

41

(iv) Sketch, on the axes in Fig. 2.2, the graph you would expect to obtain and show how you would use this graph to determine the titre value.

Explain the shape of your graph.

Fig. 2.2



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Explanation:

As NaOH is added, more neutralisation occurs which evolves more heat. The total amount of heat evolved reaches maximum at the equivalence point when all HC*l* just reacted. Past equivalence point, the graph is horizontal because no more heat is evolved/Graph is downward sloping due to heat lost to the surroundings'.

(v) Sketch, on the same axes in Fig. 2.2, the graph you would expect to obtain if aqueous ammonia of the same concentration as aqueous NaOH is used as the titrant instead.

Label this graph clearly as **Graph B**.

Explain the shape of **Graph B**.

Graph B

Ammonia is a **weak base** which dissociates partially to produce OH^-.

Heat is absorbed to **complete the dissociation/ break the O-H in water** to produce OH^-**.** Thus, the reaction is **less exothermic/ less energy is evolved.**

44	
45	

3 Inorganic qualitative analysis

In this experiment you are to explore the chemistry of some compounds of an unknown transition element **W**. You are provided with 4 samples, **FA 8**, **FA 9**, **FA 10** and **FA 11**.

FA 8	is a solid sample of a common dioxide of the unknown transition element **W**.
FA 9	is a dilute sulfuric acid, H_2SO_4.
FA 10	is a solid sample of sodium ethanedioate, $Na_2C_2O_4$.
FA 11	is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

Carry out the following experiments. Carefully record your observations. Test any gases produced.

	test	observations
(a)(i)	Transfer all of the solid sample of **FA 10** into a 100 cm^3 beaker. Add 25 cm^3 of **FA 9** to this beaker. Gently heat the beaker until the temperature of the mixture reaches about 60°C. Stir the mixture carefully. Place the beaker on the white tile. Add 2 – 3 spatula of **FA 8** to the mixture, stir the mixture carefully with thermometer and observe any changes in the temperature of the mixture. Filter the mixture into a boiling tube when you think that the reaction is completed. Leave the filtrate to stand. The filtrate contains compound **X**. Retain this filtrate for use **(a)(ii)**.	White solid ($Na_2C_2O_4$) dissolves to give a colourless solution. [accept: partially dissolves] Effervescence/ bubbles after addition (not gas evolved) Colourless, odourless gas gave white ppt with limewater Temperature of mixture rises (even though no heat is applied) Temperature rise stops/ temperature falls/ mixture starts to cool as the effervescence much less vigorous (Pale pink) filtrate turns yellow-green/pale yellow/pale orange

46	
47	

(a) **(ii)** You are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of aqueous ammonia, to separate portions of the filtrate from **(a)(i)** and **FA 11**.

In the space below, record the details of the tests performed and the observations made in a suitable table.

	Add sodium hydroxide, dropwise with shaking, followed by in excess, to separate samples.	Add aqueous ammonia, dropwise with shaking, followed by in excess, to separate samples.
Filtrate from **(a)(ii)**	(Light) brown precipitates insoluble in excess *ppt darken (on standing)	(Light) brown precipitates insoluble in excess *ppt darken (on standing)
FA 11	Off-white/ very light brown precipitates insoluble in excess *ppt darken (on standing)	Off-white/ very light brown precipitates insoluble in excess *ppt darken (on standing)

48	
49	
50	

(b) Explain how you determined when the reaction is completed in **4(a)(i)**. You should support your answer by referring to your observations.

Cessation of effervescence/ bubbles (on addition of more **FA 8**)

or

temperature stops rising/ starts to fall (on addition of more **FA 8**)

51	

(c) **(i)** Consider your observations in **(a)(ii)**.

Identify the transition metal ion formed in **(a)(i)**. Justify your choice by reference to your observations in **(a)(ii)**.

ion present is Mn^{2+}

justification off-white ppt, $Mn(OH)_2$, formed with both NaOH and NH_3 which are insoluble in excess and darkens/turned darker brown on standing.

52	

(ii) In **(a)(i)**, the reaction between **FA 8** and **FA 10** occurs under acidic conditions.

Write a balanced equation for this reaction.

$\mathbf{MnO_2} + 4H^+ + C_2O_4^{2-} \rightarrow \mathbf{Mn^{2+}} + 2H_2O + 2CO_2$

53	

(iii) State the role of **FA 8** in the reaction and support your answer by referring to your observations.

FA 8 is an oxidising agent. Colourless, odourless gas evolved gave white ppt in limewater showed that CO_2 was evolved because $C_2O_4^{2-}$ was oxidised/ Dark grey/ black MnO_2 solid is reduced to pale pink Mn^{2+} ions.

54	

(d) Deduce the nature of reaction, other than the type of reaction identified in **(c)**, occurring in **(a)(i)**.

Justify by referring to your observations.

The reaction is exothermic. The temperature increased, without further heating, as **FA 8** was added.

Accept neutralisation between MnO_2 and H_2SO_4 with correct evidence and conclusion.

55	

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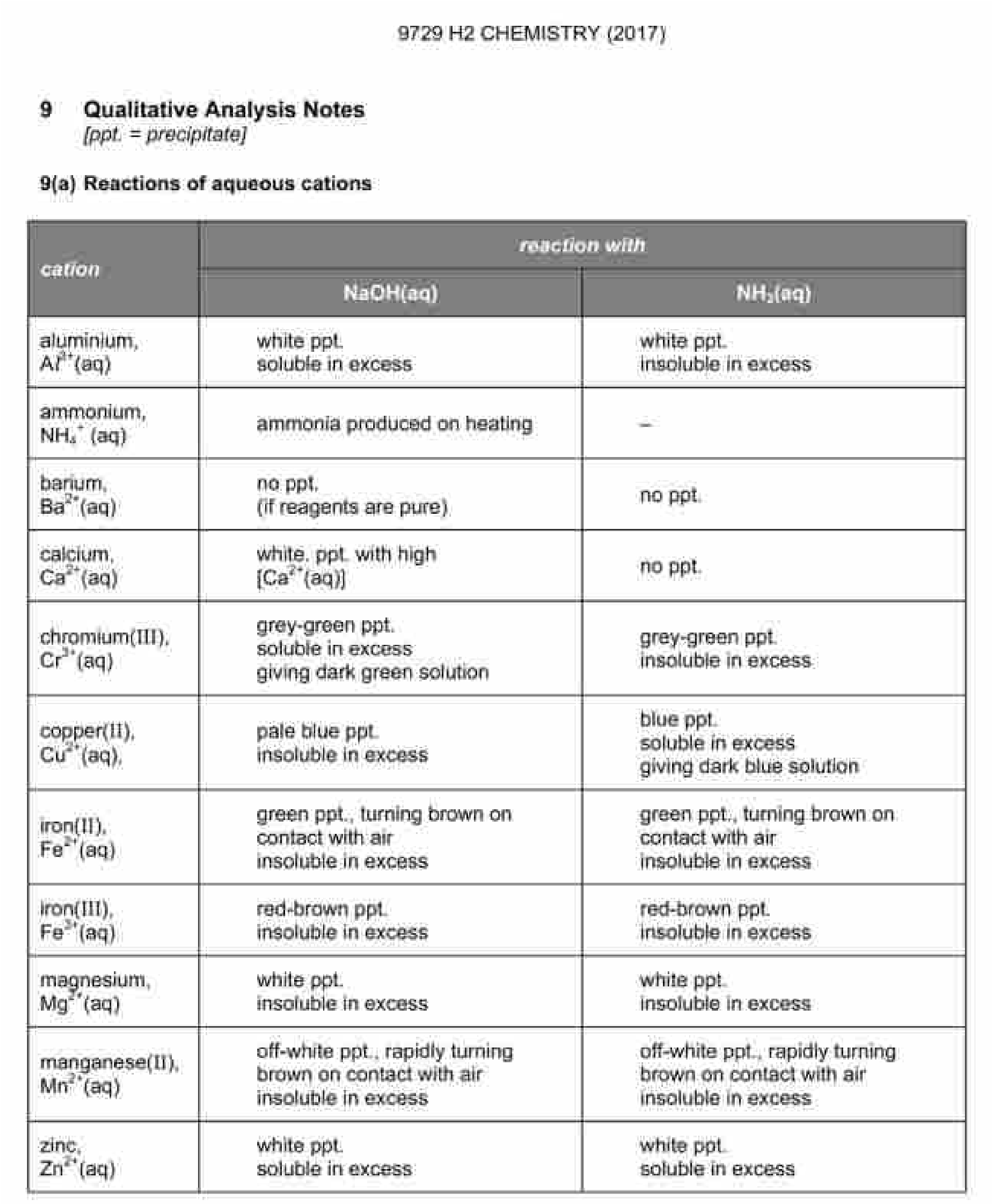


9729 H2 CHEMISTRY (2017)

9 Qualitative Analysis Notes

[ppt. = precipitate]

9(a) Reactions of aqueous cations

cation	*reaction with*	
	$NaOH(aq)$	$NH_3(aq)$
aluminium, $Al^{3+}(aq)$	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, $Ba^{2+}(aq)$	no ppt. (if reagents are pure)	no ppt.
calcium, $Ca^{2+}(aq)$	white. ppt. with high $[Ca^{2+}(aq)]$	no ppt.
chromium(III), $Cr^{3+}(aq)$	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), $Cu^{2+}(aq)$,	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), $Fe^{2+}(aq)$	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), $Fe^{3+}(aq)$	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, $Mg^{2+}(aq)$	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), $Mn^{2+}(aq)$	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, $Zn^{2+}(aq)$	white ppt. soluble in excess	white ppt. soluble in excess

9(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

9(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

9(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 Year 6 Chemistry Practical Examination 2

List of Chemical

Question 1			
Description	*Label (if any)*	*Quantity per student*	*Remarks*
0.030 mol dm^{-3} acidified iron(III) chloride Dissolve 8.11 g of $FeCl_3.6H_2O$ [C] in each dm^3 of 0.20 mol dm^{-3} hydrochloric acid. 0.20 mol dm^{-3} hydrochloric acid made by diluting 2.0 mol dm^{-3} hydrochloric acid **[H]** (preparation instructions on page 63 of the 2015 syllabus) 10-fold.	**FA 1**	150 cm^3	1 bottle per student; to be placed on each student bench.
0.060 mol dm^{-3} potassium iodide Dissolve 9.96 g of KI in each dm^3 of solution.	**FA 2**	80 cm^3	
0.0060 mol dm^{-3} sodium thiosulfate Dissolve 29.78 g of $Na_2S_2O_3.5H_2O$ in each dm^3 of solution. Dilute this solution 20-fold.	**FA 3**	150 cm^3	
20 g dm^{-3} starch solution	**Starch indicator**	80 cm^3	

The time *t* should be in the range 15 to 20s for experiment 1.

Question 2			
Description	*Label (if any)*	*Quantity per student*	*Remarks*
Powdered anhydrous $CaCO_3$ (fresh chemicals should be used, chemicals after packed in small bottle should be kept air-tight.)	**FA 4**	About 1 gram, cap in a small weighing bottle.	1 bottle per student; to be placed on each student bench.
2.00 mol dm^{-3} hydrochloric acid, HCl	**FA 5**	70 cm^3	

0.130 mol dm^{-3} sodium hydroxide, NaOH (labelled as 0.140M in the qn paper)	**FA 6**	150 cm^3	
Thymolphthalein indicator *Freshly prepared 0.04 g **thymolphthalein** in 50 mL of 95% ethanol. Dilute this **solution** to 100 mL with distilled water.	**thymolphthalein**	5 cm^3	

Question 3			
Description	*Label (if any)*	*Quantity per student*	*Remarks*
manganese(IV) oxide, MnO_2, in a capped small bottle	**FA 8**	6 g	1 set per student; to be placed on each student bench.
approximately 0.5 mol dm^{-3} sulfuric acid, H_2SO_4	**FA 9**	40 cm^3	
sodium ethanedioate, $Na_2C_2O_4$, in a capped small bottle	**FA 10**	2.8 g	
approximately 0.2 mol dm^{-3} manganese(II) sulfate, $MnSO_4$, made by dissolving, in deionised water, about 84.5 g of $MnSO_4$.H2O in each dm^3 of solution. This solution must be stored in a capped bottle	**FA 11**	20 cm^3	

Others

Bench reagents			1 bottle per student; to be placed on each student bench. *Top up NaOH(aq), NH_3(aq), limewater after each shift
Deionised water	-	1 large bottle	Each student requires about 500 cm^3, so they will top up at least once during the examination.

List of Apparatus

Description	*Quantity*	*Remarks*
100 cm^3 conical flask, labelled **X**	1	
Burette	1	Clamped with retort stand. To check the tips and replaced if chipped.
Pipette 25.0 cm^3	1	
Filter funnel	2	
250 cm^3 volumetric flask	1	
250 cm^3 conical flask	2	
Pipette filler	1	
White tile	1	
25 cm^3 measuring cylinder	2	
10 cm^3 measuring cylinder	2	
Alcohol thermometer graduated to 0.5°C	1	
Ignitor	1	
Tripod stand + wire gauze	1	
Test-tube rack + test tube holder + 1 large and 1 small brushes	1	
Boiling tube	1	
large test-tube	5	
Small test-tube	3	
Delivery tube	1	
stopwatch	1	
100 cm^3 beaker	2	
plastic teat pipettes	8	
Small spatula	1	
Glass rod	1	
Paper towel	6	
Round filter paper	2	To be placed in small ziplock bag
red, blue litmus paper strips	4 each	
Electronic weighing balance	See remarks	5/6 per lab; 1 waste beaker beside each balance
Small weighing bottle with cap	1	
Permanent marker	1	
Bunsen burner	1	

Note: Place the following on the Teacher's Bench

- 6 additional sets of apparatus
- 10 additional sets of chemicals

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **17 September 2018**

Paper 1 Multiple Choice **1 hour**

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

READ THESE INSTRUCTIONS:

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages.

1 To identify an oxide of nitrogen, the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2\,(g)} x\,NH_3 + y\,H_2O$$

The water collected weighs 0.133 g. The ammonia produced is neutralised by 18.50 cm^3 of 0.2 mol dm^{-3} HC*l*.

Which of the following could be the oxide?

1 N_2O

2 NO_2

3 NO_3

4 N_2O_4

A 3 only

B 1 and 2 only

C 2 and 3 only

D 2 and 4 only

2 This question is about sparingly soluble salts.

	AgC*l*	**AgI**	**HgI_2**
K_{sp}	1.0×10^{-10}	8.3×10^{-16}	1.1×10^{-21}

From the above information, which statements are **not** true?

A For a solution containing 1 mol dm^{-3} of NaC*l* and NaI, the concentration of chloride ions when AgI just starts to precipitate is 1 mol dm^{-3}.

B The solubility of HgI_2 is 6.50×10^{-8} mol dm^{-3}.

C The solubility of HgI_2 is the lowest.

D The units for K_{sp} for HgI_2 is $mol^3\,dm^{-9}$.

3 The following tests were performed on an aqueous solution containing bromide and iodide ions.

Step	**Test**	**Observations**
1	Add excess $AgNO_3$(aq).	A mixture of cream and yellow precipitate were formed.
2	To the mixture from step 1, add concentrated NH_3.	The cream precipitate dissolved to form a colourless solution. The yellow precipitate was insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.
4	Add Cl_2(aq) to filtrate.	Brown solution is formed.

Which of the following statements is correct?

A In step 2, the cream precipitate dissolved because the addition of concentrated NH_3 results in formation of a complex which decreases the K_{sp} of AgBr.

B In step 2, the yellow precipitate was insoluble because the K_{sp} of AgI is higher than the K_{sp} of AgBr.

C In step 2, the yellow precipitate was insoluble because the ionic product of AgI is higher than the K_{sp} of AgI.

D In step 4, a disproportionation reaction has taken place.

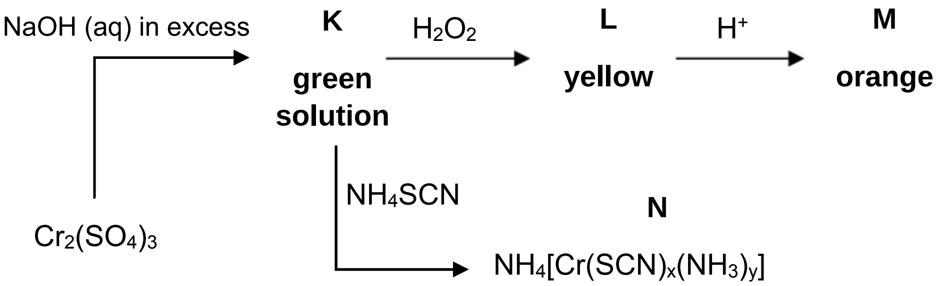
4 A stable ion of **Q** has the following properties:

- has a noble gas configuration
- has more protons than electrons
- was obtained by removing electrons from the same orbital

Which of the following could be **Q**?

A Al **B** Ca **C** Cu **D** S

5 Chromium and its compounds undergo the following reactions.



N has the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%.

Which of the following can be deduced from the above reaction scheme?

A The values of x and y in **N** are 4 and 2 respectively.

B The types of reactions that occur are ligand exchange and redox only.

C The formula of **K** is $Cr(OH)_2(H_2O)_6$.

D H_2O_2 is a reducing agent in the conversion of **K** to **L**.

6 Which one of the following statements about Group 2 elements and their compounds is correct?

A Beryllium chloride has a higher boiling point than magnesium chloride as it has a more exothermic lattice energy than magnesium chloride.

B The reducing power of Group 2 elements increases down the group.

C 1 mole of barium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate.

D Barium has a higher melting point than magnesium due to more electrons.

7 Liquefaction can be defined as a process that generates a liquid from a gas and this can be done by altering pressure. In the liquefaction of CH_4 and NH_3, the pressure needed for NH_3 is less than CH_4.

Which of the following reasons best explains this observation?

A NH_3 has stronger intermolecular forces of attraction than CH_4.

B NH_3 has weaker bond energy than CH_4.

C NH_3 molecules are bigger than CH_4 molecules.

D NH_3 molecules possess less kinetic energy than CH_4 molecules.

8 Phosphate buffers are commonly used in biological chemistry research.

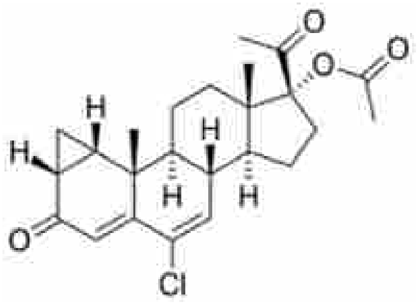
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 6.7$$

A phosphate buffer with pH 7.4 was prepared using NaH_2PO_4 and Na_2HPO_4 solutions. The total hydrogen phosphates concentration ($[HPO_4^{2-}] + [H_2PO_4^-]$) of the buffer was 0.3 mol dm^{-3}.

What are the concentrations of NaH_2PO_4 and Na_2HPO_4 used to create this buffer?

	$[NaH_2PO_4]$ / mol dm^{-3}	**$[Na_2HPO_4]$ / mol dm^{-3}**
A	0.23	0.07
B	0.07	0.23
C	0.10	0.50
D	0.05	0.25

9 Cyproterone acetate (CPA) is a drug that is used in the treatment of prostate cancer.



CPA

Which of the following statements about CPA are incorrect?

1 One mole of silver is formed when one mole of CPA is warmed with $[Ag(NH_3)_2]^+$.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 One mole of silver chloride is formed when one mole of CPA is heated with ethanolic silver nitrate.

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

10 Consider the following equilibrium:

$$2Q_2\,(g) + R_2\,(g) \rightleftharpoons 2Q_2R(g)$$

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

11 *Use of the Data Booklet is relevant to this question.*

Iodine clock reaction can be used to study how the concentration of iodide ions affect the rate of oxidation of iodide ions with peroxodisulfate ions. Peroxodisulfate ions convert iodide ions into iodine slowly.

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

The rate of the reaction can be increased by the addition of catalysts such as aqueous iron (III) ions.

A possible catalysed reaction pathway involves the following steps:

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Step 2: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Which of the following statements are **correct**?

1 Aqueous cobalt(II) ions can be used as a catalyst in this reaction.

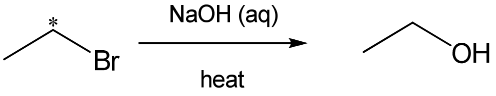
2 $S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+}.

3 The $E_{cell}^{\ominus}$ for step 2 is more positive than step 1.

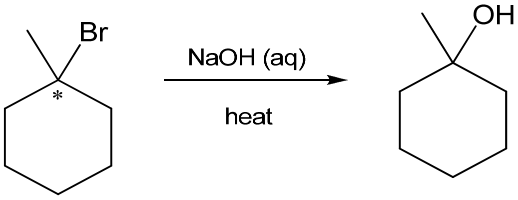
A 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

12 Which of the following reactions has no change in the hybridisation state of the carbon atom indicated with an asterisk (*) from the reactant to the **intermediate** in the mechanism?

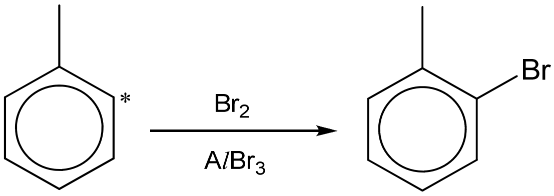
A



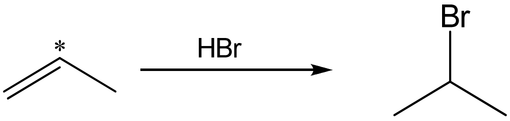
B



C



D



13 What is the volume of vapour formed when 10 cm^3 of liquid ethanol (density: 0.789 g cm^{-3}) is heated to 300 °C at a pressure of 5 bar?

A 85.5 cm^3

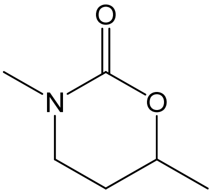
B 855 cm^3

C 163.3 cm^3

D 1633 cm^3

14 Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?

1



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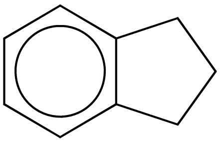

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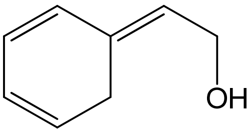


A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3

D None of the above

15 Trifluorooxonium has the formula OF_3^{n+} and its shape is trigonal pyramidal.

What is the value of *n* in trifluorooxonium?

A 1 **B** 2 **C** 3 **D** 4

16 *Use of the Data Booklet is relevant to this question.*

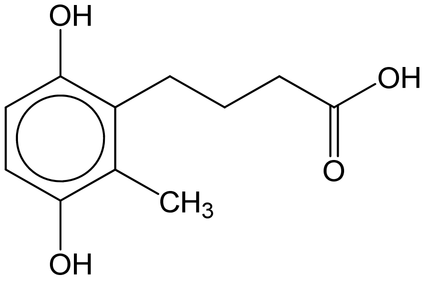
Which set of reagents, when added in the order shown below, would convert $Fe^{3+}(aq)$ to $[Fe(CN)_6]^{3-}(aq)$?

$$Fe^{3+}(aq) \xrightarrow{\text{step 1}} Fe^{2+}(aq) \xrightarrow{\text{step 2}} \mathbf{X} \xrightarrow{\text{step 3}} [Fe(CN)_6]^{3-}(aq)$$

	step 1	step 2	step 3
A	Zn(s)	$CN^-(aq)$	$SO_2(g)$
B	$I^-(aq)$	$CN^-(aq)$	$Cl_2(g)$
C	$H_2O_2(aq)$	$I^-(aq)$	$CN^-(aq)$
D	Ag(s)	$I^-(aq)$	$CN^-(aq)$

17 Compound **X** is dissolved in heavy water, D_2O. It contains a number of hydrogen atoms which can be easily be replaced by deuterium, D.

[D, deuterium = ^2H]



Compound **X**

What is the maximum number of hydrogen atoms which could be replaced by deuterium atoms in each molecule of **X**?

A 1 **B** 2 **C** 3 **D** 4

18 Which of the following, when mixed together at 298K and 1 bar, represent the standard enthalpy change of neutralisation?

1 500 cm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} KOH

2 500 cm^3 of 1 mol dm^{-3} H_2SO_4 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$

3 1 dm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$

4 1 dm^3 of 1 mol dm^{-3} H_2SO_4 and 1 dm^3 of 1 mol dm^{-3} KOH

A 1 only **B** 2 and 3 only **C** 2, 3 and 4 only **D** 1, 2, 3 and 4

19 Which of the following cannot act as a ligand?

A AlH_4^-

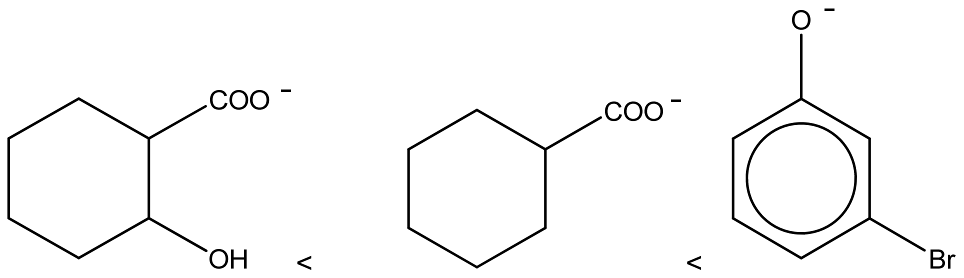
B N_2H_4

C CH_3OH

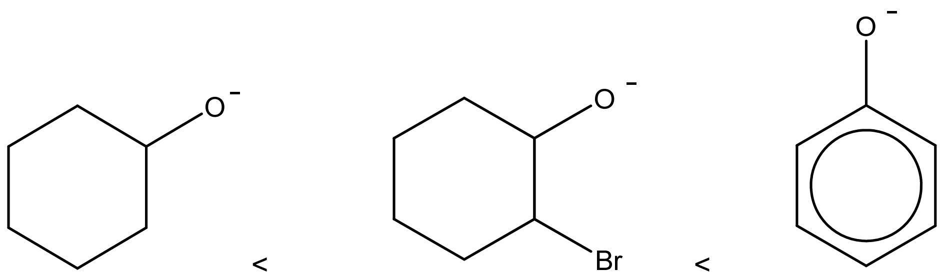
D CO

20 Which of the following shows an increasing trend in K_b?

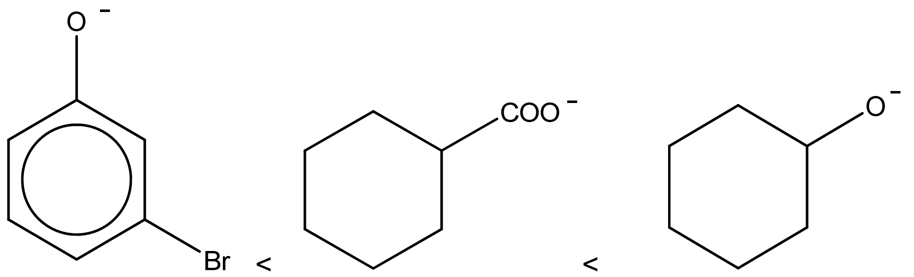
A



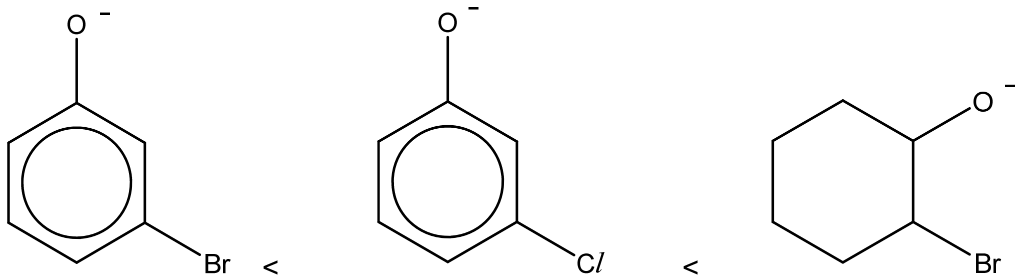
B



C



D



21 Which quantity would best indicate the strength of intermolecular hydrogen bonds in HF?

A enthalpy change of vapourisation

B enthalpy change of formation

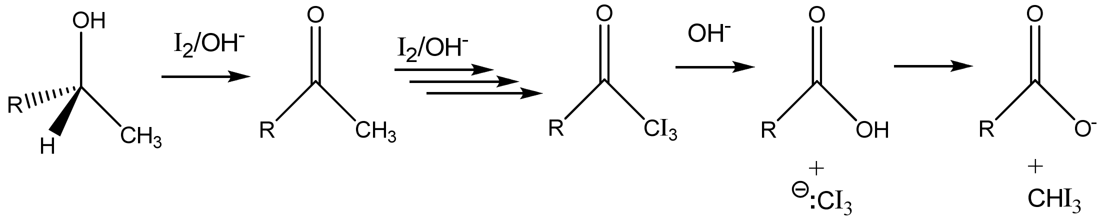
C enthalpy change of atomisation

D bond dissociation energy

22 The following data refer to cobalt as a typical transition element and calcium as an s-block element. Which of the following properties shows the correct data for both elements?

	Property	**Cobalt**	**Calcium**
A	Metallic radius / nm	0.150	0.117
B	Electrical conductivity / relative units	10.2	50
C	Melting point / °C	1495	1965
D	Density / g cm^{-3}	8.9	1.54

23 The reaction of methyl alcohols with alkaline aqueous iodine can be described by the simplified scheme as shown below:



Which of the following reactions have taken place?

1 Oxidation

2 Acid-base reaction

3 Nucleophilic addition

A 1 only **B** 1 and 2 only **C** 1 and 3 only **D** 1, 2 and 3

24 Nitrogen, ^{14}N, is the final product formed by the radioactive decay of ^{14}C, which is a first-order reaction with a half-life of 5.73 x 10^3 years.

What would be the age of a substance, originally nitrogen free, in which the molar proportion of ^{14}C : ^{14}N is 2 : 5?

A 0.29 x 10^4 years

B 1.04 x 10^4 years

C 1.58 x 10^4 years

D 1.95 x 10^4 years

[Please Turn Over

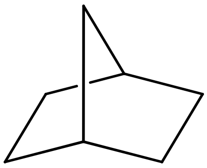
25 The properties of the oxides of four Period 3 elements **W, X, Y** and **Z** are given below.

- The oxide of **W** is insoluble in water and in dilute acid but soluble in concentrated sodium hydroxide.
- The oxide of **X** is amphoteric.
- The oxide of **Y** reacts with dilute potassium hydroxide at room temperature.
- The oxide of **Z** dissolves in water to form a solution of pH = 13.

Which of the following is correct in order of increasing atomic number?

A **Z, X, W, Y**
B **W, X, Y, Z**
C **Z, W, X, Y**
D **Z, Y, W, X**

26 Norcarane undergoes free radical substitution with limited bromine in the presence of ultraviolet light to form mono-brominated compound **Y**.



Norcarane

How many isomers of **Y** (including stereoisomers) will be formed at the end of the reaction?

A 3 **B** 4 **C** 6 **D** 8

27 The following are information for a reaction involving **X** and **Y**:

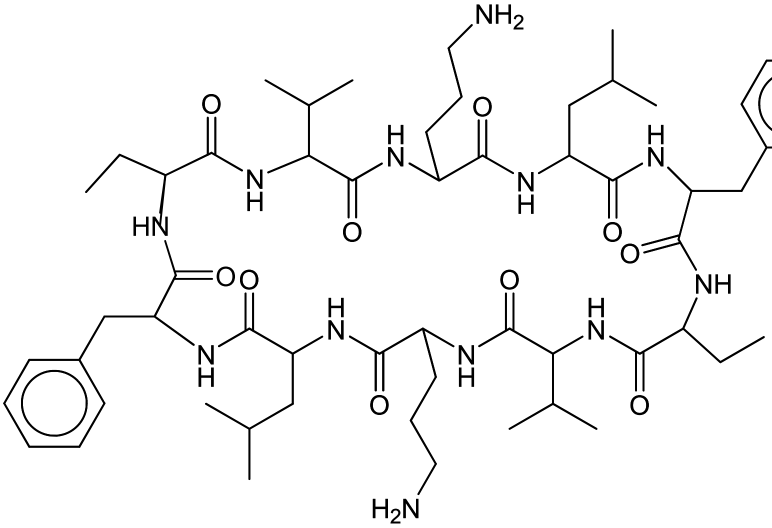
- it is first order with respect to [**X**] and zero order with respect to [**Y**].
- its rate constant doubles for each 10 °C rise in temperature

Which of the following statements are true about this reaction?

1 The half-life of the reaction remains the same when [**X**] doubles.
2 The half-life of the reaction doubles when [**Y**] is halved.
3 When the temperature of the reaction increases from 298K to 318K, the rate of the reaction will be quadrupled.
4 The rate of the reaction will change when [**X**] is halved and temperature increases from 298K to 308K.

A 1 and 2 only **B** 1 and 3 only **C** 1, 2 and 3 only **D** 2, 3 and 4 only

28 Gramicidin Soviet is an antibiotic that is effective against some fungi. It is made up of several α amino acids.



Gramicidin Soviet

Which statement about Gramicidin Soviet is correct?

A It is made up of 5 different amino acids.

B 1 mole of Gramicidin Soviet consists of 9 amide bonds.

C 1 mole of Gramicidin Soviet reacts with 10 moles of hot dilute H_2SO_4.

D Upon reaction with hot dilute NaOH, the products formed have high melting point as they can form strong intermolecular hydrogen bonding.

29 A humidity meter is made by soaking filter paper in an aqueous solution of cobalt(II) ions in HC*l* (aq). The equation for the equilibrium reaction can be represented as follows:

$$\underset{\text{pink}}{Co^{2+}(aq)} + 4Cl^{-}(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} \qquad \Delta H = +ve$$

Which of the following statements are correct?

1 On a very humid day, the filter paper will appear more pink.

2 When the filter paper is diluted with more water, there will be no colour change.

3 On a very hot day, the filter paper will appear more blue.

4 When the filter paper is placed in a sealed container under high pressure, there will be no colour change.

A 3 only **B** 2 and 4 only **C** 1, 3 and 4 only **D** 2, 3 and 4 only

[Please Turn Over

30 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$

Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Based on this information, which statements are correct?

1 Br^- is the conjugate base of HBr.

2 $N_2H_5^+$ is the Bronsted base in **Reaction 2**.

3 The order of acid strength is $HBr > N_2H_5^+ > NH_4^+$.

4 N_2H_4 is the Lewis acid in **Reaction 1**.

A 1 and 3 only **B** 1 and 4 only **C** 2 and 3 only **D** 2 and 4 only

~ END OF PAPER ~

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **17 September 2018**

Paper 1 Multiple Choice **1 hour**

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

READ THESE INSTRUCTIONS:

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages.

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
D	C	C	B	A	B	A	D	D	C

Q11	Q12	Q13	Q14	Q15	Q16	Q17	Q18	Q19	Q20
D	D	D	C	A	B	C	C	A	A

Q21	Q22	Q23	Q24	Q25	Q26	Q27	Q28	Q29	Q30
A	D	B	B	A	B	B	A	C	A

1 To identify an oxide of nitrogen, the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2\,(g)} x\,NH_3 + y\,H_2O$$

The water collected weighs 0.133 g. The ammonia produced is neutralised by 18.50 cm^3 of 0.2 mol dm^{-3} HCl.

Which of the following could be the oxide?

1 N_2O
2 NO_2
3 NO_3
4 N_2O_4

A 3 only
B 1 and 2 only
C 2 and 3 only
D 2 and 4 only

Answer: D

No. of moles of water = 0.133/18 = 0.00739

No. of moles of NH_3 = 18.50/1000 x 0.2 = 0.0037

Ratio of NH_3 to water is 1: 2

Therefore, x : y (i.e. N to O) of oxide is also 1:2

2 This question is about sparingly soluble salts.

	AgCl	**AgI**	**HgI_2**
K_{sp}	1.0×10^{-10}	8.3×10^{-16}	1.1×10^{-21}

From the above information, which statements are **not** true?

A For a solution containing 1 mol dm^{-3} of NaCl and NaI, the concentration of chloride ions when AgI just starts to precipitate is 1 mol dm^{-3}.

B The solubility of HgI_2 is 6.50×10^{-8} mol dm^{-3}.

C The solubility of HgI_2 is the lowest.

D The units for K_{sp} for HgI_2 is mol^3 dm^{-9}.

Answer: C

Option A: Since silver chloride and silver iodide has the same number of ions, the solubility is directly proportional to the K_{sp}. Hence silver iodide is precipitated before silver chloride. When silver iodide precipitates, chloride ions are still in solution and have not precipitated yet. Hence, the concentration of chloride ions is still 1 mol dm^{-3}.

Option B: Let solubility of HgI_2 be x, hence $K_{sp} = 4x^3$. $x = 6.50 \times 10^{-8}$ mol dm^{-3}

Option C: The solubility of AgCl = 1×10^{-5} mol dm^{-3}, AgI = 2.88×10^{-8} mol dm^{-3}. AgI is less soluble than HgI.

Option D: For HgI_2 $K_{sp} = [Hg^{2+}][I]^2$, hence units is (mol dm^{-3})^3 = mol^{3}dm^{-9}

3 The following tests were performed on an aqueous solution containing bromide and iodide ions.

Step	Test	Observations
1	Add excess $AgNO_3$(aq).	A mixture of cream and yellow precipitate were formed.
2	To the mixture from step 1, add concentrated NH_3.	The cream precipitate dissolved to form a colourless solution. The yellow precipitate was insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.
4	Add Cl_2(aq) to filtrate.	Brown solution is formed.

Which of the following statements is correct?

A In step 2, the cream precipitate dissolved because the addition of concentrated NH_3 results in formation of a complex which decreases the K_{sp} of AgBr.

B In step 2, the yellow precipitate was insoluble because the K_{sp} of AgI is higher than the K_{sp} of AgBr.

C In step 2, the yellow precipitate was insoluble because the ionic product of AgI is higher than the K_{sp} of AgI.

D In step 4, a disproportionation reaction has taken place.

Answer: C

The yellow precipitate remained in step 2 because IP of AgI > Ksp of AgI.

4 A stable ion of **Q** has the following properties:

- has a noble gas configuration
- has more protons than electrons
- was obtained by removing electrons from the same orbital

Which of the following could be **Q**?

A	A*l*	**B**	Ca	**C**	Cu	**D**	S

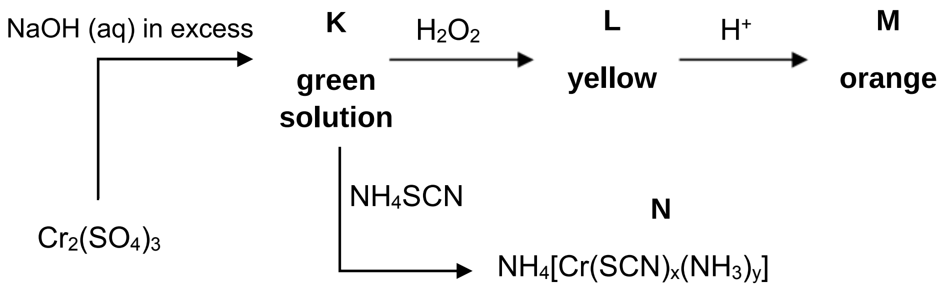
Answer: B

From the first 2 properties, **Q** has to be a main group metal.

Hence, option C and D are incorrect.

Since it was obtained by removing electrons from the same orbital, **Q** has to be either a metal in Group 1 or 2.

5 Chromium and its compounds undergo the following reactions.



N has the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%.

Which of the following can be deduced from the above reaction scheme?

A The values of x and y in **N** are 4 and 2 respectively.

B The types of reactions that occur are ligand exchange and redox only.

C The formula of **K** is $Cr(OH)_2(H_2O)_6$.

D H_2O_2 is a reducing agent in the conversion of **K** to **L**.

Answer: A

Option A: The empirical formula: Cr, 15.5%; S, 38.1%; N, 29.2%

Cr : S : N = 0.298 : 1.19 : 2.09 = 1: 4 : 7

From K to N, there should be no change in oxidation state and merely a ligand exchange. In N, the coordination number is 6 and the oxidation number of Cr = +3. Given that there is one cation NH_4^+, hence the overall charge is -1. Thus, There are $4SCN^-$ ligands to make the overall charge -1.

Option B: The conversion of L to M is also an acid base reaction where L is CrO_4^{2-} and M is $Cr_2O_7^{2-}$.

Option C: K is $Na_3[Cr(OH)_6]$ (aq). K is not a solid unlike the formula given in option C.

Option D: H_2O_2 is an oxidising agent in the conversion of K to L as the oxidation number of Cr increases from +3 to +6.

6 Which one of the following statements about Group 2 elements and their compounds is correct?

A Beryllium chloride has a higher boiling point than magnesium chloride as it has a more exothermic lattice energy than magnesium chloride.

B The reducing power of Group 2 elements increases down the group.

C 1 mole of barium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate.

D Barium has a higher melting point than magnesium due to more electrons.

Answer: B

Option A: Beryllium chloride is a simple covalent molecule while magnesium chloride is an ionic compound. Hence beryllium chloride should have a lower boiling point as it has weaker id-id interactions than the strong ionic bonds in magnesium chloride.

Option B: The E^θ value for M^{2+} / M is more negative down the group, indicating M is more easily oxidised hence its reducing power increases down the group.

Option C: Ba^{2+} has a smaller charge density than Mg^{2+} and distorts electron cloud of CO_3^{2-} to smaller extent, hence C – O bond is weakened to a smaller extent and more energy is required to decompose $BaCO_3$. Hence, less CO_2 is given off when $BaCO_3$ is decomposed.

Option D: Ba and Mg are both metallic with strong electrostatic forces of attraction between metal cation and sea of delocalised electrons. The number of electrons in the sea of delocalised electrons would be the same as both lose 2 valence electrons per atom. Ba^{2+} has a smaller charge density so the metallic bonds are weaker and less energy required to break them. Barium should have a lower melting point.

7 Liquefaction can be defined as a process that generates a liquid from a gas and this can be done by altering pressure. In the liquefaction of CH_4 and NH_3, the pressure needed for NH_3 is less than CH_4.

Which of the following reasons best explains this observation?

A NH_3 has stronger intermolecular forces of attraction than CH_4.

B NH_3 has weaker bond energy than CH_4.

C NH_3 molecules are bigger than CH_4 molecules.

D NH_3 molecules possess less kinetic energy than CH_4 molecules.

Answer: A

The process of liquefaction is making the molecules of gas come closer together via pressurisation. If the intermolecular forces between the molecules are stronger, the pressure required would be less. Since NH_3 has hydrogen bond and is stronger than instantaneous dipole-induced dipole in CH_4, pressure needed for NH_3 would be less than CH_4.

8 Phosphate buffers are commonly used in biological chemistry research.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 6.7$$

A phosphate buffer with pH 7.4 was prepared using NaH_2PO_4 and Na_2HPO_4 solutions. The total hydrogen phosphates concentration ($[HPO_4^{2-}] + [H_2PO_4^-]$) of the buffer was 0.3 mol dm^{-3}.

What are the concentrations of NaH_2PO_4 and Na_2HPO_4 used to create this buffer?

	$[NaH_2PO_4]$ / mol dm^{-3}	**$[Na_2HPO_4]$ / mol dm^{-3}**
A	0.23	0.07
B	0.07	0.23
C	0.10	0.50
D	0.05	0.25

Answer: D

$pH = pK_a + \lg [Na_2HPO_4]/ [NaH_2PO_4]$

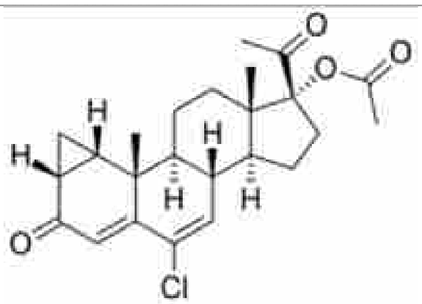
Hence, $7.4 = 6.7 + \lg [Na_2HPO_4]/ [NaH_2PO_4]$

$7/10 = \lg [Na_2HPO_4]/ [NaH_2PO_4]$

$[Na_2HPO_4]/ [NaH_2PO_4] = 5$

Hence, the answer can be C or D. However, since the ($[HPO_4^{2-}] + [H_2PO_4^-]$)= 0.30, thus D is the answer.

9 Cyproterone acetate (CPA) is a drug that is used in the treatment of prostate cancer.



CPA

Which of the following statements about CPA are incorrect?

1 One mole of silver is formed when one mole of CPA is warmed with $[Ag(NH_3)_2]^+$.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 One mole of silver chloride is formed when one mole of CPA is heated with ethanolic silver nitrate.

A	1 only	**B**	1 and 2 only	**C**	2 and 3 only	**D**	1, 2 and 3

Answer: D

Statement 1: False. No aldehyde is present.

Statement 2: False. Only one mole of yellow precipitate is formed when one mole of CPA is subjected to iodoform test.

Statement 3: False. C*l* forms a partial double bond with C=C. Hence it does not undergoes hydrolysis with $AgNO_3$

10 Consider the following equilibrium:

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

Answer: C

[Please Turn Over

Since total pressure is 3 atm and the mole ratio between Q_2 and R_2 is 2:1, their respective partial pressure is 2 atm and 1 atm.

	$2Q_2$ (g) +	R_2 (g) $\rightleftharpoons$	$2Q_2R$(g)
Initial:	2	1	0
change:	-2x	-x	+2x
equilibrium:	2 - 2x	1 – x	2x

Total pressure of gas at equilibrium = (2-2x)+(1-x) +2x = 3-x

According to question,

$2x/(3-x) = 0.20$

$x = 0.273$ atm

Thus,

partial pressure of Q_2 = 2 – 2(0.273) = 1.454 atm

partial pressure of R_2 = 1 - 0.273 = 0.727 atm

partial pressure of Q_2R = 2 x 0.273 = 0.546 atm

$K_p = (0.546)^2 / [(1.454)^2(0.727)] = 0.194\ \text{atm}^{-1}$

11 *Use of the Data Booklet is relevant to this question.*

Iodine clock reaction can be used to study how the concentration of iodide ions affect the rate of oxidation of iodide ions with peroxodisulfate ions. Peroxodisulfate ions convert iodide ions into iodine slowly.

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$

The rate of the reaction can be increased by the addition of catalysts such as aqueous iron (III) ions.

A possible catalysed reaction pathway involves the following steps:

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Step 2: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Which of the following statements are **correct**?

1 Aqueous cobalt(II) ions can be used as a catalyst in this reaction.

2 $S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+}.

3 The $E_{cell}^{\ominus}$ for step 2 is more positive than step 1.

A	2 only	**B**	1 and 3 only	**C**	2 and 3 only	**D**	1, 2 and 3

Answer: D

$Co^{3+} + e \rightleftharpoons Co^{2+}$	+ 1.89
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+ 0.77

$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ + 2.01

$I_2 + 2e \rightleftharpoons 2I^-$ + 0.54

Statement 1:

Step 1: $2Co^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Co^{3+}(aq) + 2SO_4^{2-}(aq)$

Step 2: $2I^-(aq) + 2Co^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{3+}(aq)$

$E_{cell}^{\ominus}$ for step 1: 2.01 – 1.89 = +0.12 V

$E_{cell}^{\ominus}$ for step 2: 1.89 – 0.54 = +1.35 V

Statement 2:

$S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+} as it is more easily reduced due a more positive reduction potential +2.01 vs + 0.77 V.

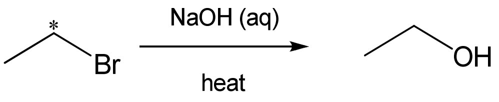
Statement 3:

$E_{cell}^{\ominus}$ for step 1: 0.77 – 0.54 = +0.23 V

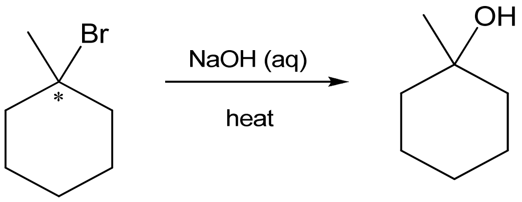
$E_{cell}^{\ominus}$ for step 2: 2.01 – 0.77 = +1.24 V

12 Which of the following reactions has no change in the hybridisation state of the carbon atom indicated with an asterisk (*) from the reactant to the **intermediate** in the mechanism?

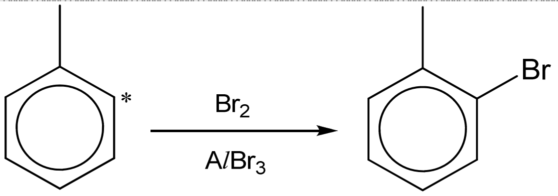
A



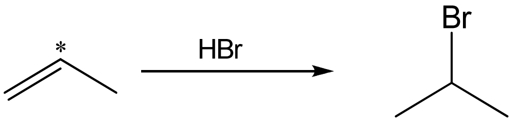
B



C



D

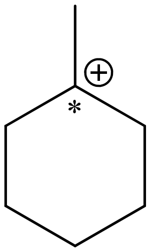


Answer: D

Option A: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N2) mechanism as it is a primary RX. There is no intermediate. The product is formed via a transition state (C atom with * will not be sp^3 hybridised anymore because it is bonded to 5 groups).

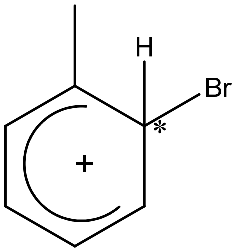
Option B: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N1) mechanism as it is a tertiary RX. Intermediate is a carbocation where the C atom with * is sp^2 hybridised.

Intermediate:



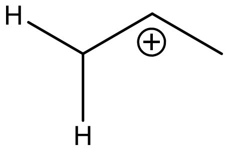
Option C: C atom with * is sp^2 hybridised in the reactant. Electrophilic substitution mechanism. The C atom with * in the intermediate is sp^3 hybridised.

Intermediate:



Option D: C atom with * is sp^2 hybridised in the reactant. Electrophilic addition mechanism. The C atom with * in the intermediate is also sp^2 hybridised.

Intermediate:



13 What is the volume of vapour formed when 10 cm^3 of liquid ethanol (density: 0.789 g cm^{-3}) is heated to 300 °C at a pressure of 5 bar?

A 85.5 cm^3

B 855 cm^3

C 163.3 cm^3

D 1633 cm^3

Answer: D

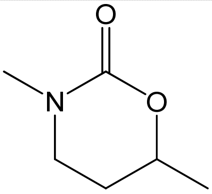
Mass of ethanol = 10 x 0.789 = 7.89

No. of moles of ethanol = 7.89/46 = 0.1715

Therefore, using pV = nRT,

V = [0.1715 x 8.31 x (300+273)] / (5 x 10^5) = 0.001633 m^3 = 1633 cm^3

14 Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?

1


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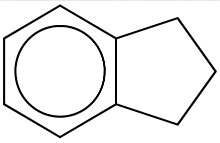

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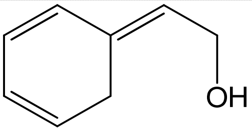


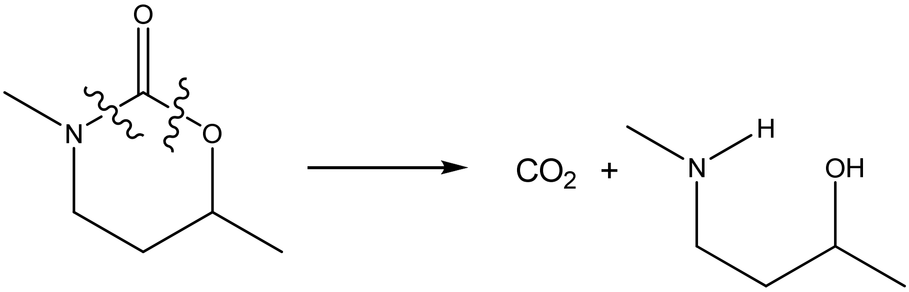
A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3

D None of the above

Answer: C

1:


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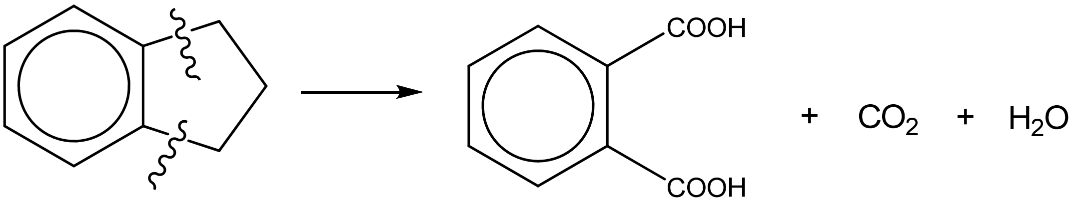

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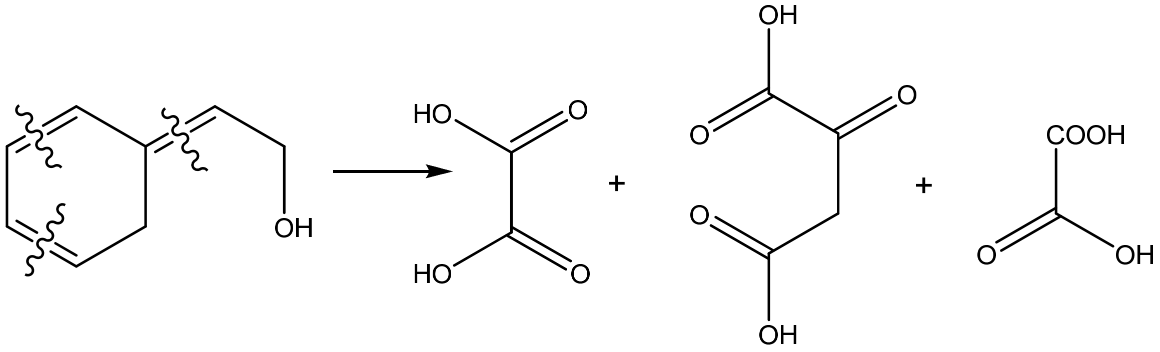
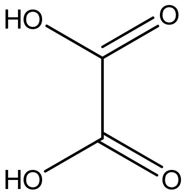
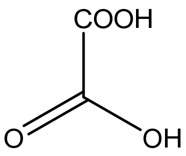




and



are further oxidised to CO_2 and H_2O

15 Trifluorooxonium has the formula OF_3^{n+} and its shape is trigonal pyramidal.

What is the value of *n* in trifluorooxonium?

A	1	**B**	2	**C**	3	**D**	4

Answer: A

Since its shape is trigonal pyramidal, that must mean that around O there are 3 bp and 1lp. The 3 bp are formed between one electron from F and 1 from O and the lp belongs to O. With only 5 valence electrons around O than the usual 6, the entire ion is short of 1 electron and hence n = 1

16 *Use of the Data Booklet is relevant to this question.*

Which set of reagents, when added in the order shown below, would convert Fe^{3+}(aq) to $[Fe(CN)_6]^{3-}$(aq)?

$$Fe^{3+}(aq) \xrightarrow{\text{step 1}} Fe^{2+}(aq) \xrightarrow{\text{step 2}} \mathbf{X} \xrightarrow{\text{step 3}} [Fe(CN)_6]^{3-}(aq)$$

	step 1	step 2	step 3
A	Zn(s)	CN^-(aq)	SO_2(g)
B	I^-(aq)	CN^-(aq)	Cl_2(g)
C	H_2O_2(aq)	I^-(aq)	CN^-(aq)
D	Ag(s)	I^-(aq)	CN^-(aq)

Answer: B

Step 1: redox

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $E^\ominus_{cell} = +0.77 - (+0.54) > 0$ V

Step 2: ligand exchange

$Fe(H_2O)_6^{2+} + 6CN^- \rightarrow Fe(CN)_6^{4-} + 6H_2O$

Step 3: redox

$Fe(CN)_6^{4-} + \frac{1}{2}Cl_2 \rightarrow Fe(CN)_6^{3-} + Cl^-$

$E^\ominus_{cell} = +1.36 - (+0.36) > 0$ V

For **A**, step 3 is incorrect as SO_2 cannot be reduced by $Fe(CN)_6^{4-}$.

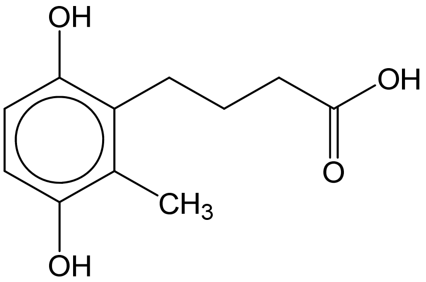
For **C**, step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^- cannot be reduced.

For **D**, step 1 is incorrect as reaction is not feasible since $E^\ominus_{cell} = +0.77 - (+0.80) < 0$ V.

Step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^- cannot be reduced.

17 Compound **X** is dissolved in heavy water, D_2O. It contains a number of hydrogen atoms which can be easily be replaced by deuterium, D.

[D, deuterium = ^2H]



Compound **X**

What is the maximum number of hydrogen atoms which could be replaced by deuterium atoms in each molecule of **X**?

A	1	**B**	2	**C**	3	**D**	4

Answer: C

Phenol and carboxylic acid will dissociate in water to form O^- and COO^- respectively.

$D_2O \rightleftharpoons D^+ + OD^-$

The D^+ can bond with the phenoxide ions and carboxylate ion. Since there are 2 phenols and 1 carboyxlic acid in compound **X**, 3 hydrogen atoms could be replaced.

18 Which of the following, when mixed together at 298K and 1 bar, represent the standard enthalpy change of neutralisation?

1	500 cm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} KOH
2	500 cm^3 of 1 mol dm^{-3} H_2SO_4 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$
3	1 dm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$
4	1 dm^3 of 1 mol dm^{-3} H_2SO_4 and 1 dm^3 of 1 mol dm^{-3} KOH

A	1 only	**B**	2 and 3 only	**C**	2, 3 and 4 only	**D**	1, 2, 3 and 4

Answer: C

Standard enthalpy change of neutralisation is when 1 mole of water is produced.

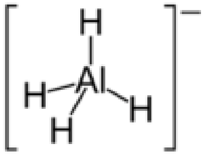
Option 1 produced 0.5 moles of water while the other options produce 1 mole of water.

19 Which of the following cannot act as a ligand?

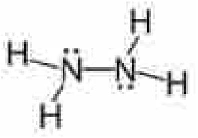
A	AlH_4^-
B	N_2H_4
C	CH_3OH
D	CO

Answer: A

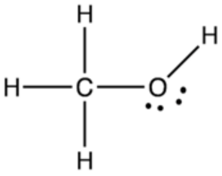
Option A: No available lone pair for dative bonding



Option B:

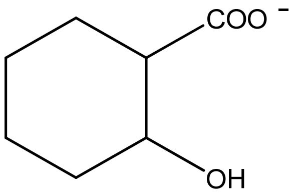
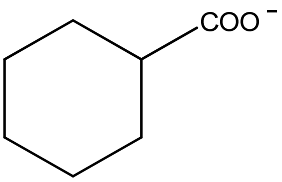
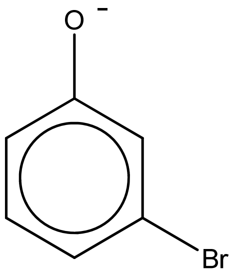
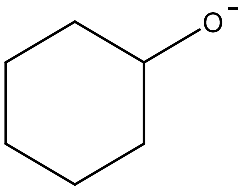
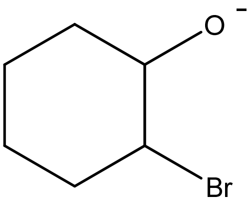
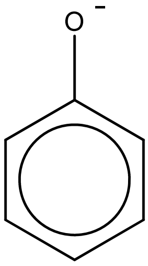
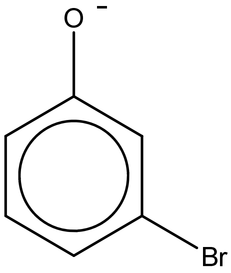
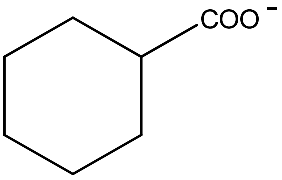
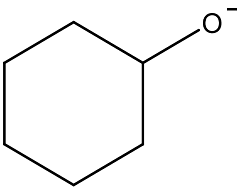
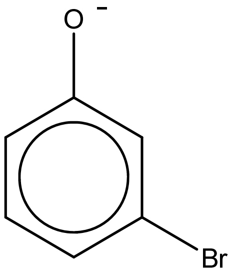
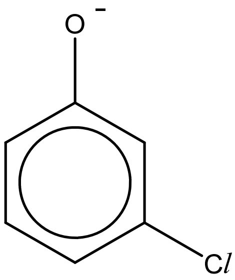
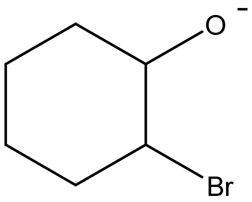


Option C:



Option D: $:C\equiv O:$

20 Which of the following shows an increasing trend in K_b ?

	A	 <  < 
	B	 <  < 
	C	 <  < 
	D	 <  < 
		Answer: A Increasing trend in K_b = increasing basicity = increasing strength of conjugate base = decreasing acidity of the original acid. Carboxylic acids are stronger acids than phenols which are stronger acids than alcohols. Hence the carboxylate ions are the weakest conjugate bases, followed by phenoxide ions, followed by alkoxide ions which are the strongest conjugate bases. Option A: OH is electron withdrawing group which stabilises the conjugate base further, hence the negative charge does not accept H^+ readily, thus it's the weakest base. Option B: Alkoxide ions are supposed to stronger conjugate bases than phenoxide ions. Option C: Phenoxide ions are supposed to be stronger conjugate bases than carboxylate ions.

Option D: C*l* is more electronegative than Br, hence the negative charge on O is less available to accept H^+ when C*l* is attached to the ring compared to Br.

21 Which quantity would best indicate the strength of intermolecular hydrogen bonds in HF?

A enthalpy change of vapourisation

B enthalpy change of formation

C enthalpy change of atomisation

D bond dissociation energy

Answer: A

Hydrogen bond is only formed between HF and NH_3 when dissolve in water. The other 3 energy change involved breaking and forming of other kinds of bonds (e.g. covalent bond) and not the hydrogen bond.

22 The following data refer to cobalt as a typical transition element and calcium as an s-block element. Which of the following properties shows the correct data for both elements?

	Property	**Cobalt**	**Calcium**
A	Metallic radius / nm	0.150	0.117
B	Electrical conductivity / relative units	10.2	50
C	Melting point / °C	1495	1965
D	Density / g cm^{-3}	8.9	1.54

Answer: D

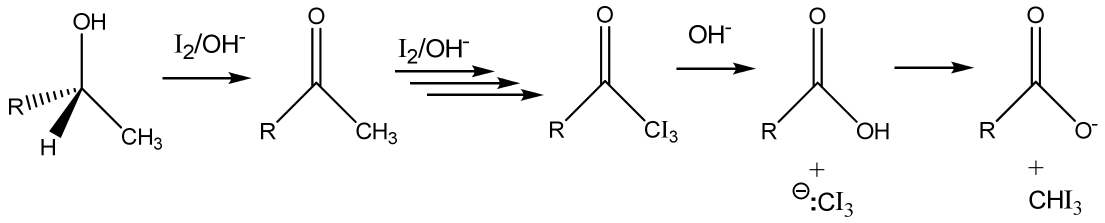
Option A: Co has more protons than Ca, hence the nuclear charge is higher than Ca. Co also has more electrons than Ca but the increase in shielding effect is minimal. Although the additional 2 electrons in Co are added in an inner sub-shell, they still provide a relatively poor shielding for the outermost 4s electrons. Hence, the valence 4s electrons in Co experiences a greater effective nuclear charge and are attracted more strongly to the nucleus than those in Ca, resulting in a smaller radius.

Option B: Cobalt should have higher conductivity than calcium due to more delocalised electrons from 3d and 4s.

Option C: Cobalt should have higher m.p than calcium. For cobalt, both 3d and 4s electrons are delocalised to form a ‘sea’ of electrons for strong metallic bonding. Hence, strong electrostatic forces holding the metallic cations (which has a larger cationic charge and smaller cationic radius) together.

Option D: While the size of the atom, measured by the metallic radius, decreases slightly from scandium to zinc, the relative atomic mass increases considerably. This results in an increase in density from scandium to zinc. The d-block metals are, in general, denser than the s-block metals.

23 The reaction of methyl alcohols with alkaline aqueous iodine can be described by the simplified scheme as shown below:



Which of the following reactions have taken place?

1 Oxidation

2 Acid-base reaction

3 Nucleophilic addition

A	1 only	**B**	1 and 2 only	**C**	1 and 3 only	**D**	1, 2 and 3

Answer: B

Statement 1: Iodoform test is an oxidation reaction. Alcohol is oxidised to a carboxylic acid (carboxylate).

Statement 2: Acid-base reaction occurs in the last step where CI_3^- acts as base to accept H^+ from OH in RCOOH (which acts as acid).

Statement 3: There is no addition reaction taking place.

24 Nitrogen, ^{14}N, is the final product formed by the radioactive decay of ^{14}C, which is a first-order reaction with a half-life of 5.73 x 10^3 years.

What would be the age of a substance, originally nitrogen free, in which the molar proportion of ^{14}C : ^{14}N is 2 : 5?

A 0.29 x 10^4 years

B 1.04 x 10^4 years

C 1.58 x 10^4 years

D 1.95 x 10^4 years

Answer: B

Original amount of ^{14}C is 7 parts (2+5).

Since radioactive decay of ^{14}C is first order,

$2/7 = (1/2)^n$ where n is the no. of half-life that took place for ^{14}C.

$n = 1.807$

Therefore, age of the substance is $1.807 \times 5.73 \times 10^3 = 1.04 \times 10^4$ years.

25 The properties of the oxides of four Period 3 elements **W, X, Y** and **Z** are given below.

- The oxide of **W** is insoluble in water and in dilute acid but soluble in concentrated sodium hydroxide.
- The oxide of **X** is amphoteric.
- The oxide of **Y** reacts with dilute potassium hydroxide at room temperature.
- The oxide of **Z** dissolves in water to form a solution of pH = 13.

Which of the following is correct in order of increasing atomic number?

A **Z, X, W, Y**

B **W, X, Y, Z**

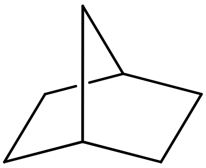
C **Z, W, X, Y**

D **Z, Y, W, X**

Answer: A

W is Silicon. X is Aluminium. Y is either Phosphorus or Sulfur. Z is Sodium.

26 Norcarane undergoes free radical substitution with limited bromine in the presence of ultraviolet light to form mono-brominated compound **Y**.

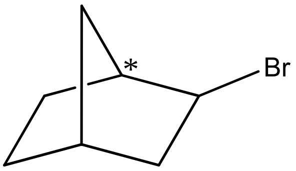


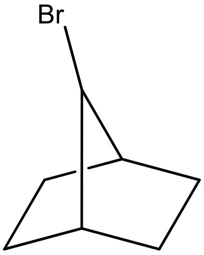
Norcarane

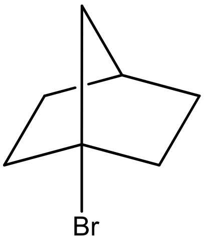
How many isomers of **Y** (including stereoisomers) will be formed at the end of the reaction?

A	3	**B**	4	**C**	6	**D**	8

Answer: B







There are 3 structural isomers. One of them has a chiral carbon (C*) so there are 4 isomers including stereoisomers.

27 The following are information for a reaction involving **X** and **Y**:

- it is first order with respect to [**X**] and zero order with respect to [**Y**].
- its rate constant doubles for each 10 °C rise in temperature

Which of the following statements are true about this reaction?

1 The half-life of the reaction remains the same when [**X**] doubles.

2 The half-life of the reaction doubles when [**Y**] is halved.

3 When the temperature of the reaction increases from 298K to 318K, the rate of the reaction will be quadrupled.

4 The rate of the reaction will change when [**X**] is halved and temperature increases from 298K to 308K.

A	1 and 2 only	**B**	1 and 3 only	**C**	1, 2 and 3 only	**D**	2, 3 and 4 only

Answer: B

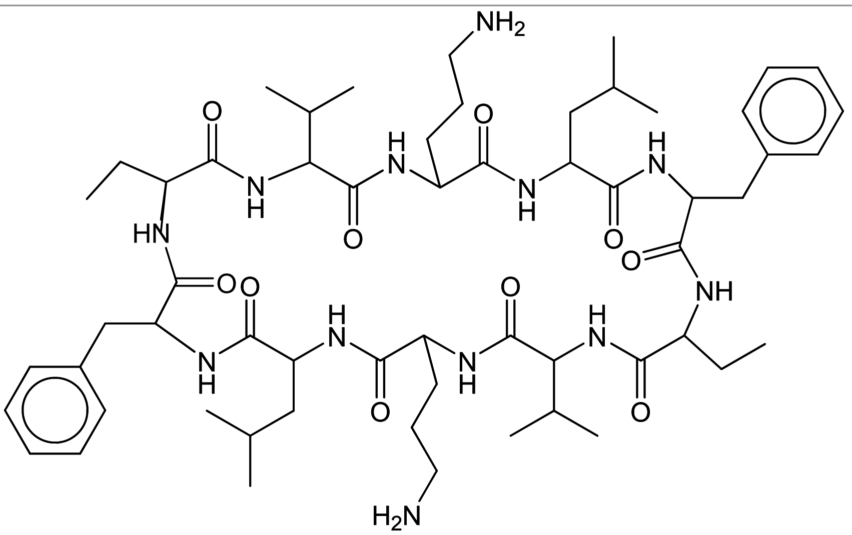
Statement 1 is correct as half-life is not affected by change in [X].

Statement 2 is wrong as [Y] does not affect the rate of reaction at all.

Statement 3 is correct as temperature increased by 20 °C and that would cause rate to increase 4 times.

Statement 4 is wrong as rate will not change due to it decreased 2 times due to [X] is halved but increase 2 times due to temperature increase by 10 °C.

28 Gramicidin Soviet is an antibiotic that is effective against some fungi. It is made up of several α amino acids.



Gramicidin Soviet

Which statement about Gramicidin Soviet is correct?

A It is made up of 5 different amino acids.

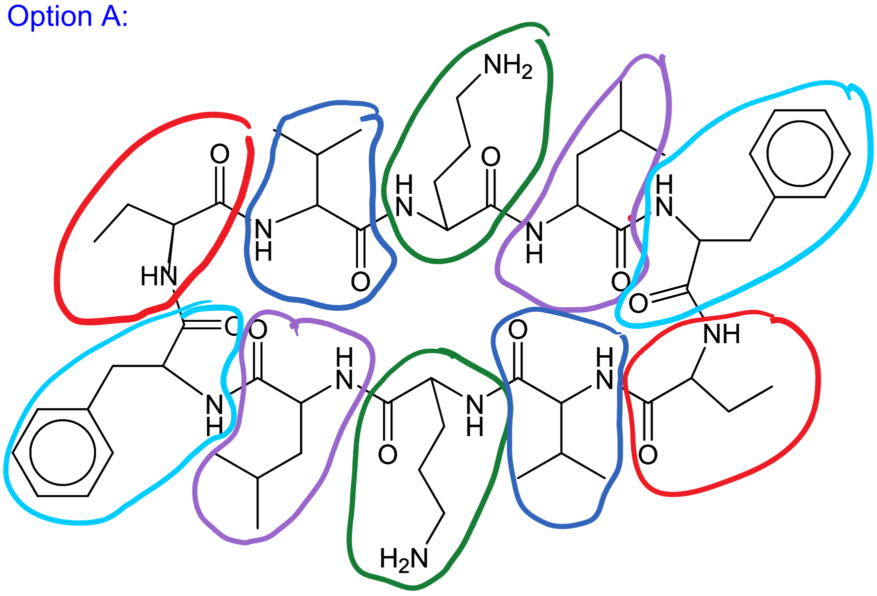
B 1 mole of Gramicidin Soviet consists of 9 amide bonds.

C 1 mole of Gramicidin Soviet reacts with 10 moles of hot dilute H_2SO_4.

D Upon reaction with hot dilute NaOH, the products formed have high melting point as they can form strong intermolecular hydrogen bonding.

Answer: A

Option A:



Gramicidin Soviet

There are 5 different amino acids (marked by the different colours).

Option B: There are 10 amide bonds.

Option C: 10 moles of amide bonds will be hydrolysed by 10 moles of hot dilute H_2SO_4. However, there are amine groups in the side-chains which would also be neutralised by dilute H_2SO_4. Hence, more than 10 moles of hot dilute H_2SO_4 will react with 1 mole of Gramicidin Soviet.

Option D: Upon reaction with hot dilute NaOH, the products formed are ionic salts (the COOH groups obtained after hydrolysis of amide bonds will be neutralised to form COO^-). These salts have high melting point as they can form strong electrostatic forces of attraction between ions, and NOT form intermolecular hydrogen bonding.

29 A humidity meter is made by soaking filter paper in an aqueous solution of cobalt(II) ions in HC*l* (aq). The equation for the equilibrium reaction can be represented as follows:

$$\underset{\text{pink}}{Co^{2+}(aq)} + 4Cl^{-}(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} \qquad \Delta H = +ve$$

Which of the following statements are correct?

1 On a very humid day, the filter paper will appear more pink.

2 When the filter paper is diluted with more water, there will be no colour change.

3 On a very hot day, the filter paper will appear more blue.

4 When the filter paper is placed in a sealed container under high pressure, there will be no colour change.

A	3 only	**B**	2 and 4 only	**C**	1, 3 and 4 only	**D**	2, 3 and 4 only

Answer: C

Statements 1 and 2: When humidity increase and solution is diluted, amount of water increases and all the ions will be diluted. Since reactants have 5 ions and product only has 1 ion, the concentration of reactants will drop more than the products. Hence, by LCP, equilibrium position will shift to the left and the filter paper will appear more pink. Thus statement 1 is correct but not statement 2.

Statement 3: it is correct as on a hot day, temperature increase and by LCP, equilibrium position will shift to the right to favor the endothermic reaction to absorb the excess heat and hence the filter paper will appear more blue.

Statement 4: since pressure only affects gaseous species and there are no gaseous species in this reaction, equilibrium position is not affected and hence there is no colour change.

30 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$

Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Based on this information, which statements are correct?

1 Br^- is the conjugate base of HBr.

2 $N_2H_5^+$ is the Bronsted base in **Reaction 2**.

3 The order of acid strength is HBr > $N_2H_5^+$ > NH_4^+.

4 N_2H_4 is the Lewis acid in **Reaction 1**.

A 1 and 3 only **B** 1 and 4 only **C** 2 and 3 only **D** 2 and 4 only

Answer: A

Statement 1: HBr is a bronsted acid as it donates a proton. Hence the **product formed (bromide ion) is a conjugate base.**

Statement 2: $N_2H_5^+$ is the Bronsted acid in **Reaction 2 as it donates a proton**.

Statement 3: Since the POE lies to the right for both reactions, HBr is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+.

Statement 4: N_2H_4 is the Lewis base in **Reaction 1** as it donates a lone pair of electrons for dative bonding to a proton from HBr.

~ END OF PAPER ~

Name		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **12 September 2018**

Paper 2 Structured Questions **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's use:

Question	1	2	3	4	5	Total
Marks	/ 19	/ 20	/ 10	/ 7	/ 19	/ 75

This document consists of **20** printed pages (including this page).

Answer **all** the questions.

1 Glucose oxidase (GOx) is an enzyme found in certain species of insects and fungi that catalyses the oxidation of glucose to gluconic acid.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + O_2 + H_2O \xrightarrow{\text{GOx}} \underset{\text{gluconic acid}}{C_6H_{12}O_7} + H_2O_2$$

(a) Write two half-equations to show that this is a redox reaction. **[2]**

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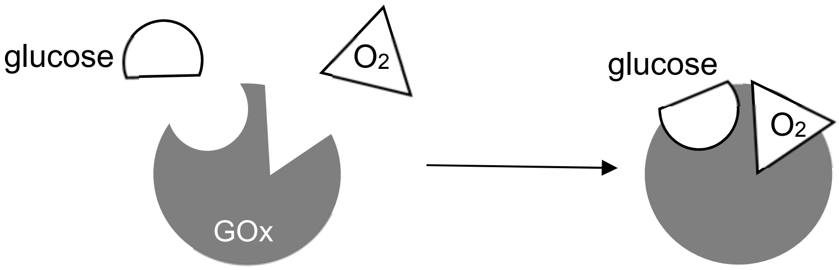
(b) The binding of reactants to GOx can be simplified with a diagram as shown below.



(i) Explain why GOx can be described as a *biological catalyst*. **[2]**

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(ii) Based on the diagram above, suggest why the sign of ΔS is negative for the reaction. **[1]**

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1 (b) (iii) Sketch a graph showing how the rate of this GOx-catalysed reaction varies with the concentration of glucose.

[1]

(c) The overall equation can be re-expressed to show the change in functional group.

$$C_5H_{11}O_5CHO + O_2 + H_2O \longrightarrow C_5H_{11}O_5COOH + H_2O_2$$

glucose → gluconic acid

Calculate the enthalpy change of reaction for the conversion of glucose into gluconic acid. Use relevant data from the *Data Booklet*. **[2]**

1 (d) Experiments were done to determine the kinetics of the reaction.

In the first investigation, the following reaction mixture was prepared.

initial [glucose] = 5.00×10^{-3} mol dm^{-3}

initial [GOx] = 1.00×10^{-2} mol dm^{-3}

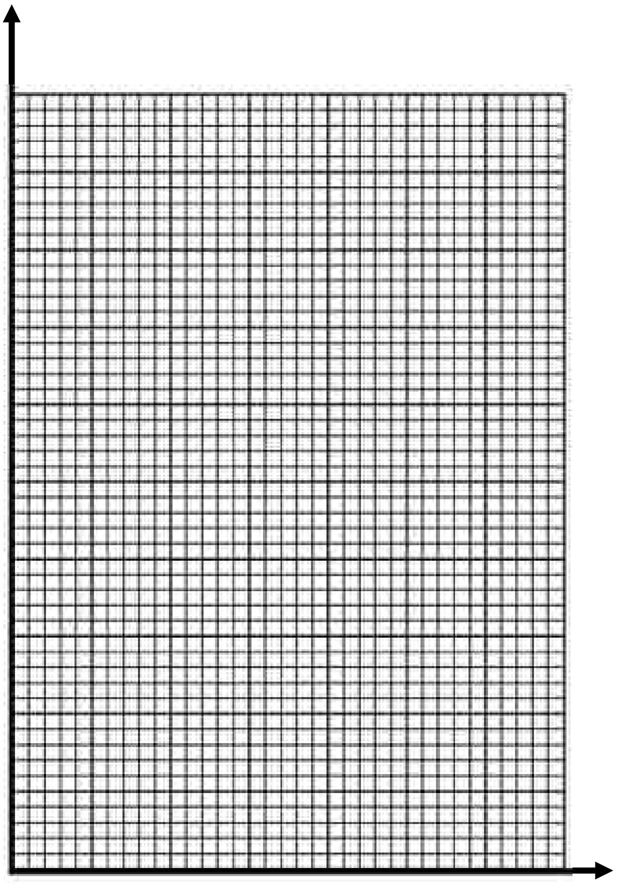
initial [O_2] = 1.00×10^{-2} mol dm^{-3}

The following results in **Table 1** were obtained.

Table 1

***t*/s**	**[glucose] / mol dm^{-3}**
0	5.00×10^{-3}
10	3.40×10^{-3}
20	2.50×10^{-3}
30	1.80×10^{-3}
60	6.00×10^{-4}

1 (d) (i) To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.



[2]

(ii) Hence, deduce the order of reaction with respect to [glucose], showing all your working and drawing clearly on your graph. **[2]**

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1 (d) (iii) In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table 2

Investigation	**Initial [O_2] (mol dm^{-3})**	**Initial [GOx] (mol dm^{-3})**	**Initial rate (mol dm^{-3} s^{-1})**
1	1.00×10^{-2}	1.00×10^{-2}	**Y**
2	5.00×10^{-3}	1.00×10^{-2}	2.00×10^{-4}
3	5.00×10^{-3}	2.50×10^{-3}	5.00×10^{-5}

Use your graph in **(d)(i)** to determine the initial rate **Y**, showing all your working and drawing clearly on your graph. Hence, use the information in **Table 2** to determine the orders of reaction with respect to [O_2] and [GOx]. Explain your reasoning.

[3]

1 **(e)** GOx can be used in a biosensor to convert glucose present in body fluids into gluconic acid. The amount of hydrogen peroxide produced is then reduced electrochemically to determine the amount of glucose present.

A 0.1 cm^3 of blood sample from a patient was tested to diagnose if he was at risk of diabetes. The diagnosis is based on the concentration of glucose in the blood.

Condition	**[glucose] in blood (x 10^{-3} mol dm^{-3})**
Normal	less than 5.6
Pre-diabetes	5.6 − 6.9
Diabetes	More than 6.9

The biosensor gave a current of 1.01 mA for 1 min. (1000 mA = 1A)

(i) Calculate the number of moles of hydrogen peroxide produced. Hence, diagnose the condition of the patient. **[3]**

(ii) Before the test, the blood sample has to be treated to remove some components present. Suggest why a treated blood sample was necessary for the biosensor to give an accurate reading. **[1]**

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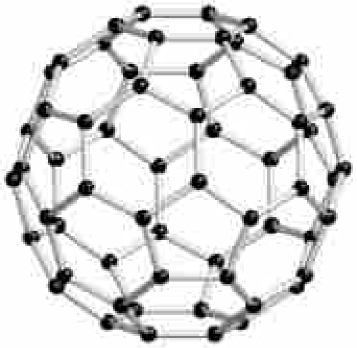
[Total: 19]

[Please Turn Over

2 This question deals with carbon and silicon which are both elements in Group 14.

(a) C_{60} and diamond are allotropes of carbon. C_{60} is a simple covalent molecule while diamond is a giant covalent molecule. State the type of bonding and describe the lattice structure of solid C_{60}.



C_{60} **[2]**

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(b) 0.144 g of C_{60} was placed in a 100 cm^3 container of hydrogen gas at 20 °C and 1.00×10^5 Pa.

The reaction occurred as shown in the equation.

$$C_{60}\,(s) + xH_2\,(g) \rightarrow C_{60}H_{2x}\,(s)$$

When all the C_{60} had reacted, the pressure was found to be 2.21×10^4 Pa at the same temperature.

(i) Calculate the amount, in moles, of C_{60} that reacted. **[1]**

2 **(b)** **(ii)** Calculate the amount, in moles, of hydrogen gas that reacted with C_{60}. **[2]**

(iii) Use your answers from **(i)** and **(ii)** to deduce the molecular formula of the hydrocarbon, $C_{60}H_{2x}$. **[2]**

(c) **(i)** Graphite is another allotrope of carbon. State the type of hybridisation and draw the arrangement of the hybrid orbitals about each C atom. **[2]**

(ii) Graphite is a good conductor of electricity. Explain, with reference to orbital overlap, how graphite has a high electrical conductivity. **[2]**

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2 **(c)** **(iii)** The values for the enthalpy change of combustion of graphite and diamond are given in the table below.

Substance	**Enthalpy change of combustion / kJ mol^{-1}**
Graphite	−394
Diamond	−396

The products of the combustion reactions of graphite and diamond are carbon dioxide and water.

Suggest why the enthalpy change of combustion of graphite is less exothermic than that of diamond. **[1]**

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(d) Silicon is another element in Group 14 which shows the same kind of bonding and structure as diamond.

(i) When silicon reacts with magnesium, Mg_2Si forms. Mg_2Si is thought to contain the Si^{4-} ion. Compare and explain the difference between the atomic and anionic radii of silicon. **[2]**

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2 **(d)** **(ii)** Suggest why the second ionisation energy of silicon is lower than that of aluminium. **[2]**

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(iii) Solid Mg_2Si reacts with dilute hydrochloric acid to form gaseous SiH_4 and a solution of magnesium chloride only. Write an equation, including state symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid. **[1]**

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(iv) Describe the reaction, if any, of $NaCl$ and $SiCl_4$ with water, relating any differences to their bonding. Give relevant equations for any reactions and suggest the pH values of each resulting solution. **[3]**

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[Total: 20]

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH_3SH.

(a) State the bond angle about the oxygen atom in CH_3OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH_3SH. **[3]**

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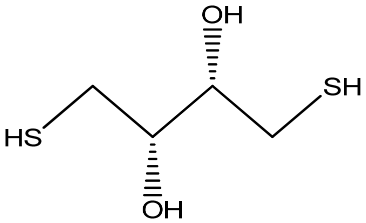
(b) Thiols can be converted to produce compounds called disulfides. This type of reaction is common in protein structures where it forms disulfide linkages (**–S–S–**) between two thiols as shown in the following equation:

$$2\ RS\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + H_2$$

Based on the above equation, suggest two disulfide products that could be formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted. **[1]**

(c) Dithiothreitol (**DTT**) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$. It has both the functional group of an alcohol and a thiol. The structure of **DTT** is given below.



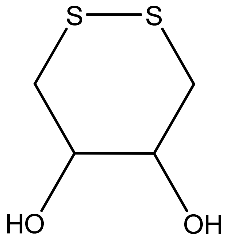
DTT can be oxidised under suitable conditions to form product **X** with molecular formula, $C_4S_2O_2H_8$.

3 **(c)** **(i)** Draw the structural formula of product **X**. **[1]**

(ii) Product **X** can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions.

Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows. **[3]**

3 **(d)** **DTT** can be oxidised to form a stable six-membered ring with an internal disulfide bond as shown in the following structure.



The oxidised form of **DTT** has a restricted rotation about the C-C bond with the two –OH groups hence enabling it to exhibit cis-trans isomerism.
Draw the cis-trans isomers of the oxidised form of **DTT**. **[2]**

[Total: 10]

4 Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO_2 free radicals. The reaction mechanism is given below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$$

(a) Define *free radical*. **[1]**

....

....

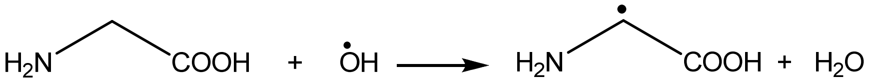
4 (b) Draw the dot-and-cross diagram for HO_2 free radical. **[1]**

(c) State the type of catalysis that takes place between iron(II) sulfate and hydrogen peroxide and state the property of iron(II) sulfate that allows it to carry out its function as a catalyst in the above decomposition reaction. **[2]**

Type of catalysis: ……………………..……….

Property: ………………………………………………………………………………

(d) OH radicals can modify amino acids. They behave similarly to chlorine radicals by abstracting a hydrogen in the propagation step of free radical substitution mechanisms. This is represented using glycine as shown below.



glycine

(i) Suggest why the rate of propagation is slower when glycine exists as an anion. **[1]**

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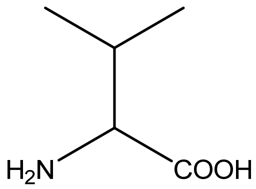
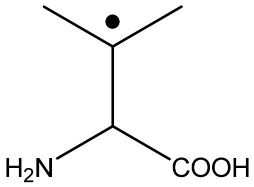
[Please Turn Over

4 (d) (ii) Valine is another amino acid that can react with OH radicals. The structure of valine is as shown below.

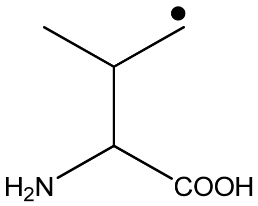


Valine

Valine reacts with OH radicals to form three radical products, of which two are shown below.



&



Product A **Product B**

Suggest a reason why product **A** is more stable. **[1]**

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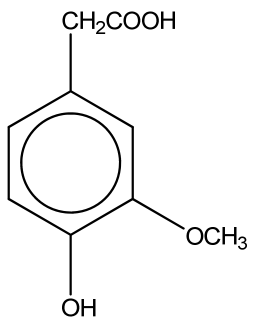
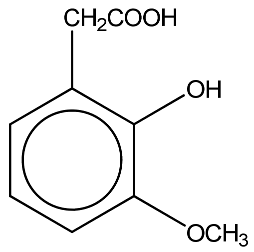
(iii) Draw the structural formula of the third radical product for the above reaction in **(ii)**. **[1]**

[Total: 7]

5 **(a)** The concentration of hydrogen peroxide can be determined by fluorescence reaction between homovanillic acid (HVA) and hydrogen peroxide. HVA can be found in urine and can be found to exist in two constitutional forms as shown below.



HVA - I



HVA-II

(i) There are two pK_a values associated with **HVA - I**: 3.7 and 5.3. Explain the difference in the pK_a values. **[2]**

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(ii) Draw the structural formula of the monoanion produced from the first dissociation of **HVA – II**.

Hence, explain why the first pK_a value of **HVA – II** is much lower than the first pK_a value of **HVA – I.** **[2]**

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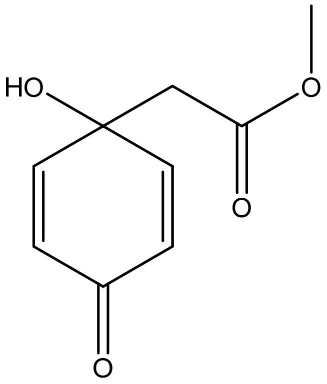
5 (a) (iii) An isomer of HVA is jacaranone which is used in cancer treatments. Its structure is given below.



jacaranone

Identify the functional groups present in jacaranone. **[2]**

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(iv) Suggest a simple chemical test which could distinguish between **HVA - I** and jacaranone. Write the balanced equation for the positive test. **[3]**

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Balanced equation:

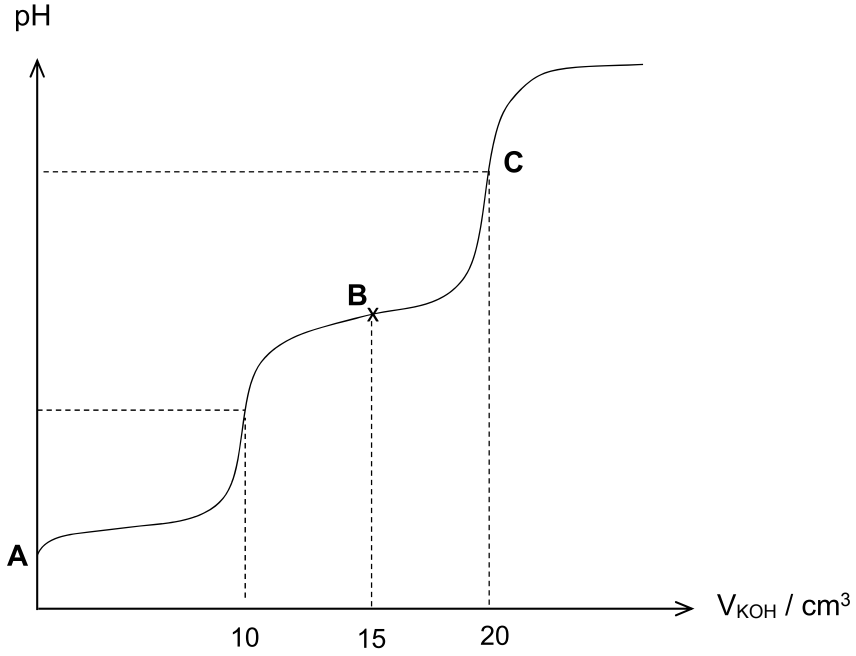
5 (a) (v) Draw all the carbon-containing products formed when jacaranone is heated with acidified $KMnO_4$. **[3]**

(b) **HVA - I**, $C_9H_{10}O_4$, is a weak dibasic acid which dissociates in water as follows:

$$C_9H_{10}O_4 \rightleftharpoons C_9H_9O_4^- + H^+ \qquad pK_{a1} = 3.7$$

$$C_9H_9O_4^- \rightleftharpoons C_9H_8O_4^{2-} + H^+ \qquad pK_{a2} = 5.3$$

A quantitative analysis was performed on a 25.0 cm^3 sample of **HVA - I**. It was titrated against 0.75 mol dm^{-3} of potassium hydroxide. The resulting pH curve was plotted as shown below.



(i) Calculate the concentration of **HVA - I** present in the sample. **[2]**

5 **(b)** **(ii)** Using the first pK_a value, calculate the initial pH at point **A**. **[2]**

(iii) State the pH at point **B** and hence, explain the significance of point **B**. **[2]**

pH: ………………..

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(iv) Write an equation to show that pH at point **C** is more than 7. **[1]**

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[Total: 19]

~ END OF PAPER ~

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

12 September 2018

2 hours

Chemistry (9729)

Paper 2 Structured Questions

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's use:

Question	1	2	3	4	5	Total
Marks	19	20	10	7	19	75

This document consists of **20** printed pages (including this page).

Answer **all** the questions.

1 Glucose oxidase (GOx) is an enzyme found in certain species of insects and fungi that catalyses the oxidation of glucose to gluconic acid.

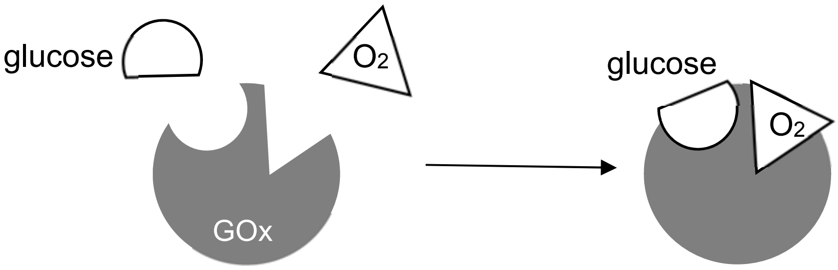
$$\underset{\text{glucose}}{C_6H_{12}O_6} + O_2 + H_2O \xrightarrow{\text{GOx}} \underset{\text{gluconic acid}}{C_6H_{12}O_7} + H_2O_2$$

(a) Write two half-equations to show that this is a redox reaction. **[2]**

$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

(b) The binding of reactants to GOx can be simplified with a diagram as shown below.



(i) Explain why GOx can be described as a *biological catalyst*. **[2]**

GOx allows certain reactants to bind specifically to it for the conversion into products.

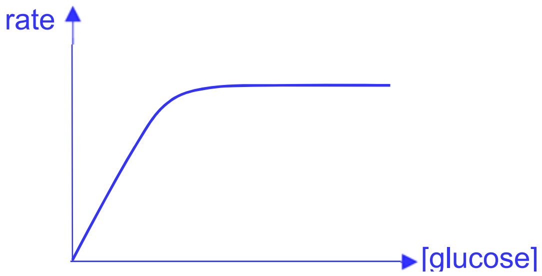
GOx speeds up the rate of reaction by providing an alternative pathway of lower activation energy. OR It is regenerated / remained chemically unchanged at the end of the reaction.

(ii) Based on the diagram above, suggest why the sign of ΔS is negative for the reaction. **[1]**

The 2 reactants and GOx must come together to form one large entity. OR There is a decrease in number of (gaseous) particles.

Hence, the products are less disordered than the reactants.

(iii) Sketch a graph showing how the rate of this GOx-catalysed reaction varies with the concentration of glucose. **[1]**



(c) The overall equation can be re-expressed to show the change in functional group.

$$C_5H_{11}O_5CHO + O_2 + H_2O \longrightarrow C_5H_{11}O_5COOH + H_2O_2$$

glucose gluconic acid

Calculate the enthalpy change of reaction for the conversion of glucose into gluconic acid. Use relevant data from the *Data Booklet*. **[2]**

Bonds broken in reactant: C–H, ~~C=O~~, O=O, ~~2O–H~~

Bonds formed in product: ~~C=O~~, C–O, O–H + ~~2O–H~~ + O–O

$\Delta H = (410 + 496) - (360 + 460 + 150) = -64.0 \text{ kJ mol}^{-1}$

(d) Experiments were done to determine the kinetics of the reaction.

In the first investigation, the following reaction mixture was prepared.

initial [glucose] = 5.00×10^{-3} mol dm^{-3}

initial [GOx] = 1.00×10^{-2} mol dm^{-3}

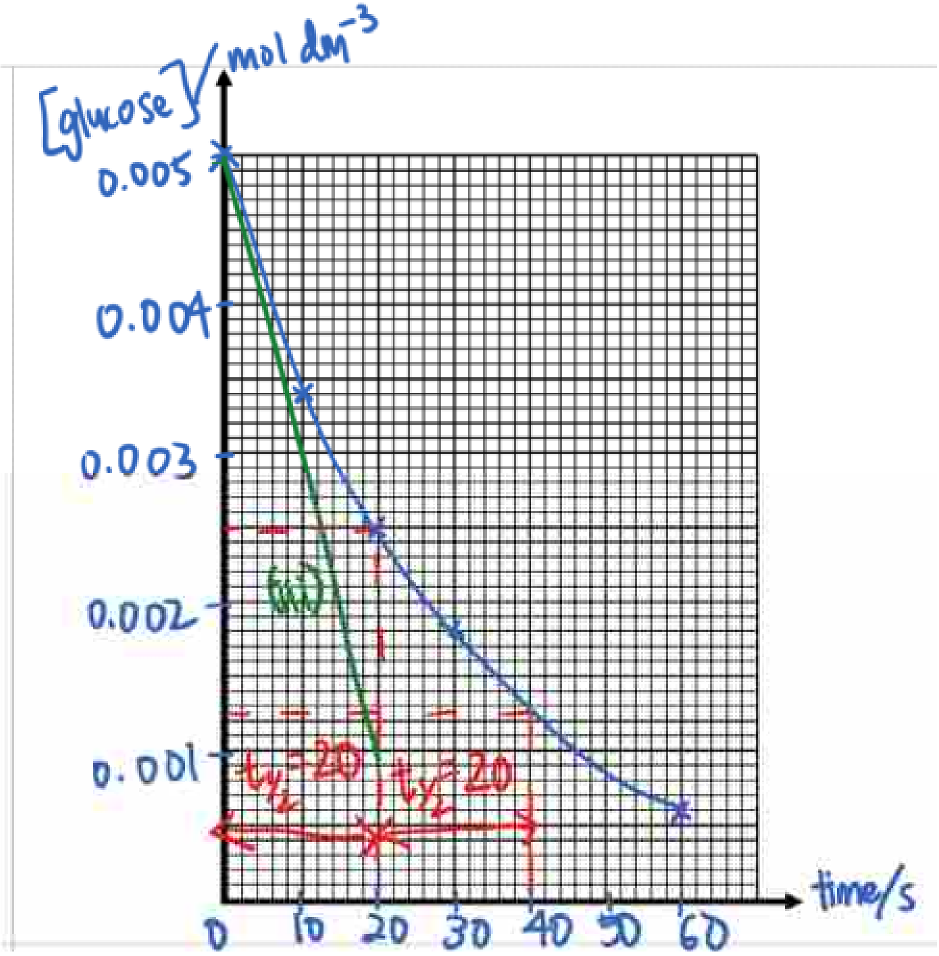
initial [O_2] = 1.00×10^{-2} mol dm^{-3}

The following results in **Table 1** were obtained.

Table 1

t/s	[glucose] / mol dm^{-3}
0	5.00×10^{-3}
10	3.40×10^{-3}
20	2.50×10^{-3}
30	1.80×10^{-3}
60	6.00×10^{-4}

(i) To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.



[2]

Guidelines for scale:

x-axis: *t*/s, 1 big square = 20s

y-axis: [glucose] / mol dm^{-3}, 1 big square = 1.0 X 10^{-3} mol dm^{-3}

(ii) Hence, deduce the order of reaction with respect to [glucose], showing all your working and drawing clearly on your graph. **[2]**

Show two $t_{1/2}$ clearly on the graph.

Since $t_{1/2}$ is (approximately) constant at 20s, the reaction is first order with respect to [glucose].

In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table 2

Investigation	**Initial [O_2] (mol dm^{-3})**	**Initial [GOx] (mol dm^{-3})**	**Initial rate (mol dm^{-3} s^{-1})**
1	1.00 x 10^{-2}	1.00 x 10^{-2}	**Y**
2	5.00 x 10^{-3}	1.00 x 10^{-2}	2.00 x 10^{-4}
3	5.00 x 10^{-3}	2.50 x 10^{-3}	5.00 x 10^{-5}

(iii) Use your graph in **(d)(i)** to determine the initial rate **Y**, showing all your working and drawing clearly on your graph. Hence, use the information in **Table 2** to determine the orders of reaction with respect to [O_2] and [GOx]. Explain your reasoning. **[3]**

$$\mathbf{Y} = \frac{(5.0 \text{ X } 10^{-3} - 1.0 \text{ X} 10^{-3})}{20} = 2.00 \text{ X } 10^{-4}$$

Using investigation 1 and 2, when [O_2] is halved, the initial rate remains the same. Hence, the reaction is zero order with respect to [O_2].

Using investigation 2 and 3, when [GOx] decreases 4 times, the initial rate decreases 4 times. Hence, the reaction is first order with respect to [GOx].

(e) GOx can be used in a biosensor to convert glucose present in body fluids into gluconic acid. The amount of hydrogen peroxide produced is then reduced electrochemically to determine the amount of glucose present.

A 0.1 cm^3 of blood sample from a patient was tested to diagnose if he was at risk of diabetes. The diagnosis is based on the concentration of glucose in the blood.

Condition	**[glucose] in blood (x 10^{-3} mol dm^{-3})**
Normal	less than 5.6
Pre-diabetes	5.6 – 6.9
Diabetes	More than 6.9

The biosensor gave a current of 1.01 mA for 1 min. (1000 mA = 1A)

(i) Calculate the number of moles of hydrogen peroxide produced. Hence, diagnose the condition of the patient. **[3]**

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Amt of charge = $1.01 \times 10^{-3} \times 60 = 0.0606$ C

Amt of e^- = $0.0606 / 96500 = 6.2798 \times 10^{-7}$ mol

Amt of H_2O_2 = $6.2798 \times 10^{-7} / 2 = 3.14 \times 10^{-7}$ mol (3sf)

Amt of glucose = amt of H_2O_2 = 3.14×10^{-7} mol

[glucose] = $3.14 \times 10^{-7} / (0.1 \times 10^{-3})$ = 3.14×10^{-3} mol dm^{-3}

The patient is normal.

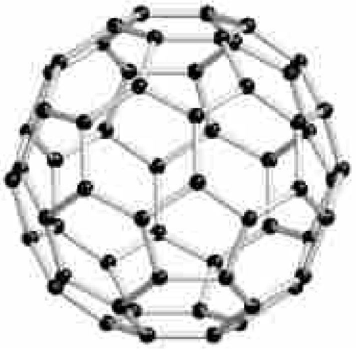
(ii) Before the test, the blood sample has to be treated to remove some components present. Suggest why a treated blood sample was necessary for the biosensor to give an accurate reading. **[1]**

The blood has to be treated to remove some components that can be reduced or oxidised by the biosensor or GOx .

[Total: 19]

2 This question deals with carbon and silicon which are both elements in Group 14.

(a) C_{60} and diamond are allotropes of carbon. C_{60} is a simple covalent molecule while diamond is a giant covalent molecule. State the type of bonding and describe the lattice structure of solid C_{60}.



C_{60}

[2]

Type of bonding: Within each C_{60} molecule, there is strong covalent bonds between carbon atoms.

Describe lattice structure: C_{60} exists as a regular lattice of simple covalent molecules with instantaneous dipole-induced dipole interactions between C_{60} molecules.

(b) 0.144 g of C_{60} was placed in a 100 cm^3 container of hydrogen gas at 20 °C and 1.00×10^5 Pa.

The reaction occurred as shown in the equation.

$$C_{60}(s) + xH_2(g) \rightarrow C_{60}H_{2x}(s)$$

When all the C_{60} had reacted, the pressure was found to be 2.21×10^4 Pa at the same temperature.

(i) Calculate the amount, in moles, of C_{60} that reacted. **[1]**

Amount of C_{60} = $0.144 / 720 = 2 \times 10^{-4}$

(ii) Calculate the amount, in moles, of hydrogen gas that reacted with C_{60}. **[2]**

$pV = nRT$

$\therefore \Delta n = (p1 - p2)V / RT$

$\Delta n = (1.00 \times 10^5 - 2.21 \times 10^4).100 \times 10^{-6} / 8.31 \times 293 = 0.00320$ mol

(iii) Use your answers from **(i)** and **(ii)** to deduce the molecular formula of the hydrocarbon, $C_{60}H_{2x}$. **[2]**

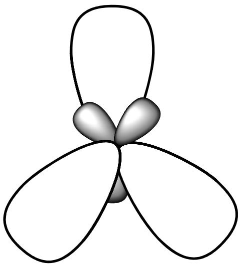
$C_{60}:H_2 = 2.00 \times 10^{-4} : 0.00320 = 1:16$

X = 16

$C_{60}H_{32}$

(c) **(i)** Graphite is another allotrope of carbon. State the type of hybridisation and draw the arrangement of the hybrid orbitals about each C atom. **[2]**

sp^2



(ii) Graphite is a good conductor of electricity. Explain, with reference to orbital overlap, how graphite has a high electrical conductivity. **[2]**

The unhybridised p orbitals on each carbon are overlapping sideways.

This side–on overlap results in the formation of a π-electron cloud.

The π electrons are delocalised and account for the high electrical conductivity of graphite.

(c) **(iii)** The values for the enthalpy change of combustion of graphite and diamond are given in the table below.

Substance	**Enthalpy change of combustion / kJ mol^{-1}**
Graphite	−394
Diamond	−396

The products of the combustion reactions of graphite and diamond are carbon dioxide and water.

Suggest why the enthalpy change of combustion of graphite is less exothermic than that of diamond. **[1]**

The C-C bonds in graphite are stronger than that in diamond. (or words to the effect, e.g. graphite is energetically more stable than diamond / has lower energy content)

(d) Silicon is another element in Group 14 which shows the same kind of bonding and structure as diamond.

(i) When silicon reacts with magnesium, Mg_2Si forms. Mg_2Si is thought to contain the Si^{4-} ion. Compare and explain the difference between the atomic and anionic radii of silicon. **[2]**

The number of protons in both the atom and its anion is the same, hence **nuclear charge remains constant**. The anion has **more electrons** and hence **valence electrons are less strongly attracted to the nucleus**, resulting in **larger anionic radius in** Si^{4-} when compared to Si.

(ii) Suggest why the second ionisation energy of silicon is lower than that of aluminium. **[2]**

Al^+ : $[Ne]3s^2$

Si^+ : $[Ne]3s^23p^1$

The second electron to be removed from Si is in the p orbital which is further away from the nucleus than the s orbital and it faces additional shielding effect from the 3s electrons. Less energy required to remove it.

(iii) Solid Mg_2Si reacts with dilute hydrochloric acid to form gaseous SiH_4 and a solution of magnesium chloride only. Write an equation, including state symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid. **[1]**

$Mg_2Si(s) + 4HCl\ (aq) \rightarrow SiH_4(g) + 2MgCl_2(aq)$

(iv) Describe the reaction, if any, of NaC*l* and SiC*l*$_4$ with water, relating any differences to their bonding. Give relevant equations for any reactions and suggest the pH values of each resulting solution. **[3]**

As covalent character of chlorides increases, the more complete the hydrolysis / the more acidic the solution is.

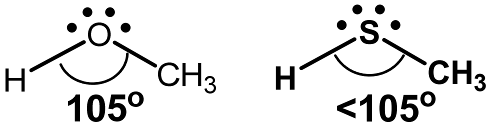
NaC*l* **dissolves** in water to form a neutral solution of **pH 7**. SiC*l*$_4$ undergoes complete hydrolysis to form an acidic solution of **pH 2**.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2\ (s) + 4HCl(aq)$

[Total: 20]

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH_3SH.

(a) State the bond angle about the oxygen atom in CH_3OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH_3SH. **[3]**



Both CH_3OH and CH_3SH have 2 bond pairs of electrons and 2 lone pairs of electrons around O and S stoms respectively. In CH_3OH, **oxygen has a greater electronegativity than sulfur** in CH_3SH.

The **bond pair of electrons are more strongly attracted to oxygen**, resulting in **greater repulsion between the bond pairs** in CH_3OH.

Hence, the **H-S-C bond angle in CH_3SH is less than 105°**

(b) Thiols can be converted to produce compounds called disulfides. This type of reaction is common in protein structures where it forms disulfide linkages (**–S–S–**) between two thiols as shown in the following equation:

$$2\ RS\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + H_2$$

Based on the above equation, suggest two disulfide products that could be formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted.

[1]

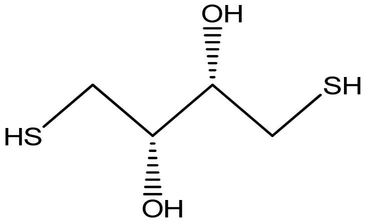
Any two of the three below:

$HOCH_2CH_2S\text{-}SCH_2CH_2OH$,

$HOCH_2CH_2S\text{-}SCH(CH_3)CH_2OH$,

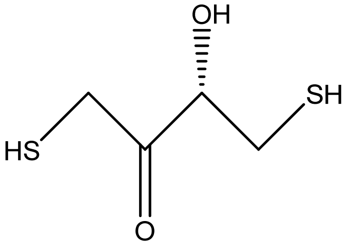
$HOCH_2CH(CH_3)S\text{-}SCH(CH_3)CH_2OH$

(c) Dithiothreitol (**DTT**) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$. It has both the functional group of an alcohol and a thiol. The structure of **DTT** is given below.



DTT can be oxidised under suitable conditions to form product **X** with molecular formula, $C_4S_2O_2H_8$.

(i) Draw the structural formula of product **X**. **[1]**



(ii) Product **X** can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions.

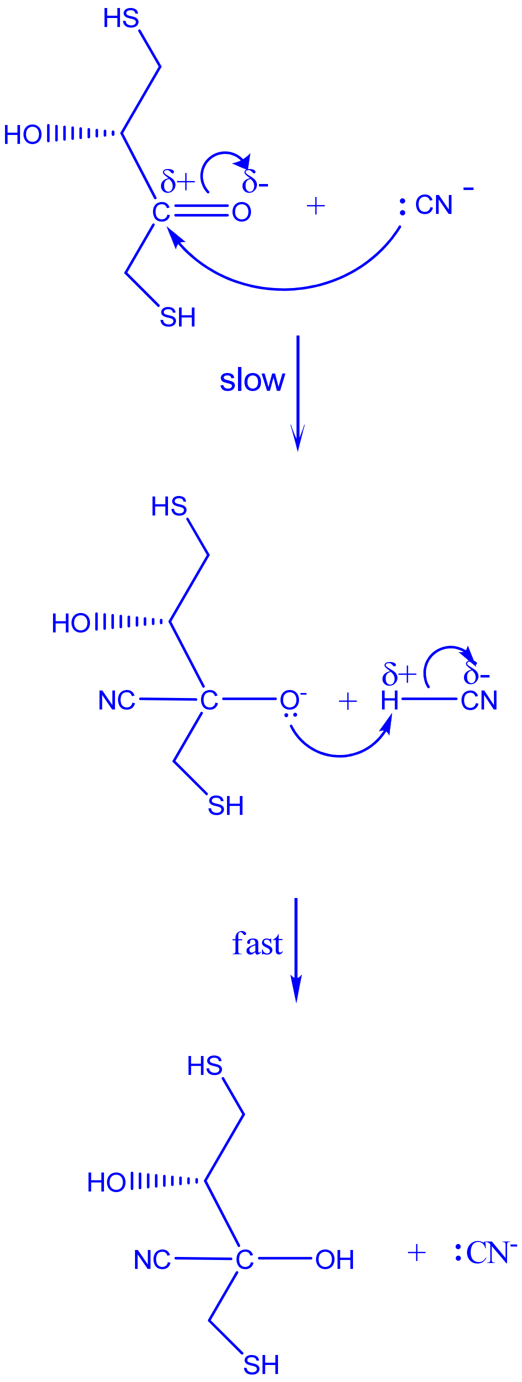
Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows. **[3]**

Conditions: Trace amount of NaOH (aq) or NaCN (aq), 10 – 20 °C

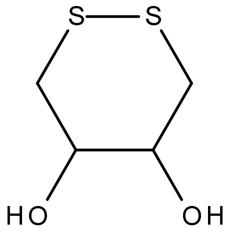
$NaOH + HCN \rightarrow Na^+ + CN^- + H_2O$

OR

$NaCN \rightarrow Na^+ + CN^-$

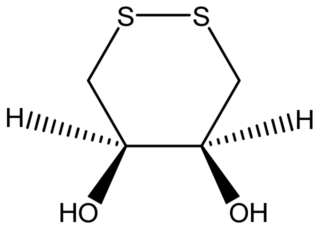

HS
HO
δ+
δ-
C
O
+
: CN -
SH
slow
HS
HO
NC
C
O-
+
δ+
δ-
H
CN
SH
fast
HS
HO
NC
C
OH
+
:CN-
SH

(d) **DTT** can be oxidised to form a stable six-membered ring with an internal disulfide bond as shown in the following structure.

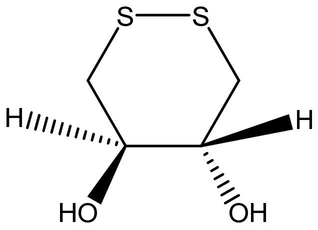


The oxidised form of **DTT** has a restricted rotation about the C-C bond with the two –OH groups hence enabling it to exhibit cis-trans isomerism.
Draw the cis-trans isomers of the oxidised form of **DTT**.

[2]



cis



trans

[Total: 10]

4 Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO_2 free radicals. The reaction mechanism is given below.

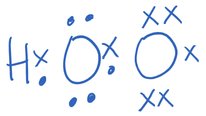
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$$

(a) Define *free radical*. **[1]**

Free radical is an atom or group of atoms having an **unpaired / single / lone / odd electron**.

(b) Draw the dot-and-cross diagram for HO_2 free radical. **[1]**

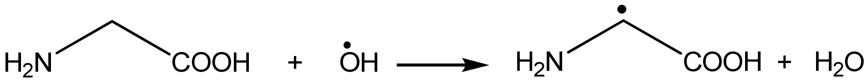


(c) State the type of catalysis that takes place between iron(II) sulfate and hydrogen peroxide and state the property of iron(II) sulfate that allows it to carry out its function as a catalyst in the above decomposition reaction. **[2]**

Homogeneous catalysis.

Iron can exist in **variable oxidation states**.

(d) OH radicals can modify amino acids. They behave similarly to chlorine radicals by abstracting a hydrogen in the propagation step of free radical substitution mechanisms. This is represented using glycine as shown below.

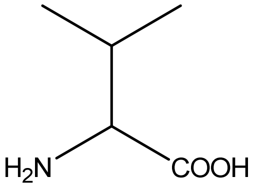


glycine

(i) Suggest why the rate of propagation is slower when glycine exists as an anion. **[1]**

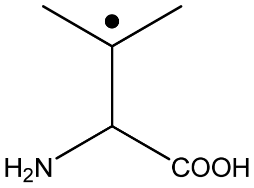
When glycine exists as an anion, the negatively-charged ion and electron on the OH radical will **repel** one another.

(ii) Valine is another amino acid that can react with OH radicals. The structure of valine is as shown below.

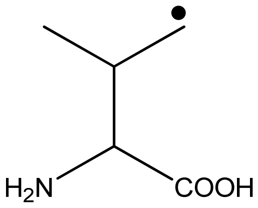


valine

Valine reacts with OH radicals to form three radical products, of which two are shown below.



&

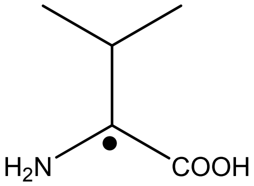


Product A **Product B**

Suggest a reason why product **A** is more stable. **[1]**

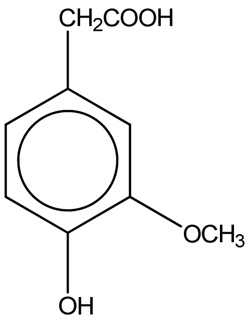
There are more **electron-donating alkyl groups in A** to stabilise the electron deficiency on the carbon with the radical.

(iii) Draw the structural formula of the third radical product for the above reaction in **(ii)**. **[1]**

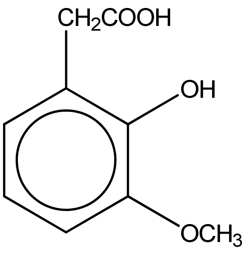


[Total: 7]

5 **(a)** The concentration of hydrogen peroxide can be determined by fluorescence reaction between homovanillic acid (HVA) and hydrogen peroxide. HVA can be found in urine and can be found to exist in two constitutional forms as shown below.



HVA - I



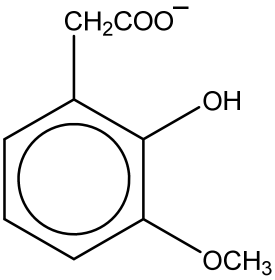
HVA-II

(i) There are two pK_a values associated with **HVA - I**: 3.7 and 5.3. Explain the difference in the pK_a values. **[2]**

The negative charge delocalises over the O-C-O bond of the carboxylate ion, while the negative charge delocalises into the benzene ring of the phenoxide ion. However the resonance effect is greater for carboxylate ion / carboxylate ion is more stable, hence carboxylic acid is a stronger acid / carboxylic acid has a lower pKa.

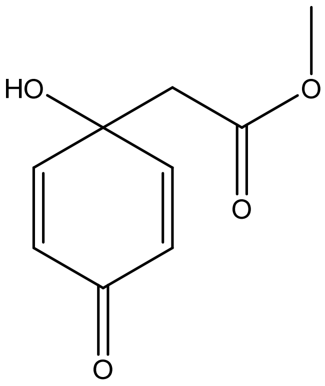
(ii) Draw the structural formula of the monoanion produced from the first dissociation of **HVA – II**.

Hence, explain why the first pK_a value of **HVA – II** is much lower than the first pK_a value of **HVA – I.** **[2]**



The **<u>monoanion formed from HVA-II is more stable than the monoanion from HVA-I</u>** as it is able to **<u>form intramolecular hydrogen bonding / ion-dipole interactions.</u>**

An isomer of HVA is jacaranone which is used in cancer treatments. Its structure is given below.



jacaranone

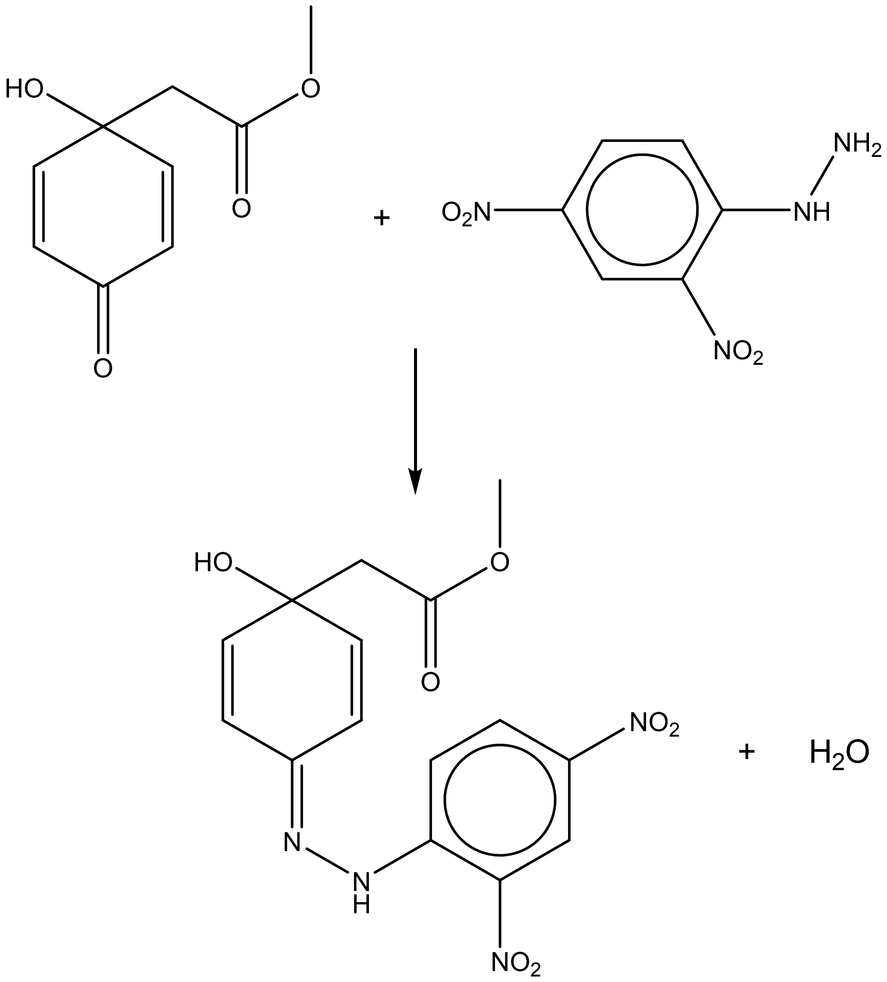
(iii) Identify the functional groups present in jacaranone. **[2]**

Tertiary alcohol, ester, alkene, ketone

(iv) Suggest a simple chemical test which could distinguish between **HVA - I** and jacaranone. Write the balanced equation for the positive test. **[3]**

Add **<u>2,4-dinitrophenylhydrazine</u>** to each compound separately and warm.

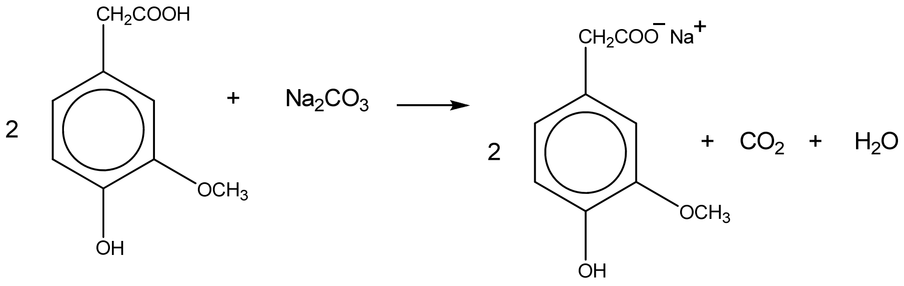
<u>Orange ppt seen with jacaranone</u>.



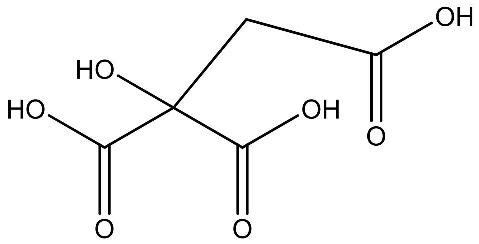
OR

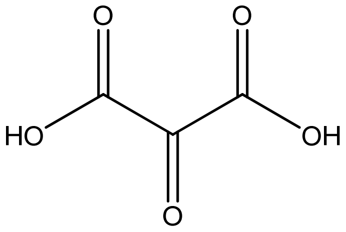
Add **Na_2CO_3** to each compound separately.

Effervescence is seen for HVA-I and gas forms white ppt in limewater.



(v) Draw all the carbon-containing products formed when jacaranone is heated with acidified $KMnO_4$. **[3]**





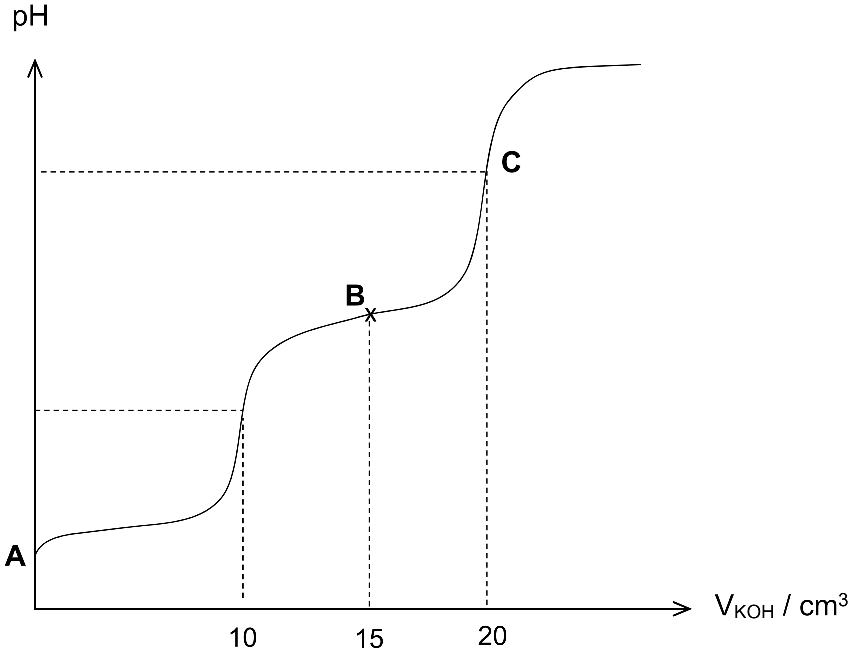
CO_2

(b) **HVA - I**, $C_9H_{10}O_4$, is a weak dibasic acid which dissociates in water as follows:

$$C_9H_{10}O_4 \rightleftharpoons C_9H_9O_4^- + H^+ \qquad pK_{a1} = 3.7$$

$$C_9H_9O_4^- \rightleftharpoons C_9H_8O_4^{2-} + H^+ \qquad pK_{a2} = 5.3$$

A quantitative analysis was performed on a 25.0 cm^3 sample of **HVA - I**. It was titrated against 0.75 mol dm^{-3} of potassium hydroxide. The resulting pH curve was plotted as shown below.



(i) Calculate the concentration of **HVA - I** present in the sample. **[2]**

Amount of KOH = 0.75 x 0.020 = 0.015 mol

Mole ratio of KOH : **HVA - I** = 2 : 1

Amount of **HVA - I** = 0.015 / 2 = 0.0075 mol

[**HVA - I**] = 0.0075 / 0.025 = **0.300** mol dm^{-3}

(ii) Using the first pK_a value, calculate the initial pH at point **A**. **[2]**

$K_a = 10^{-3.7} = 1.995 \times 10^{-4}$

$K_a = [H^+]^2 / [\mathbf{HVA - I}]$

$[H^+] = (1.995 \times 10^{-4} \times 0.300)^{1/2} = 7.736 \times 10^{-3}$ mol dm^{-3}

pH = $-\lg(7.736 \times 10^{-3})$ = **<u>2.11</u>**

(iii) State the pH at point **B** and hence, explain the significance of point **B**. **[2]**

pH = 5.3

It has <u>equal concentrations of salt and acid</u>. OR It has <u>equal ability</u> to remove small amount of H^+ and OH^-. OR Maximum buffer capacity.

(iv) Write an equation to show that pH at point **C** is more than 7. **[1]**

$C_9H_8O_4^{2-} + H_2O \rightleftharpoons C_9H_9O_4^- + OH^-$

[Total: 19]

~ END OF PAPER ~

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

Chemistry (9729) **14 September 2018**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A

Answer **all** questions. Marks **[60]**

Section B

Answer **one** question. Marks **[20]**

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

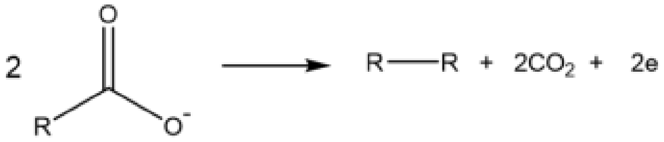
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages including this page.

Section A

Answer **all** the questions in this section.

1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. **[1]**

(b) **(i)** Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. **[2]**

(ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of pV/RT against p for one mole of **each** gas at the same temperature. Briefly explain your answer. **[2]**

1 **(c)** The cathodic reaction for the Kolbe reaction can be represented by the following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^-$.

Write an overall equation for the Kolbe reaction involving ethanoate ions. Hence, calculate $\Delta G^\ominus$ for the Kolbe reaction given that the $E^\ominus_{cell}$ value for the reaction is +2.28 V.

[2]

(d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:

Step 1: Dissociation of carboxylic acid to form a carboxylate ion.

Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO•.

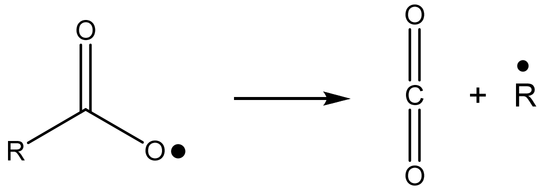
Step 3: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.

Step 4: Formation of a covalent bond between two alkyl radicals.

(i) Using ethanoic acid as a starting reagent, suggest suitable equations for **Steps 1, 2** and **4** on how ethane can be produced using the Kolbe reaction. **[3]**

(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in **Step 3** can be represented by the following equation: $RCOO\bullet \rightarrow CO_2 + R\bullet$

Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.



[1]

(e) In another separate experiment, a new alkane **A**, C_6H_{12}, was produced. When reacted with bromine under ultraviolet light, **A** produced only **one isomeric monobromo** compound, **B**, which does not have a chiral centre. Draw the skeletal formulae of **A** and **B**. **[2]**

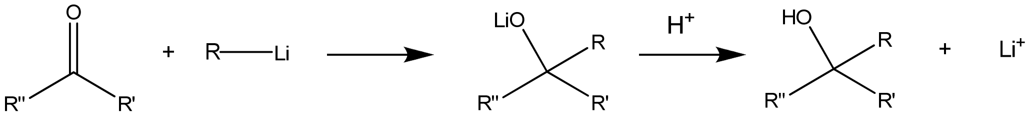
1 **(f)** **(i)** Using monohalogenoethane, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions. **[2]**

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs. **[2]**

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

$$\text{R-Br} + 2\text{Li} \rightarrow \text{R-Li} + \text{LiBr}$$

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R’ and R’’ are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. **[2]**

[Total: 19]

2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.

(a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe^{2+} is treated by electrocoagulation.

$$4Fe^{2+}\,(aq) + 10H_2O\,(l) + O_2\,(g) \rightleftharpoons 4Fe(OH)_3\,(s) + 8H^+\,(aq)$$

(i) By considering the interaction it forms with water, explain why Fe^{2+} cannot be easily removed from wastewater. **[1]**

(ii) State a suitable physical method to remove $Fe(OH)_3$ from the wastewater. **[1]**

(iii) Using *Le Chatelier's Principle*, suggest why the wastewater has to be kept alkaline for a more effective removal of Fe^{2+}. **[1]**

(iv) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature would affect the rate of the electrocoagulation process. **[3]**

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

$$NH_3\,(aq) + 2O_2\,(g) \rightleftharpoons NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$$

(i) Write the expression for the equilibrium constant, K_c, for this reaction given that K_c has units of $mol^{-1}\,dm^3$. **[1]**

(ii) 12 mol of oxygen gas was pumped into 1000 dm^3 of wastewater containing 5 mol of NH_3. After nitrification, the resulting treated wastewater had a pH of 4.2.

Calculate the value of K_c. Leave your answer to 3 significant figures. **[3]**

(iii) State how the K_c in **(ii)** would change when the amount of NH_3 in wastewater is increased to 10 mol. **[1]**

(iv) The nitrification process was carried out at room temperature. It was observed that the outer surface of the reaction vessel was cold after some time.

By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia. **[2]**

2 **(b)** **(v)** Construct a suitable energy cycle using the following equations to show how the enthalpy change of reaction, ΔH_r, can be determined.

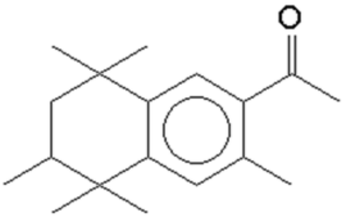
$NH_3\,(aq) + 2O_2\,(g) \longrightarrow NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$ ΔH_r

$NH_3(aq) + O_2(g) + H_2(g) \longrightarrow NH_2OH(aq) + H_2O(l)$ ΔH_1

$NH_2OH(aq) + H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow NO_3^-(aq) + 2H_2(g) + H^+(aq)$ ΔH_2

$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$ ΔH_3 **[3]**

(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, $C_{18}H_{26}O$, is one such organic compound found commonly in sludge. It has a melting point of 54.5°C.



tonalide

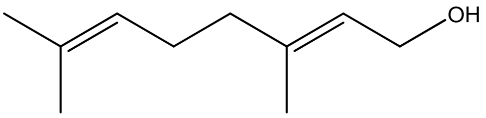
(i) Write an equation which describes the standard enthalpy change of combustion of tonalide. **[1]**

(ii) The enthalpy change of combustion of tonalide is -865 kJ mol^{-1}.
Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide. **[2]**

(iii) The sign of the entropy change of combustion of tonalide is positive. Briefly explain the effect of temperature on the spontaneity of combustion of tonalide. **[1]**

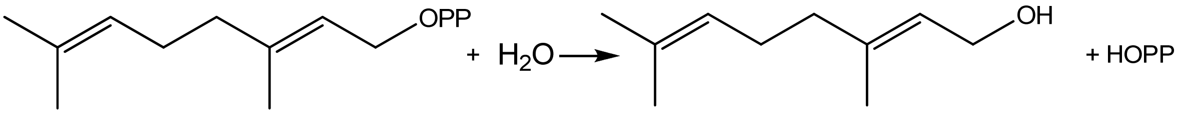
[Total: 20]

3 Geraniol, $C_{10}H_{18}O$, is commonly used in perfumes and food flavourings.



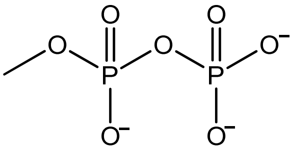
Geraniol

It is produced from geranyl diphosphate as shown in the following equation.



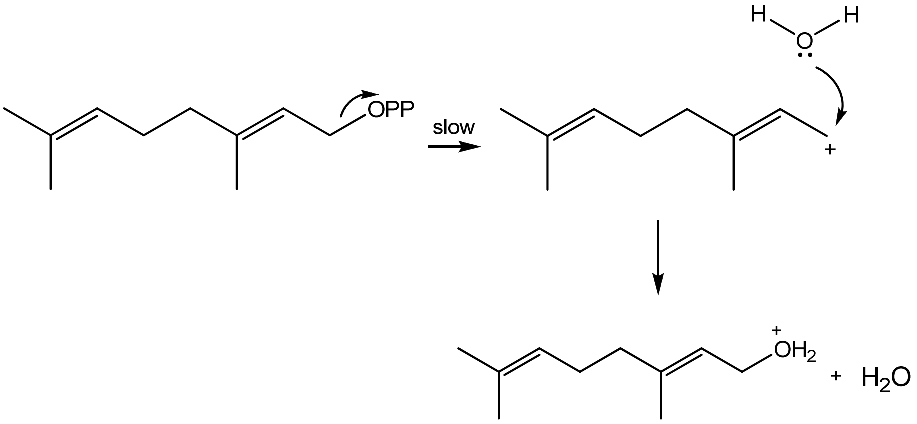
Geranyl diphosphate

where OPP :

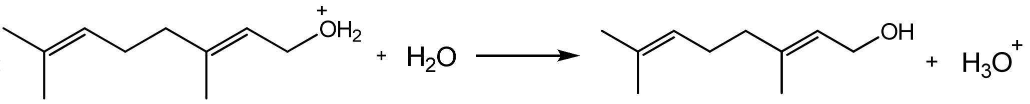


(a) The mechanism of this reaction consists of the following:

Reaction I:



Reaction II:

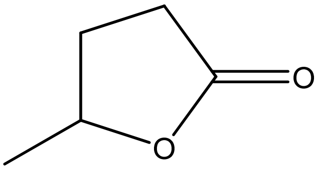


(i) State the mechanism in reaction **I**. **[1]**

(ii) Explain why the mechanism in reaction **I** takes place in two steps instead of one step. **[1]**

(iii) State the role of water in reaction **II**. **[1]**

3 **(a)** **(iv)** The following compound can be synthesised from geraniol.



Propose a reaction scheme for this synthesis. **[4]**

(v) Explain what is meant by constitutional isomers and draw a constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine. **[2]**

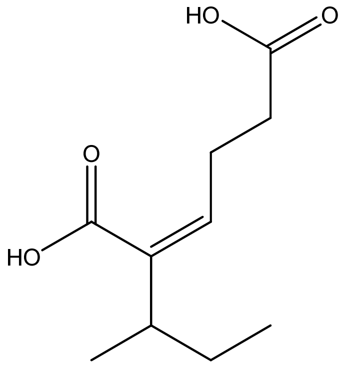
(b) Geranyl diphosphate can be synthesised using P_4O_{10}.

(i) Write an equation for the reaction of P_4O_{10} in water and describe the effect of the resulting solution on universal indicator solution. **[2]**

(ii) Naturally occurring phosphorus contains the isotopes ^{31}P, ^{32}P and ^{33}P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively. **[2]**

(c) Geraniol is a by-product of the metabolism of sorbic acid, C_5H_7COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt. **[3]**

3 **(d)** Another constitutional isomer of geraniol is compound **X**. **X** does not react with 2,4-dinitrophenylhydrazine. **X** produces effervescence when sodium metal is added to it. When hot acidified $K_2Cr_2O_7$ is added to **X**, orange solution remains. On addition of aqueous bromine to **X**, the orange solution decolourises and compound **Y** is formed. **X** reacts with hot acidified $KMnO_4$ to form compound **Z** only. When **Z** is reacted with excess concentrated H_2SO_4 at 170 °C, the following product is obtained.



X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

[5]

[Total: 21]

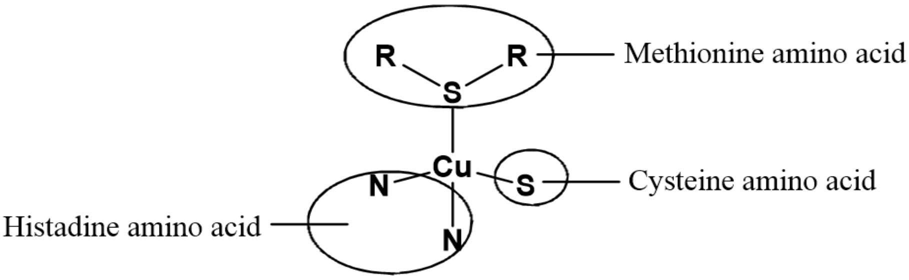
Section B

Answer **one** question in this section.

4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.

(a) Explain what is meant by the term *transition element*. **[1]**

(b) **(i)** Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu^{2+} in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu^{2+} act as ligands.



Define the term *ligand*. **[1]**

(ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu^+ complex which has a deep blue colour.

State the electronic configuration of Cu^+. **[1]**

(iii) The deep blue colour seen is considered to be unusual.

Suggest a reason why this is so. **[1]**

(c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is $Cu_3(CO_3)_2(OH)_2$ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.

(i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH^- may be produced from a saturated solution of sodium carbonate. **[1]**

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid.

Suggest an explanation why the proposed method is not ideal. **[1]**

4 **(c)** **(iii)** Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm^3 of 0.550 mol dm^{-3} sulfuric acid. The resulting solution was topped up to 250 cm^3 using deionised water.

Step 2: 25.0 cm^3 of the solution required 15.55 cm^3 of 0.200 mol dm^{-3} sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

$$Cu_3(CO_3)_2(OH)_2 + \boldsymbol{a}\ H_2SO_4 \rightarrow \boldsymbol{a}\ CuSO_4 + \boldsymbol{b}\ H_2O + \boldsymbol{c}\ CO_2$$

Complete the balancing of the above equation by deducing values for ***a***, ***b*** and ***c***. Hence, calculate the percentage of azurite in the rock sample.

[3]

(iv) Using your knowledge on the thermal decomposition of carbonates and given that $Cu(OH)_2$ thermally decomposes to form CuO and H_2O, write an equation for the thermal decomposition of azurite.

Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. **[3]**

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm^{-3} sodium carbonate solution and 0.100 mol dm^{-3} potassium hydroxide solution. Calculate the concentration of Cu^{2+} required to begin precipitating $CuCO_3$ and $Cu(OH)_2$ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

K_{sp} of $CuCO_3$ = 7.08×10^{-9} $mol^2\ dm^{-6}$

K_{sp} of $Cu(OH)_2$ = 4.8×10^{-20} $mol^3\ dm^{-9}$

[3]

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations.

[2]

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

[3]

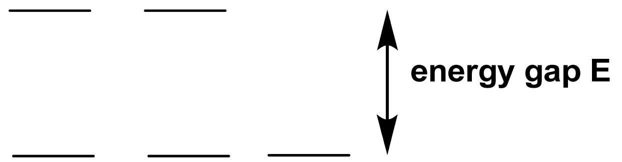
[Total: 20]

5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.

(a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe^{2+} ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

(i) A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.

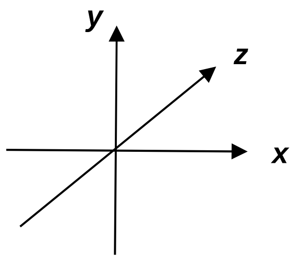
Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe^{2+} in oxyhaemoglobin.



[1]

(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.

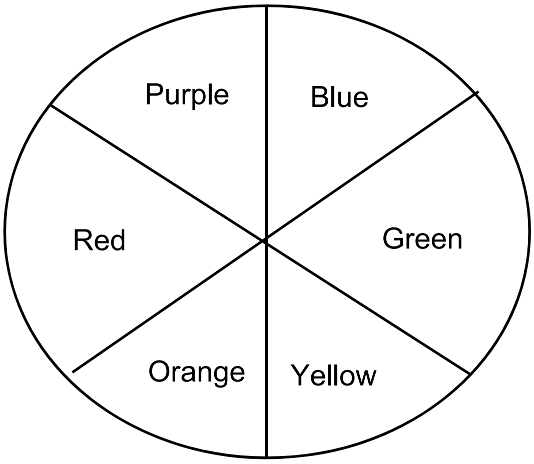
Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



[3]

5 (a) (iii) Explain why oxyhaemoglobin is red. **[2]**

(iv) The complementary colours are shown using the following colour wheel.



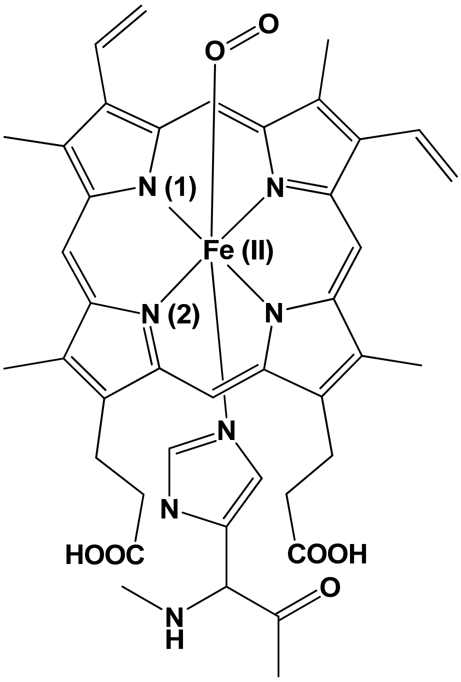
The wavelength of each colour component in visible light is as provided.

Colour	**Purple**	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength / nm	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750

Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

[2]

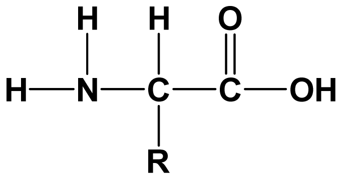
5 (a) (v) Fe^{2+} complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled **(1)** and the bond angle around the N atom labelled **(2)**. **[2]**

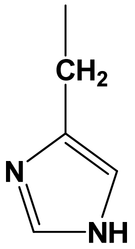
(vi) Besides Fe^{2+}, Fe^{3+} may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. **[1]**

5 **(a)** **(vii)** Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



$$H_2N-CH(R)-COOH$$

In each chain, histidine, leucine and glycine amino acids can be found.

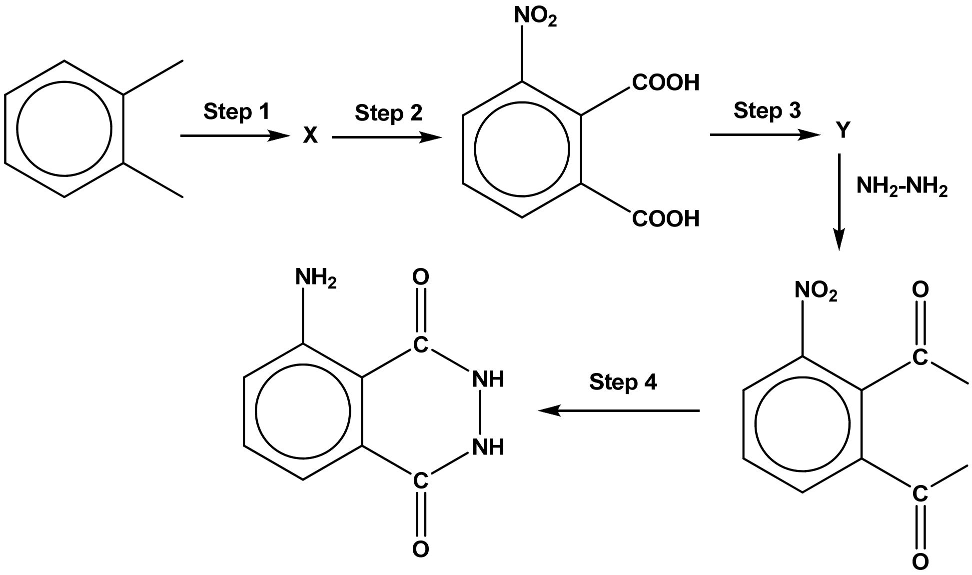
Amino acid	**R group**
Histidine	
Leucine	$-CH_2CH(CH_3)_2$
Glycine	-H

Draw the structural formula of a tripeptide with the sequence histidine-leucine-glycine at pH 2. **[2]**

(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. **[1]**

5 (b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood.

The synthetic route for luminol is as shown.



Luminol

(i) State the reagents and conditions for **steps 1** to **3**. **[3]**

(ii) Draw the structures for intermediate products **X** and **Y**. **[2]**

(iii) For **Step 4**, $Na_2S_2O_4$ is commonly used as the reagent.

State the role of $Na_2S_2O_4$. **[1]**

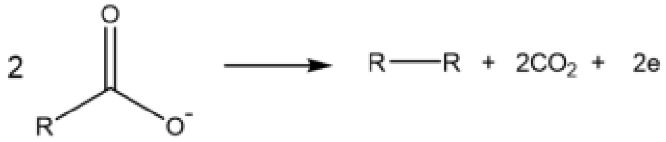
[Total: 20]

END OF PAPER

Section A

Answer **all** the questions in this section.

1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. **[1]**

Alkanes have C-C and C-H bonds which are strong and non-polar.

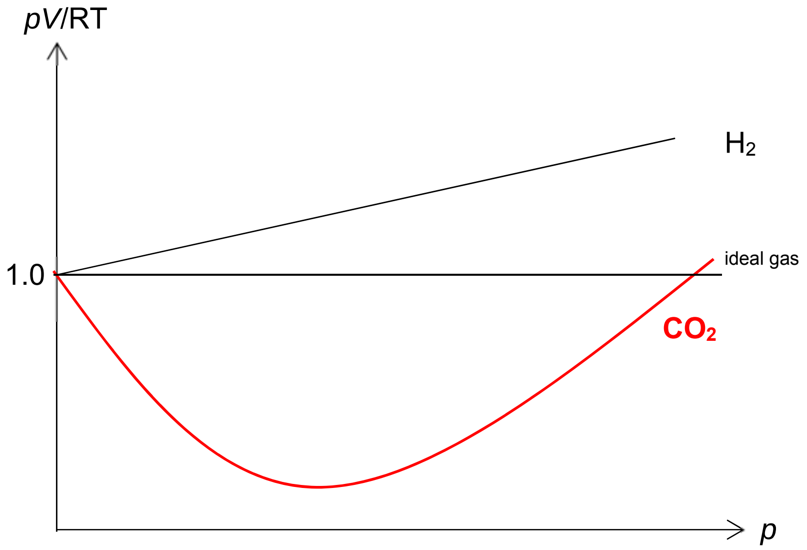
(b) **(i)** Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. **[2]**

Q = It = 32 x 60 x 5 = 9600 C

Amt of CO_2 = Amt of e = Q/F = 9600/(96500) = 0.09948 mol

Vol of CO_2 collected = 0.09948 x 22.7 = 2.26 dm^3

(ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of *pV*/RT against *p* for one mole of **each** gas at the same temperature. Briefly explain your answer. **[2]**



CO_2 deviates more from ideal behaviour because it experiences <u>stronger instantaneous dipole-induced dipole interactions / intermolecular forces</u> between the molecules compared to H_2 which has a smaller electron cloud.

(c) The cathodic reaction for the Kolbe reaction can be represented by the following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^-$.

Write an overall equation for the Kolbe reaction involving ethanoate ions. Hence, calculate $\Delta G^\ominus$ for the Kolbe reaction given that the $E^\ominus_{cell}$ value for the reaction is +2.28 V. **[2]**

$2CH_3COO^- \rightarrow CH_3\text{-}CH_3 + 2CO_2 + 2e$

$2H_2O + 2e \rightarrow H_2 + 2OH^-$

Overall: $2CH_3COO^- + 2H_2O \rightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2OH^-$

$\Delta G^\ominus = -nFE = -(2)(96500)(2.28) = -440\ \text{kJ mol}^{-1}$

(d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:

Step 1: Dissociation of carboxylic acid to form a carboxylate ion.

Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO•.

Step 3: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.

Step 4: Formation of a covalent bond between two alkyl radicals.

(i) Using ethanoic acid as a starting reagent, suggest suitable equations for **Steps 1, 2** and **4** on how ethane can be produced using the Kolbe reaction. **[3]**

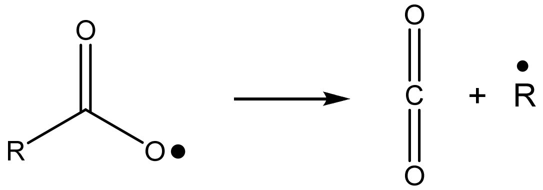
Step 1: $CH_3COOH \rightarrow CH_3COO^- + H^+$

Also accept "$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$".

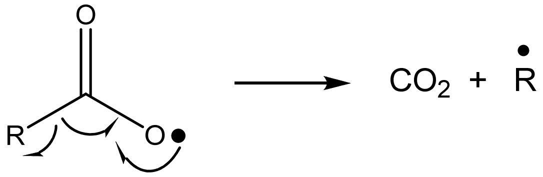
Step 2: $CH_3COO^- \rightarrow CH_3COO\bullet + e$

Step 4: $CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$ (accept C_2H_6 also)

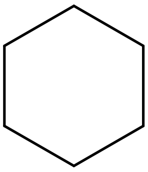
(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in **Step 3** can be represented by the following equation: $RCOO\bullet \rightarrow CO_2 + R\bullet$
Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.

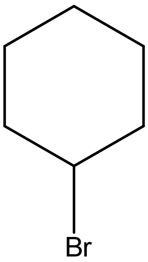


[1]



(e) In another separate experiment, a new alkane **A**, C_6H_{12}, was produced. When reacted with bromine under ultraviolet light, **A** produced only **one isomeric monobromo** compound, **B**, which does not have a chiral centre. Draw the skeletal formulae of **A** and **B**. **[2]**





(f) **(i)** Using monohalogenoethane, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions. **[2]**

The hydrolysis of C_2H_5X will increases in reactivity (C_2H_5Cl < C_2H_5Br) . This is because the bond length / bond energy of C-Cl <C-Br, hence, it is most difficult to overcome C-Cl bond > C-Br bond.

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs. **[2]**

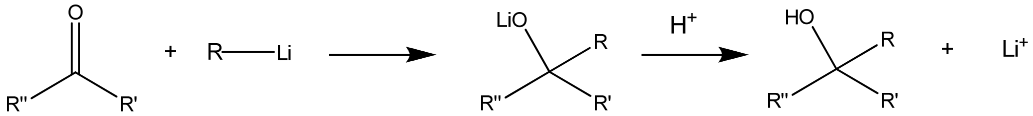
CFCs produce chlorine radicals, which in turn initiate the chain reaction breaking down ozone molecules, O_3 to O_2.

Alkanes are flammable.

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

$$R\text{-}Br + 2Li \rightarrow R\text{-}Li + LiBr$$

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R' and R'' are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. **[2]**

Ethanal, 1-bromobutane

OR Bromomethane, Pentanal

[Total: 19]

2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.

(a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe^{2+} is treated by electrocoagulation.

$$4Fe^{2+}\,(aq) + 10H_2O\,(l) + O_2\,(g) \qquad 4Fe(OH)_3\,(s) + 8H^+\,(aq)$$

(i) By considering the interaction it forms with water, explain why Fe^{2+} cannot be easily removed from wastewater. **[1]**

It forms ion-dipole interaction with water. Hence, it is soluble in water and cannot be easily removed.

OR

It forms dative bond with water to form a soluble complex of $[Fe(H_2O)_6]^{2+}$. Hence it cannot be easily removed.

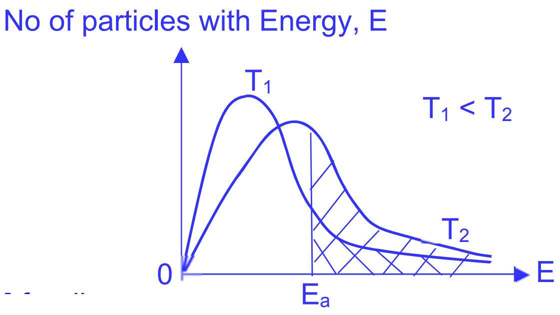
(ii) State a suitable physical method to remove $Fe(OH)_3$ from the wastewater. **[1]**

filtration

(iii) Using *Le Chatelier's Principle*, suggest why the wastewater has to be kept alkaline for a more effective removal of Fe^{2+}. **[1]**

As $[OH^-]$ is high / $[H^+]$ is low, the position of the equilibrium shifts right to increase $[H^+]$. Hence, more Fe^{2+} would be oxidised/removed as $Fe(OH)_3$.

(iv) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature would affect the rate of removal of Fe^{2+}. **[3]**



When T increases, the KE of the reacting particles increases. Hence, there are more particles with $E \geq E_a$ and the frequency of effective collision increases. The rate of removal of Fe^{2+} would increase.

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

$$NH_3\,(aq) + 2O_2\,(g) \rightleftharpoons NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$$

(i) Write the expression for the equilibrium constant, K_c, for this reaction given that K_c has units of $mol^{-1}\,dm^3$. **[1]**

$K_c = [NO_3^-][H^+] / [NH_3]\,[O_2]^2$

(ii) 12 mol of oxygen gas was pumped into 1000 dm^3 of wastewater containing 5 mol of NH_3. After nitrification, the resulting treated wastewater had a pH of 4.2. Calculate the value of K_c. Leave your answer to 3 significant figures. **[3]**

	$NH_3(aq)$	$+ 2O_2$	$\rightleftharpoons$	$NO_3^-(aq)$	$H^+(aq)$	H_2O
Initial conc / mol dm^{-3}	0.005	0.012		0	0	
Eqm conc / mol dm^{-3}	$0.005 - 10^{-4.2}$ $= 0.0049369$	$0.012 - 2 \times 10^{-4.2}$ $=$ 0.011873		$10^{-4.2}$	$10^{-4.2}$	

$$K_c = \frac{(10^{-4.2})^2}{(4.9369 \text{ X } 10^{-3})(1.1873 \text{ X } 10^{-2})^2} = 5.72 \text{ X } 10^{-3}\ mol^{-1}\,dm^3 \text{ (3sf)}$$

(iii) State how the K_c in **(ii)** would change when the amount of NH_3 in wastewater is increased to 10 mol. **[1]**

K_c would remain the same.

(iv) The nitrification process was carried out at room temperature. It was observed that the outer surface of the reaction vessel was cold after some time. **[2]**

By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia.

The (forward) reaction is endothermic. Hence, we can increase the temperature to shift the equilibrium position right, so as to absorb the excess heat, which allows more NH_3 to be converted.

(v) Construct a suitable energy cycle using the following equations to show how the enthalpy change of reaction, ΔH_r, can be determined. **[3]**

$NH_3\ (aq) + 2O_2\ (g) \qquad NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l)$ $\quad \Delta H_r$

$NH_3(aq) + O_2(g) + H_2(g) \qquad NH_2OH(aq) + H_2O(l)$ $\quad \Delta H_1$

$NH_2OH(aq) + H_2O(l) + \frac{1}{2}O_2(g) \qquad NO_3^-(aq) + 2H_2(g) + H^+(aq)$ $\quad \Delta H_2$

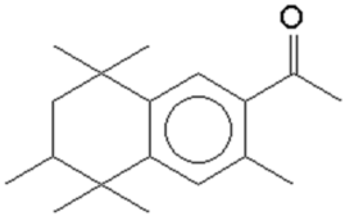
$2H_2O(l) \qquad 2H_2(g) + O_2(g)$ $\quad \Delta H_3$

$$\begin{tikzcd}
NH_3(aq) + 2O_2(g) + H_2(g) \arrow[r, phantom, "\Delta H_r"] \arrow[d, "\Delta H_1"] & NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l) + H_2\ (g) \arrow[ddl, "\frac{1}{2}\Delta H_3"'] & \\
NH_2OH\ (aq) + H_2O\ (l) + O_2\ (g) \arrow[d, "\Delta H_2"] & & \Delta H_3 \\
NO_3^-\ (aq) + 2H_2\ (g) + H^+\ (aq) + \frac{1}{2}\ O_2\ (g) & &
\end{tikzcd}$$

$\Delta H_r + \frac{1}{2}\ \Delta H_3 = \Delta H_1 + \Delta H_2$

$\Delta H_r = \Delta H_1 + \Delta H_2 - \frac{1}{2}\ \Delta H_3$

(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, $C_{18}H_{26}O$, is one such organic compound found commonly in sludge. It has a melting point of 54.5°C.



tonalide

(i) Write an equation which describes the standard enthalpy change of combustion of tonalide. **[1]**

$C_{18}H_{26}O\ (s) + 24O_2\ (g) \rightarrow 18CO_2\ (g) + 13H_2O\ (l)$

(ii) The enthalpy change of combustion of tonalide is −865 kJ mol^{-1}. **[2]**

Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide.

Amt of tonalide = 900 / (18 X 12.0 + 26 X 1.0 + 16.0) = 3.4883 mol

Amt of heat released (100%) = 865 X 3.4883 = 3017.4 kJ

Amt of energy harnessed (70%) = 3017.4 X 0.7 = 2110 kJ (3sf)

(iii) The sign of the entropy change of combustion of tonalide is positive. Briefly explain the effect of temperature on the spontaneity of combustion of tonalide. **[1]**

$\Delta G = \Delta H - T\Delta S$

$T\Delta S > 0$

$\Delta H < 0$

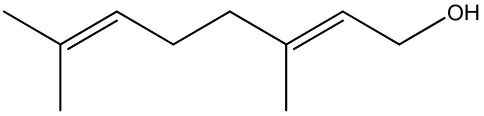
ΔG becomes more negative at higher temperatures. Hence, the combustion is more feasible.

OR

ΔG is always negative at all temperatures. Hence, the combustion is feasible at all temperatures.

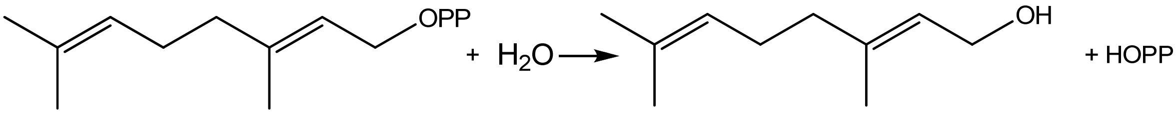
[Total: 20]

3 Geraniol, $C_{10}H_{18}O$, is commonly used in perfumes and food flavourings.



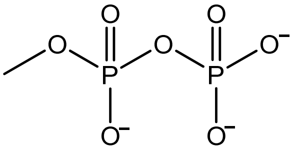
Geraniol

It is produced from geranyl diphosphate as shown in the following equation.

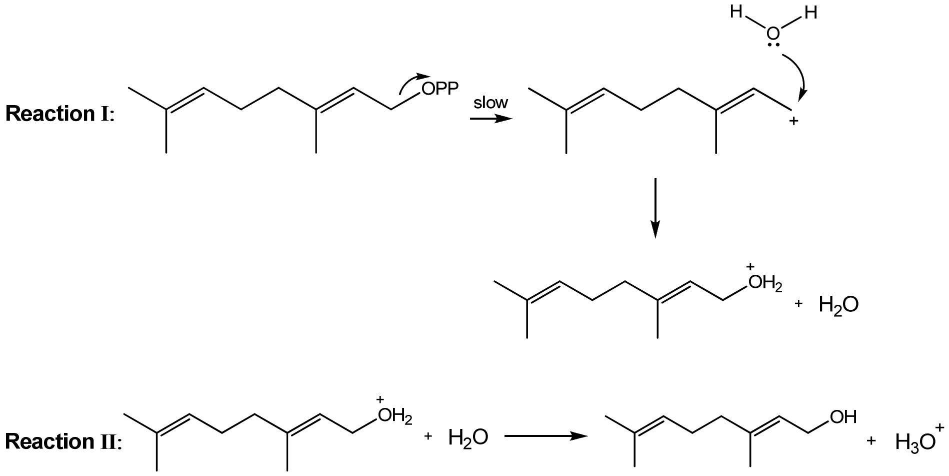


Geranyl diphosphate

where OPP :



(a) The mechanism of this reaction consists of the following:



(i) State the mechanism in reaction I. **[1]**

Nucleophilic substitution

(ii) Explain why the mechanism in reaction **I** takes place in two steps instead of one step.

OPP is a **bulky group** which creates **steric hindrance** for the nucleophile to attack the carbon bonded to OPP / **transition state is unstable**.

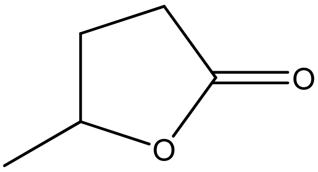
OR

OPP is negatively charged so it repels the approaching nucleophile (H_2O).

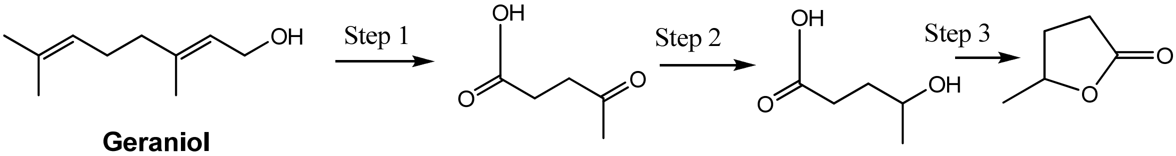
(iii) State the role of water in reaction **II**. **[1]**

It acts as a **<u>Bronsted-Lowry / Lewis base</u>** (as it accepts H^+ to form H_3O^+) or **<u>nucleophile</u>**.

(iv) The following compound can be synthesised from geraniol. **[4]**



Propose a reaction scheme for this synthesis.



Geraniol

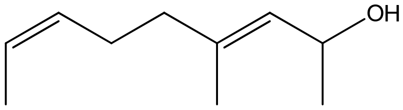
Step 1: $KMnO_4$, H_2SO_4 (aq), heat

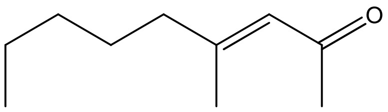
Step 2: $NaBH_4$ or Hydrogen / Nickel, heat

Step 3: concentrated sulfuric acid, heat

(v) Explain what is meant by constitutional isomers and draw a constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine. **[2]**

They are compounds with the <u>same molecular formula</u> but <u>different structural formulae</u>





OR Any other structure with same molecular formula with R-CO(CH_3) or R-CH(OH)CH_3

(b) Geranyl diphosphate can be synthesised using P_4O_{10}.

(i) Write an equation for the reaction of P_4O_{10} in water and describe the effect of the resulting solution on universal indicator solution. **[2]**

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

Universal indicator will turn red / orange.

(ii) Naturally occurring phosphorus contains the isotopes ^{31}P, ^{32}P and ^{33}P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively. **[2]**

Isotopes are elements with the same atomic number / same number of protons but different mass number / due to different number of neutrons.

relative atomic mass = (0.911 x 31) + (0.079 x 32) + (0.01 x 33) = 31.1

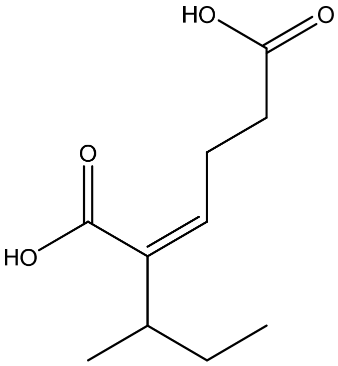
(c) Geraniol is a by-product of the metabolism of sorbic acid, C_5H_7COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt. **[3]**

$C_5H_7COOH + OH^- \rightarrow C_5H_7COO^- + H_2O$

$C_5H_7COO^- + H^+ \rightarrow C_5H_7COOH$

A large reservoir of acid and salt will help to remove a small amount of base and acid respectively to ensure that the pH remains **relatively/almost** constant/resists pH changes.

(d) Another constitutional isomer of geraniol is compound **X**. **X** does not react with 2,4-dinitrophenylhydrazine. **X** produces effervescence when sodium metal is added to it. When hot acidified $K_2Cr_2O_7$ is added to **X**, orange solution remains. On addition of aqueous bromine to **X**, the orange solution decolourises and compound **Y** is formed. **X** reacts with hot acidified $KMnO_4$ to form compound **Z** only. When **Z** is reacted with excess concentrated H_2SO_4 at 170 °C, the following product is obtained. **[5]**

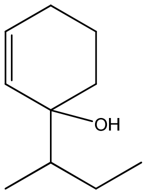


X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

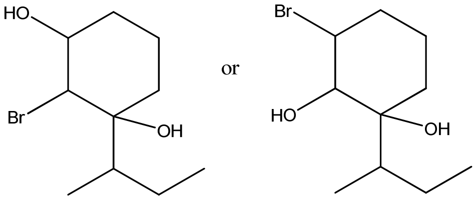
Observations	**Deductions**
X does not react with 2,4-DNPH.	**X** is not an aldehyde or ketone / not a carbonyl compound.
X produces effervescence when Na added.	Redox. Gas is H_2. **X** contains hydroxyl group (or –OH group or alcohol).
Orange solution remains when hot $K_2Cr_2O_7$ added to **X**.	**X** contains tertiary alcohol.
On addition of aqueous bromine to **X**, the orange solution turns colourless.	**X** undergoes electrophilic addition. **X** contains C=C (or alkene).
X reacts with hot acidified $KMnO_4$ to produce **Z** only.	Oxidation **X** is a cyclic compound
Z reacts with excess concentrated H_2SO_4 at 170 °C.	Elimination
X, **Y** and **Z** are all able to rotate the plane of polarised light.	All 3 compounds have chiral carbon.

Structures

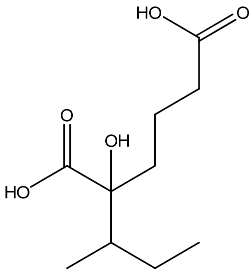
X:



Y:



Z:



[Total: 21]

Section B

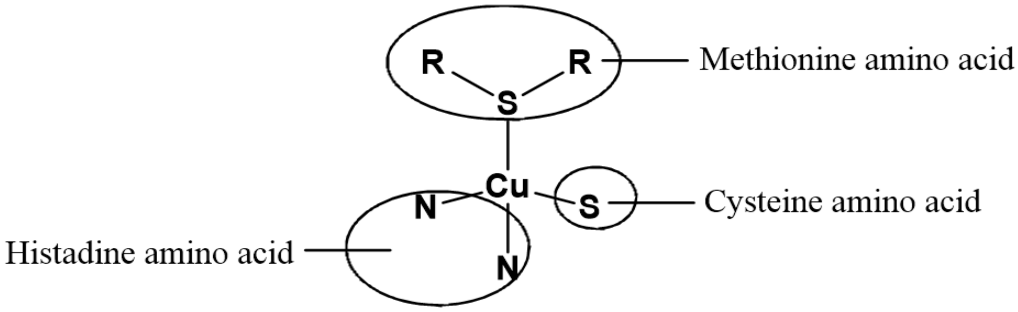
Answer **one** question in this section.

4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.

(a) Explain what is meant by the term *transition element*. **[1]**

It is a **d-block element** which forms **one or more stable ions** with **partially filled d subshells**.

(b) **(i)** Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu^{2+} in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu^{2+} act as ligands.



Define the term *ligand*. **[1]**

It is an **ion or molecule** which contains **at least 1 atom bearing a lone pair of electrons** which can be **donated into a low-lying vacant orbital of a central metal atom or ion** by forming a **dative bond**.

(ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu^+ complex which has a deep blue colour.

State the electronic configuration of Cu^+. **[1]**

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(iii) The deep blue colour seen is considered to be unusual.

Suggest a reason why this is so. **[1]**

The **d orbitals in Cu^+ are completely filled** and therefore, **no d-d transition** can occur and the complex should not be coloured.

(c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is $Cu_3(CO_3)_2(OH)_2$ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.

(i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH^- may be produced from a saturated solution of sodium carbonate. **[1]**

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid.

Suggest an explanation why the proposed method is not ideal. **[1]**

The solid is **insoluble** and **cannot be directly titrated**.

OR

The solid hydroxide and carbonate (especially) will be **too slow to react** with the sulfuric acid.

OR

The **end-point will not be accurately determined**.

(iii) Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm³ of 0.550 mol dm⁻³ sulfuric acid. The resulting solution was topped up to 250 cm³ using deionised water.

Step 2: 25.0 cm³ of the solution required 15.55 cm³ of 0.200 mol dm⁻³ sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

$$Cu_3(CO_3)_2(OH)_2 + \boldsymbol{a}\ H_2SO_4 \rightarrow \boldsymbol{a}\ CuSO_4 + \boldsymbol{b}\ H_2O + \boldsymbol{c}\ CO_2$$

Complete the balancing of the above equation by deducing values for ***a***, ***b*** and ***c***. Hence, calculate the percentage of azurite in the rock sample. **[3]**

$Cu_3(CO_3)_2(OH)_2 + 3\ H_2SO_4 \rightarrow 3\ CuSO_4 + 4\ H_2O + 2\ CO_2$

Amount of NaOH = Amount of excess H_2SO_4 = ½ x 15.55/1000 x 0.2 = 1.55×10^{-3} mol

Amount of excess H_2SO_4 in 250 cm³ = 10 x 1.55×10^{-3} = 0.0155 mol

Amount of H_2SO_4 reacted with azurite = (130/1000 x 0.55) – 0.0155 = 0.05595 mol

Amount of azurite = 0.05595 / 3 = 0.01865 mol

Mass of azurite = 0.01865 x 344.5 = 6.42 g

% azurite in rock sample = 6.425 / 7 x 100% = 91.8% (to 3 sf)

(iv) Using your knowledge on the thermal decomposition of carbonates and given that $Cu(OH)_2$ thermally decomposes to form CuO and H_2O, write an equation for the thermal decomposition of azurite.

Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. **[3]**

$Cu_3(CO_3)_2(OH)_2 \rightarrow 3\ CuO + H_2O + 2\ CO_2$

Mass of azurite in 1 mol = 344.5 g

Mass of H_2O in 1 mol = 18 g

Mass of CO_2 in 2 mol = 2 x 44 = 88 g

% loss in mass = (18+88) / 344.5 x 100% = 30.76% ≈ 30.8% (to 3 sf)

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm^{-3} sodium carbonate solution and 0.100 mol dm^{-3} potassium hydroxide solution. Calculate the concentration of Cu^{2+} required to begin precipitating $CuCO_3$ and $Cu(OH)_2$ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

K_{sp} of $CuCO_3$ = 7.08×10^{-9} $mol^2\ dm^{-6}$

K_{sp} of $Cu(OH)_2$ = 4.8×10^{-20} $mol^3\ dm^{-9}$

[3]

When $Cu(OH)_2$ first precipitates,

$[Cu^{2+}] = 4.8 \times 10^{-20} / (0.1)^2 = \underline{\mathbf{4.8 \times 10^{-18}\ mol\ dm^{-3}}}$

When $CuCO_3$ first precipitates,

$[Cu^{2+}] = 7.08 \times 10^{-9} / 0.1 = \underline{\mathbf{7.08 \times 10^{-8}\ mol\ dm^{-3}}}$

$\underline{\mathbf{Cu(OH)_2}}$ will precipitate first.

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations.

[2]

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \mathbf{Cu(OH)_2(s)} + 6H_2O\,(l)$ **---- eqm (1)**

blue solution **blue precipitate**

When <u>excess</u> aqueous NH_3 is added, **<u>ligand exchange</u>** occurs to form a deep blue solution.

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4\,H_2O$ --- eqm (2)

deep blue solution

The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ decreases the concentration of $[Cu(H_2O)_6]^{2+}$ causing **<u>position of equilibrium (1) to shift to the left in order to replenish $[Cu(H_2O)_6]^{2+}$</u>**. Hence, blue ppt of $Cu(OH)_2$ dissolves, forming the deep blue solution.

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

[3]

Impure copper ore can be purified using electrolysis. The impure copper is placed at the anode, while pure copper is used as the cathode. The electrolyte used is aqueous $CuSO_4$.

When an electric current is applied, copper at the **anode (+)**, together with Zn are oxidised to their ions owing to their relatively less positive $E^\ominus$ values. Hence, Cu^{2+} and Zn^{2+} then migrate to the cathode / remain in solution.

Ag will not be oxidised as it has a relatively positive $E^\ominus$ values and it falls off the electrode and accumulate at the bottom as anodic sludge.

At the cathode, only Cu^{2+} ions are reduced to Cu, which is deposited on the pure copper electrode, due to its more positive $E^\ominus$.

Zn^{2+} remain as ions in the solution as they do not reduce to metals easily.

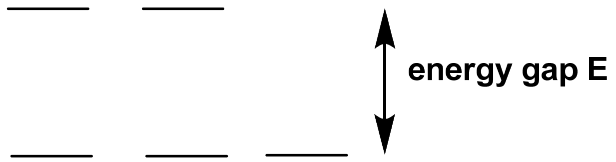
[Total: 20]

5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.

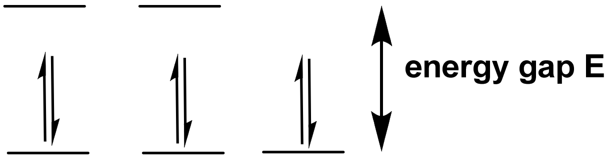
(a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe^{2+} ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

(i) A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.

Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe^{2+} in oxyhaemoglobin.

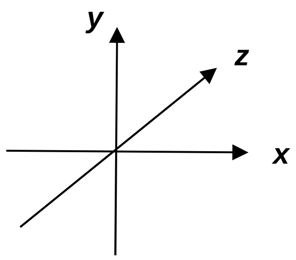


[1]



(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.

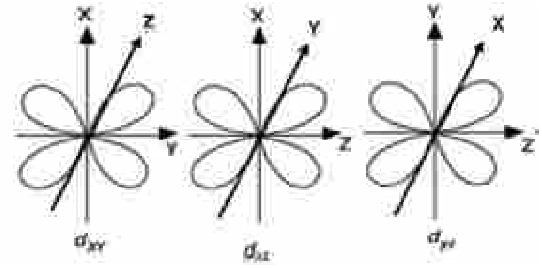
Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



[3]

In octahedral complexes, the lone pair of electrons on the 6 ligands **approach Fe^{2+} along the axes**. This results in **electronic repulsion**, which causes the energy level of $3d_{x2-y2}$ and $3d_{z2}$ to be higher.

Either one:

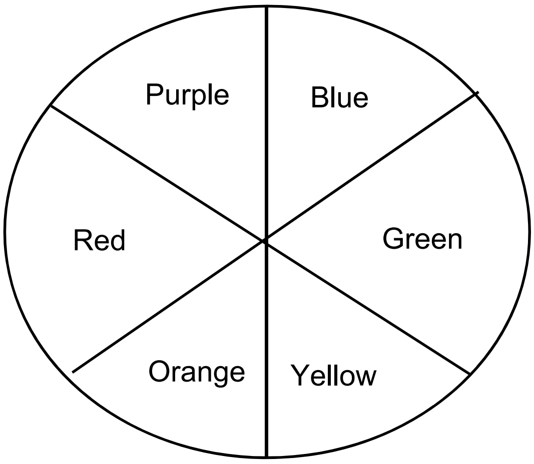


(iii) Explain why oxyhaemoglobin is red. **[2]**

When a **d electron from the lower energy d orbital absorbs light energy (visible light with wavelength corresponding to this energy gap)**, it is **promoted to the higher energy d orbital** and this is d-d transition.

The **red colour seen is complementary to the colour absorbed / red colour is not absorbed**.

(iv) The complementary colours are shown using the following colour wheel.



The wavelength of each colour component in visible light is as provided.

Colour	**Purple**	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength / nm	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750

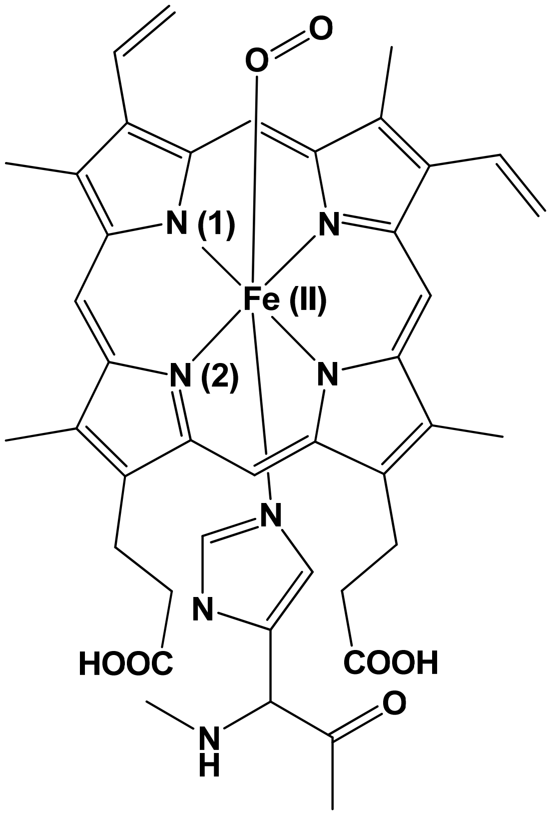
Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

[2]

O_2 causes a larger energy gap between the 3d orbitals.

Oxyhaemoglobin absorbs **green colour which is of lower wavelength / higher energy than the orange colour** that deoxyhaemoglobin absorbs.

(v) Fe^{2+} complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled **(1)** and the bond angle around the N atom labelled **(2)**.

[2]

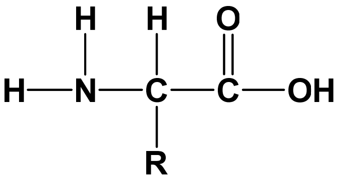
Charge around N(1): 1−

Bond angle around N(2): 120□

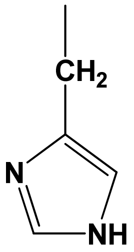
(vi) Besides Fe^{2+}, Fe^{3+} may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. **[1]**

The **energy of 3d and 4s electrons are close in proximity**. Hence, the electrons in 3d and 4s orbitals may be shared or lost to give variable oxidation states.

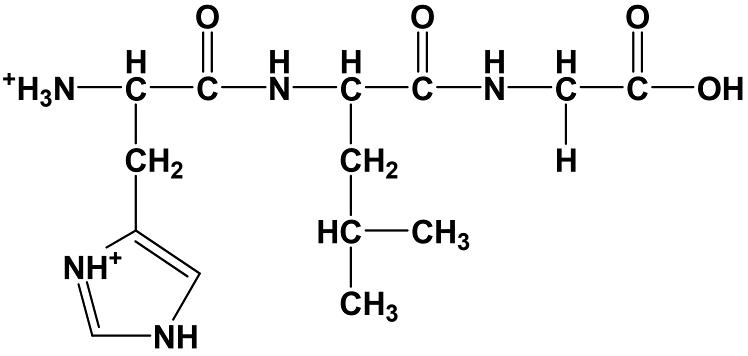
(vii) Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



In each chain, histidine, leucine and glycine amino acids can be found.

Amino acid	**R group**
Histidine	
Leucine	$-CH_2CH(CH_3)_2$
Glycine	$-H$

Draw the structural formula of a tripeptide with the sequence histidine-leucine-glycine at pH 2. **[2]**

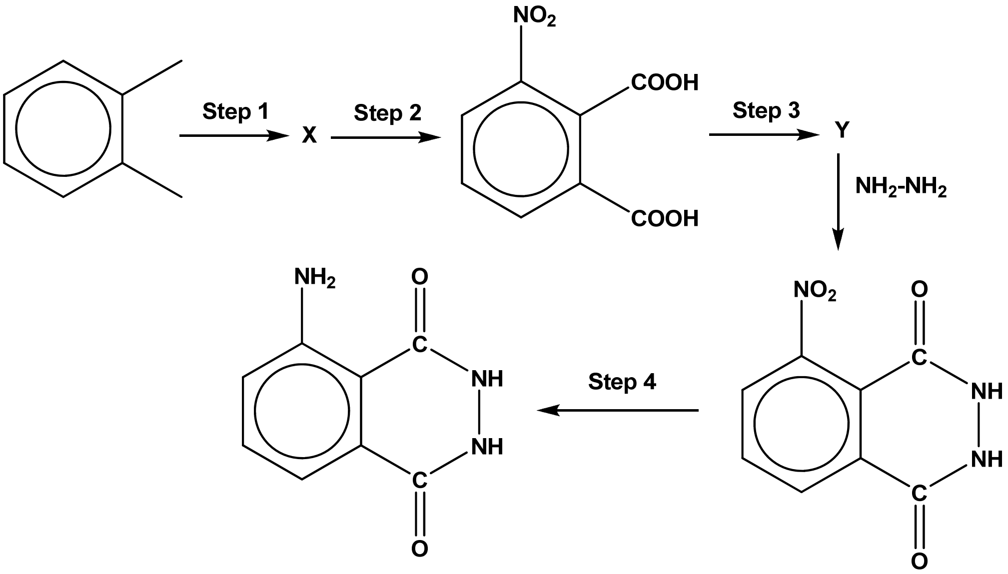


(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. **[1]**

(6 mol dm^{-3}) **concentrated** HC*l* (Any mineral acid), **prolonged heating** / several hours (for 24h)

(b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood.

The synthetic route for luminol is as shown.



Luminol

(i) State the reagents and conditions for **steps 1** to **3**. **[3]**

Step 1: Concentrated sulfuric acid, concentrated nitric acid, < 55 □C

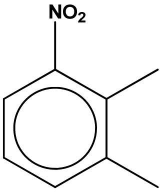
Step 2: $KMnO_4$, H_2SO_4 (aq), heat

Step 3: PCl_5 or $SOCl_2$

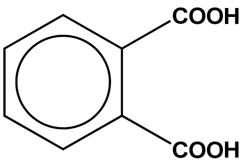
Note: Steps 1 and 2 can be interchangable but temperature > 55°C

(ii) Draw the structures for intermediate products **X** and **Y**. **[2]**

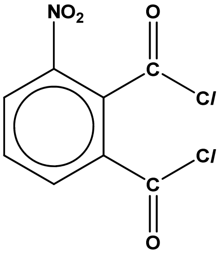
X:



or



Y:



(iii) For **Step 4**, $Na_2S_2O_4$ is commonly used as the reagent.

State the role of $Na_2S_2O_4$. **[1]**

Reducing agent

[Total: 20]

Name:		**Shift:**	
Class:		**Laboratory:**	

ST ANDREW'S JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

PAPER 4 PRACTICAL

Chemistry **28 August 2018**

Higher 2 **2 hours 30 minutes**

READ THESE INSTRUCTIONS FIRST.

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** the questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 16 and 17.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
Total	

This document consists of **17** printed pages including this page.

Answer all the questions in the spaces provided.

1 Determination of percentage by mass of sodium carbonate in a mixture of sodium carbonate and sodium hydrogen carbonate

The complete reaction between sodium carbonate and hydrochloric acid can be represented as shown:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

However, when sodium carbonate is titrated against hydrochloric acid, it reacts with hydrochloric acid in two separate stages.

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$ ———————— ***reaction 1***

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ ———————— ***reaction 2***

When a mixture of sodium carbonate and sodium hydrogen carbonate is titrated against hydrochloric acid using thymolphthalein indicator, the blue colour of the indicator is discharged when sodium carbonate is partially neutralised as represented by ***reaction 1***.

Screened methyl orange is then added and a further quantity of hydrochloric acid is necessary to bring about a colour change when ***reaction 2*** is complete. This further amount of acid reacts with both the sodium hydrogen carbonate formed in ***reaction 1*** as well as the sodium hydrogen carbonate present initially in the mixture.

(a) In this experiment, you will determine the amount of Na_2CO_3 and $NaHCO_3$ in **FA 1** by following the procedures below.

FA 1 is a solution containing sodium carbonate, Na_2CO_3 and sodium hydrogen carbonate, $NaHCO_3$.

FA 2 is an aqueous solution containing 0.50 mol dm^{-3} of hydrochloric acid, HC*l*.

1. Pipette 25.0 cm^3 of **FA 1** into a conical flask.

2. Add 5 drops of thymolphthalein indicator and titrate **FA 1** against **FA 2** in a burette.

3. When the blue colour is discharged, note and record the burette reading in the table provided on page 3. This end–point may not be easily seen. Therefore, you are advised to put a white tile under your conical flask to help you. If you are unsure if the blue colour has discharged or not, you may also add a few more drops of thymolphthalein to the solution.
   Do not discard this mixture!
   *(The volume of **FA 2** required to reach the first end–point need not be consistent but it should not exceed 15 cm^3.)*

4. Add 3 drops of screened methyl orange to this mixture and **continue** the titration until the second end–point is reached. Record the final burette reading in the same table provided on page 3.

5. Perform sufficient titrations to obtain consistent results for the **second end–point**, which is the total volume of **FA 2** required.

Results

	1	2	3	
Final burette reading (with screened methyl orange) / cm^3				
Final burette reading (with thymolphthalein) / cm^3				
Initial burette reading / cm^3				
Total volume of **FA 2** used to reach the second end–point / cm^3				
Place a tick for the consistent results				

[4]

(b) ***x*** is the average volume of **FA 2** required to reach the first end point.

y is the average **further** volume of **FA 2** required to reach the second end–point.

From your 2 consistent titration results, calculate ***x*** and ***y***.

x = ……………………

y = …………………… **[2]**

(c) **(i)** Using ***x***, calculate the amount, in moles, of Na_2CO_3 in 25.0 cm^3 of **FA 1**.

Number of moles of Na_2CO_3 = ………………………

[1]

(c) **(ii)** Using ***y***, calculate the total amount, in moles, of $NaHCO_3$ in the reaction mixture.

Total number of moles of $NaHCO_3$ = ……………………… **[1]**

(d) From your answers in **(c)**, calculate the amount, in moles, of $NaHCO_3$ in 25.0 cm^3 of **FA 1**.

Number of moles of $NaHCO_3$ = ……………………… **[1]**

(e) Calculate the percentage by mass of sodium carbonate in **FA 1**, which is a mixture of $NaHCO_3$ and Na_2CO_3.
[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

[2]

(f) A student decides to carry out the same experiment in **(a)** by using a pH meter to determine the percentage by mass of Na_2CO_3 in the mixture.

Given that pK_b of CO_3^{2-} = 3.68 and pK_b of HCO_3^- = 7.62, sketch a graph to show how the pH of the mixture changes as HC*l* is added. You may use your titre values in any set of experiments obtained in **(a)** for the volume of HC*l* at the two equivalence points.

[2]

Planning

(g) Unlike Group 2 carbonates, solid sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. However, for solid sodium hydrogencarbonate, $NaHCO_3$, it will form sodium carbonate, steam and carbon dioxide when heated.

(i) Write an equation, with state symbols, to represent the thermal decomposition of sodium hydrogen carbonate.

………………………………………………………………………………………………………. **[1]**

(g) **(ii)** Given the above information, you are to devise a plan to determine the percentage by mass of $NaHCO_3$ in a solid mixture of $NaHCO_3$ and Na_2CO_3.

You may assume you are provided with

- a boiling tube
- a pair of tongs
- 10 g of $NaHCO_3$ and Na_2CO_3 solid mixture
- a heat resistant mat
- equipment normally found in a school or college laboratory

In your plan, you should include details of:

- procedure you would follow, including the apparatus you would use and the safety precautions to take,
- measurements you would take,
- a brief outline of how the results can be used to determine the percentage by mass of $NaHCO_3$ in the mixture. You may make assumptions for the masses involved and use appropriate molar mass values to solve this.
  [A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

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.... **[6]**

[Total: 20]

2 Determination of n in the complex ion formula $[Cu(NH_3)_n]^{2+}$

Many transition metal ions possess the ability to form complexes with ligands, which can either be organic or inorganic molecules/ions.

In this experiment, you will determine the value of n in the formula $[Cu(NH_3)_n]^{2+}(aq)$, which is the complex ion formed when aqueous NH_3 is added to $Cu^{2+}(aq)$.

Different volumes of $CuSO_4$ solution and aqueous ammonia are mixed and the corresponding temperature changes are measured.

FA 3 is 0.5 mol dm^{-3} $CuSO_4$ solution
FA 4 is 2.0 mol dm^{-3} aqueous ammonia

(a) Measure and record the temperatures of the given solutions **FA 3** and **FA 4**.

$T_{FA\ 3}$ = ………………………..°C

$T_{FA\ 4}$ = ………………………..°C **[1]**

(b) Carry out the following procedures and prepare a table for your results on **page 8**.
Your table should include i) $V_{FA\ 3}$, ii) $V_{FA\ 4}$, iii) T_{initial}, iv) $T_{\max}$, v) temperature rise, ΔT and vi) colour of solution and precipitate (if any).

Procedures:

Experiment 1

- Measure 9.00 cm^3 of **FA 3** from a burette into a boiling tube.
- Add into the boiling tube 1.00 cm^3 of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as $T_{\max}$.
- Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in **experiment 2**.

Experiment 2

- Measure 8.00 cm^3 of **FA 3** from a burette into the boiling tube.
- Add into the boiling tube 2.00 cm^3 of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as $T_{\max}$. Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in subsequent experiments.

Experiments 3 – 9

Perform 7 more experiments, each time reducing the volume of **FA 3** by 1.00 cm^3 but increasing the volume of **FA 4** by 1.00 cm^3 such that the total volume of solution is kept constant at 10.00 cm^3.

The weighted average initial temperature, T_{intial}, of **FA 3** and **FA 4** can be calculated by using the formula:

$$T_{\text{initial}} = \frac{(V_{\text{FA 3}} \times T_{\text{FA 3}}) + (V_{\text{FA 4}} \times T_{\text{FA 4}})}{V_{\text{FA 3}} + V_{\text{FA 4}}}$$

where $V_{FA\,3}$ and $V_{FA\,4}$ are the volumes of **FA 3** and **FA 4** in the mixture

$T_{FA\,3}$ and $T_{FA\,4}$ are the temperatures of **FA 3** and **FA 4** measured in **(a)** **[5]**

Calculate T_{initial} for each experiment and include it in your table of results.

(c) Plot a graph of temperature rise, ΔT, against volume of **FA 4**. Your plot should consist of **two** best–fit **straight lines**.

[3]

(d) **(i)** Show on your graph how the volume of **FA 4** that corresponds to the highest temperature rise can be determined.

Volume of **FA 4** with highest temperature rise = ... cm^3

Hence, calculate the volume of **FA 3** that corresponds to this volume of **FA 4**.

Volume of **FA 3** = ... cm^3 **[3]**

(d) **(ii)** Calculate the amount, in moles, of aqueous ammonia in the volume of **FA 4** with the highest temperature rise.

Amount of NH_3(aq) = **……………………..**

[1]

(iii) Calculate the amount, in moles, of Cu^{2+} ions in the volume of **FA 3** that you have determined in **(i)**.

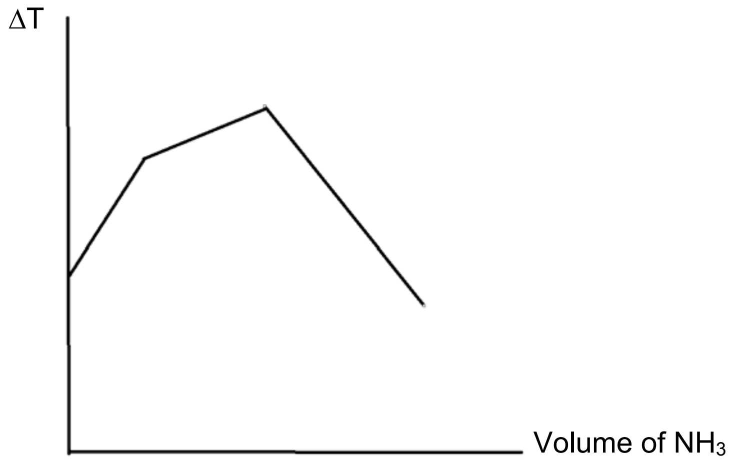
Amount of Cu^{2+}(aq) = **……………………..**

[1]

(iv) Calculate the number of moles of NH_3 bonded with one mole of Cu^{2+} ions in the solution and hence, deduce the value of n in the formula $[Cu(NH_3)_n]^{2+}$.

n = ……….. **[1]**

(e) The graph of ∆T against volume of NH_3 should theoretically look like the one below, with a combination of two straight lines with different positive gradients before the change in temperature starts to decrease.



With reference to the observations that you have recorded in the table on page 8, explain, with the aid of two relevant equations, why the graph is a combination of two straight lines with different positive gradients.

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……… **[3]**

(f) Suggest an improvement that you will make to this experiment to improve the accuracy of the results obtained.

……………………………………………………………………………………………………

…………………………………………………………………………………………………… **[1]**

Planning

(g) Chromium cations can also form complexes. A student was given a solid which has a formula of either $[Cr(H_2O)_5Cl]Cl_2$ or $[Cr(H_2O)_4Cl_2]Cl$. The relative formula mass of the compound is 248.5.

When dissolved in water, the chloride ions not involved in the complex ion would be liberated into the solution.

$$[Cr(H_2O)_5Cl]Cl_2(s) \rightarrow [Cr(H_2O)_5Cl]^{2+}(aq) + 2Cl^-(aq)$$

$$[Cr(H_2O)_4Cl_2]Cl(s) \rightarrow [Cr(H_2O)_4Cl_2]^{+}(aq) + Cl^-(aq)$$

To determine the formula of the solid given, a student prepared a 250 cm^3 of standard solution using 29.80 g of the given solid. He then determined the amount of free chloride ions by titrating 25.0 cm^3 of the standard solution against 0.3 mol dm^{-3} silver(I) nitrate solution while using some potassium chromate(VI) as an indicator. When silver(I) nitrate solution was added, a white precipitate of $AgCl$ was formed.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

When all the free chloride ions had precipitated, a red–brown precipitate of silver chromate(VI) was formed to signify that the end–point had been reached.

(i) The teacher commented that the student should have reduced the mass of solid used by half for the preparation of standard solution.
Explain, with the aid of suitable calculations, why 29.80 g is not a suitable mass to be used. **[2]**

(g) **(ii)** You are to describe how the student should prepare the standard solution by using his teacher's proposal.

In your answer, include

- the procedures involved in the preparation of the standard solution,
- the apparatus and equipment used to prepare the standard solution.

[2]

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[Total: 23]

3 Identifying cations in an unknown sample

(a) You are given **FA 5**, which is an aqueous solution containing two cations and one anion. One of the cations is Cu^{2+}. The other cation can be found from the list in the **Qualitative Analysis Notes** provided on page 16.

Perform the tests described in Table 3.1. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

	Tests	Observations
1.	To 1 cm depth of **FA 5**, add 2 cm depth of **FA 1** (from question 1).	
2.	Add about 3 cm^3 of dilute aqueous ammonia to 1 cm^3 of **FA 5.** Filter the mixture and note the appearance of both the filtrate and residue. Add dilute sulfuric acid dropwise to the filtrate till in excess.	
3.	Add a spatula of solid potassium iodide to 3 cm^3 of **FA 5.** Filter the mixture and note the appearance of the filtrate. Add 1 cm^3 of hexane to the filtrate and shake well.	

[5]

(b) Consider your observations in Table 3.1.

(i) State the other cation which is present in **FA 5**.

……………………………………………………………………………………………………. **[1]**

(ii) **FA 5** turns Universal Indicator paper red. With reference to this and your observations in test 1, write an ionic equation to represent the reaction between **FA 1** and **FA 5**.

……………………………………………………………………………………………………. **[1]**

(iii) With reference to test 3, suggest the identity of the species which was responsible for the observations seen when hexane was added to the filtrate. Hence, suggest the property of **FA 5**.

……………………………………………………………………………………………………. **[2]**

Planning

(c) **FA 5** also contains an anion. To determine the identity, a student heated **FA 5** with A*l* and NaOH(aq). A gas was evolved and it turned moist red litmus paper blue.

(i) Based on the observations given, state the possible identities of the anions.

……………………………………………………………………………………………………. **[1]**

(ii) You are provided with the reagents NaOH(aq), NH_3(aq), HNO_3(aq) and $AgNO_3$(aq).

Suggest a test to confirm the identity of the anion in **FA 5**. State the expected observations.

DO NOT carry out the test.

Test: ……………………………………………………………………………………………

…………………………………………………………………………………………………….

Expected observation for each of the possible anions in **(i)**.

…………………………………………………………………………………………………….

……………………………………………………………………………………………………. **[2]**

[Total: 12]

~ END OF PAPER ~

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

Cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off–white ppt. rapidly turning brown on contact with air insoluble in excess	off–white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

Halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange–red
iodine, I_2	black solid / purple gas	brown	purple

Name:		**Shift:**	
Class:		**Laboratory:**	

ST ANDREW'S JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

PAPER 4 PRACTICAL

Chemistry **28 August 2018**

Higher 2 **2 hours 30 minutes**

READ THESE INSTRUCTIONS FIRST.

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided above.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** the questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 16 and 17.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
Total	

This document consists of **17** printed pages including this page.

Answer all the questions in the spaces provided.

1 Determination of percentage by mass of sodium carbonate in a mixture of sodium carbonate and sodium hydrogen carbonate

The complete reaction between sodium carbonate and hydrochloric acid can be represented as shown:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

However, when sodium carbonate is titrated against hydrochloric acid, it reacts with hydrochloric acid in two separate stages.

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$ ---------------- ***reaction 1***

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ ---------------- ***reaction 2***

When a mixture of sodium carbonate and sodium hydrogen carbonate is titrated against hydrochloric acid using thymolphthalein indicator, the blue colour of the indicator is discharged when sodium carbonate is partially neutralised as represented by ***reaction 1***.

Screened methyl orange is then added and a further quantity of hydrochloric acid is necessary to bring about a colour change when ***reaction 2*** is complete. This further amount of acid reacts with both the sodium hydrogen carbonate formed in ***reaction 1*** as well as the sodium hydrogen carbonate present initially in the mixture.

(a) In this experiment, you will determine the amount of Na_2CO_3 and $NaHCO_3$ in **FA 1** by following the procedures below.

FA 1 is a solution containing sodium carbonate, Na_2CO_3 and sodium hydrogen carbonate, $NaHCO_3$.

FA 2 is an aqueous solution containing 0.50 mol dm^{-3} of hydrochloric acid, HC*l*.

1. Pipette 25.0 cm^3 of **FA 1** into a conical flask.

2. Add 5 drops of thymolphthalein indicator and titrate **FA 1** against **FA 2** in a burette.

3. When the blue colour is discharged, note and record the burette reading in the table provided on page 3. This end-point may not be easily seen. Therefore, you are advised to put a white tile under your conical flask to help you. If you are unsure if the blue colour has discharged or not, you may also add a few more drops of thymolphthalein to the solution.
   Do not discard this mixture!
   *(The volume of **FA 2** required to reach the first end-point need not be consistent but it should not exceed 15 cm^3.)*

4. Add 3 drops of screened methyl orange to this mixture and **continue** the titration until the second end-point is reached. Record the final burette reading in the same table provided on page 3.

5. Perform sufficient titrations to obtain consistent results for the **second end-point**, which is the total volume of **FA 2** required.

Results

	1	2	3	
Final burette reading (with screened methyl orange) / cm^3	30.80	40.50	30.60	
Final burette reading (with thymolphthalein) / cm^3	12.50	22.10	12.30	
Initial burette reading / cm^3	0.00	10.00	0.00	
Total volume of **FA 2** used to reach the second end-point / cm^3	30.80	30.50	30.60	
Place a tick for the consistent results		✓	✓	

[4]

[2] for accuracy of total volume of FA 2

[1] for 2 dp for all burette readings

[1] for correct sequence of burette readings, putting ticks for two total volume of FA 2 that are within 0.10 cm^3

(b) ***x*** is the average volume of **FA 2** required to reach the first end point.

y is the average **further** volume of **FA 2** required to reach the second end-point.

From your 2 consistent titration results, calculate ***x*** and ***y***.

$x = (12.10 + 12.30) / 2 = 12.20\ (cm^3)$

$$y = \frac{(40.50 - 22.10) + (30.60 - 12.30)}{2} = \frac{18.40 + 18.30}{2} = 18.35\ (cm^3)$$

[1] for correct calculations of x from the results in (a), in 2 dp
[1] for correct calculations of y from the results in (a), in 2 dp

x = ...

[2]

y = ...

(c) **(i)** Using ***x***, calculate the amount, in moles, of Na_2CO_3 in 25.0 cm^3 of **FA 1**.
ecf from (b); 0m if never use answer from (b)

No of moles of HCl = 12.20/1000 x 0.50 = 6.10 x 10^{-3} mol
No of moles of Na_2CO_3 = 6.10 x 10^{-3} mol **[1]**

Number of moles of Na_2CO_3 = ...

[1]

(c) **(ii)** Using ***y***, calculate the total amount, in moles, of $NaHCO_3$ in the reaction mixture.

ecf from (b); 0m if never use answer from (b)

No of moles of HC*l* = 18.35/1000 x 0.50 = 9.18 x 10 $^{-3}$ mol
Total no of moles of $NaHCO_3$ = 9.18 x 10 $^{-3}$ mol **[1]**

Total number of moles of $NaHCO_3$ = ……………………… **[1]**

(d) From your answers in **(c)**, calculate the amount, in moles, of $NaHCO_3$ in 25.0 cm^3 of **FA 1**.

No of moles of $NaHCO_3$ formed from Na_2CO_3 = 6.10 x 10 $^{-3}$ mol

No of moles of $NaHCO_3$ in **FA 1** = 9.18 x 10 $^{-3}$ – 6.10 x 10 $^{-3}$

= 3.08 x 10^{-3} mol **[1]**

i.e (c)(ii) – (c)(i)

Number of moles of $NaHCO_3$ = ……………………… **[1]**

(e) Calculate the percentage by mass of sodium carbonate in **FA 1**, which is a mixture of $NaHCO_3$ and Na_2CO_3.
[A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

Mass of $NaHCO_3$ in **FA 1** = 3.08 x 10 $^{-3}$ x 84.0 **i.e ((d) x 84)**

= 0.259 g

Mass of Na_2CO_3 in **FA 1** = 6.10 x 10 $^{-3}$ x 106.0 **i.e ((c)(i) x 106)**

= 0.647 g

[1] for correct calculation of mass of $NaHCO_3$ and Na_2CO_3

% by mass of Na_2CO_3 in **FA 1** = 0.647 / (0.647 + 0.259) x 100%

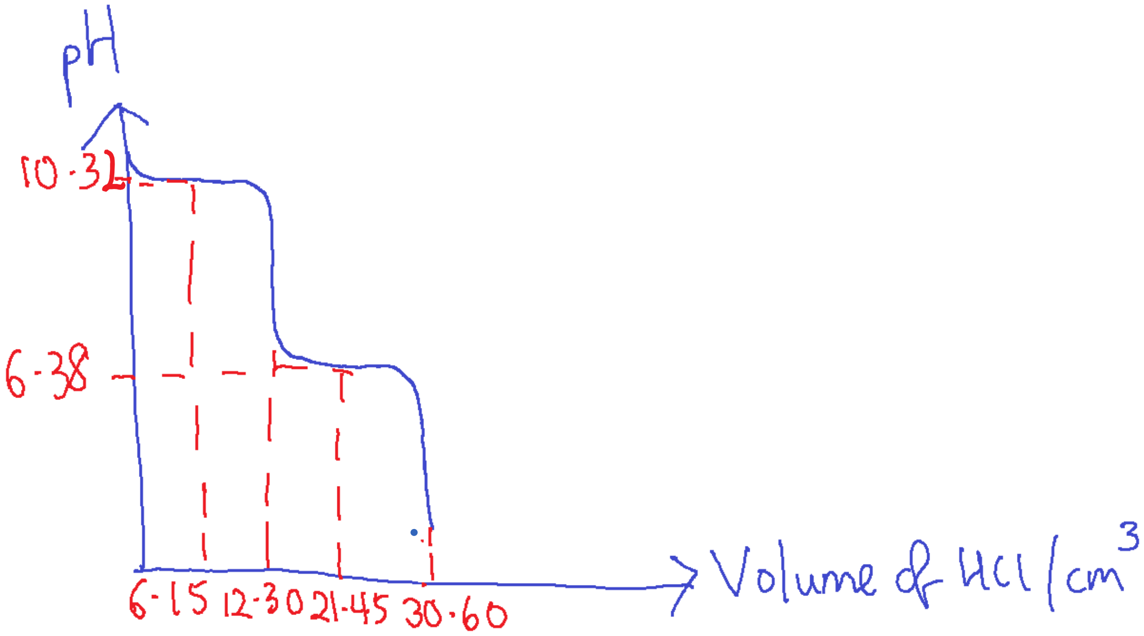
= 71.4 % **[1]** **[2]**

Apply ecf within part if student use wrong Mr for calculation of mass

(f) A student decides to carry out the same experiment in **(a)** by using a pH meter to determine the percentage by mass of Na_2CO_3 in the mixture.

Given that pK_b of CO_3^{2-} = 3.68 and pK_b of HCO_3^- = 7.62, sketch a graph to show how the pH of the mixture changes as HC*l* is added. You may use your titre values in any set of experiments obtained in **(a)** for the volume of HC*l* at the two equivalence points.

[2]



[1] for correct shape in the right direction with correct axes and unit

[1] for correct labelling of volumes at MBCs, pH at MBCs, 2 equivalence volumes using any set of titre volumes (including x and y)

Planning

(g) Unlike Group 2 carbonates, solid sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. However, for solid sodium hydrogencarbonate, $NaHCO_3$, it will form sodium carbonate, steam and carbon dioxide when heated.

(i) Write an equation, with state symbols, to represent the thermal decomposition of sodium hydrogen carbonate.

$2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$ **[1]**

Mole ratio 1 : ½ : ½ : ½ is acceptable

.... **[1]**

(g) **(ii)** Given the above information, you are to devise a plan to determine the percentage by mass of $NaHCO_3$ in a solid mixture of $NaHCO_3$ and Na_2CO_3.

You may assume you are provided with

- a boiling tube
- a pair of tongs
- 10 g of $NaHCO_3$ and Na_2CO_3 solid mixture
- a heat resistant mat
- equipment normally found in a school or college laboratory

In your plan, you should include details of:

- procedure you would follow, including the apparatus you would use and the safety precautions to take,
- measurements you would take,
- a brief outline of how the results can be used to determine the percentage by mass of $NaHCO_3$ in the mixture. You may make assumptions for the masses involved and use appropriate molar mass values to solve this.
  [A_r: Na, 23.0; H, 1.0; C, 12.0; O, 16.0]

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……………………………………………………………………………………………… **[6]**

Procedure **[4]**

1. Weigh the dry empty boiling tube using a weighing balance.
2. **Place 10 g (or any mass as defined) of sample powder in the boiling tube and weigh again**. Record the mass reading.
3. Using the tongs provided, **gently heat** the boiling tube with the sample using a Bunsen burner for about 2-3 minutes, **before strongly heating** the tube for another 5 minutes.
4. **Cool the boiling tube on a heat resistant mat before weighing the tube and sample**. Record the mass reading.
5. **Repeat the heat-cool-weigh process till consistent mass** is obtained.

Treatment of results:

Let the mass of solid mixture used be 10 g

Let the final mass (of Na_2CO_3) obtained be y g

Mass of H_2O and CO_2 = (10 – y) g

Mass of 1mol of H_2O and 1 mol of CO_2 = 18.0 + 44.0 = 62.0 g

Amount of H_2O and CO_2 evolved = 2(10 – y) / 62.0 mol **[1]**

= amount of $NaHCO_3$

OR

Amount of H_2O and CO_2 evolved = (10 – y) / 62.0 mol **[1]**

Amount of $NaHCO_3$ = 2(10 – y) / 62.0 mol

Mass of $NaHCO_3$ = [2(10 – y) / 62] x 84 g

% by mass = $\frac{84(10-y)}{31 \text{ x } 10}$ x 100% **[1]**

[Total: 20]

2 Determination of n in the complex ion formula $[Cu(NH_3)_n]^{2+}$

Many transition metal ions possess the ability to form complexes with ligands, which can either be organic or inorganic molecules/ions.

In this experiment, you will determine the value of *n* in the formula $[Cu(NH_3)_n]^{2+}(aq)$, which is the complex ion formed when aqueous NH_3 is added to $Cu^{2+}(aq)$.

Different volumes of $CuSO_4$ solution and aqueous ammonia are mixed and the corresponding temperature changes are measured.

FA 3 is 0.5 mol dm^{-3} $CuSO_4$ solution
FA 4 is 2.0 mol dm^{-3} aqueous ammonia

(a) Measure and record the temperatures of the given solutions **FA 3** and **FA 4**.

$T_{FA\ 3}$ = ...27.6............ °C

$T_{FA\ 4}$ = ...26.6............ °C **[1]**

[1] for temperatures recorded to 1 dp.

(b) Carry out the following procedures and prepare a table for your results on **page 8**.
Your table should include i) $V_{FA\ 3}$, ii) $V_{FA\ 4}$, iii) $T_{initial}$, iv) T_{max}, v) temperature rise, ΔT and vi) colour of solution and precipitate (if any).

Procedures:

Experiment 1

- Measure 9.00 cm^3 of **FA 3** from a burette into a boiling tube.
- Add into the boiling tube 1.00 cm^3 of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as T_{max}.
- Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in **experiment 2**.

Experiment 2

- Measure 8.00 cm^3 of **FA 3** from a burette into the boiling tube.
- Add into the boiling tube 2.00 cm^3 of **FA 4** from another burette.
- Note the temperature rise while stirring to ensure that you do not miss the highest temperature reached. Record this temperature as T_{max}. Note and record the colour of precipitate (if any) and the colour of solution observed.
- Discard the content in the boiling tube and wash the boiling tube thoroughly. Wipe the thermometer dry for use in subsequent experiments.

Experiments 3 - 9

Perform 7 more experiments, each time reducing the volume of **FA 3** by 1.00 cm^3 but increasing the volume of **FA 4** by 1.00 cm^3 such that the total volume of solution is kept constant at 10.00 cm^3.

Expt	$V_{FA\ 3}$ / cm^3	$V_{FA\ 4}$ / cm^3	T_{initial} / °C	T_{max} / °C	ΔT / °C	Observation
1	9.00	1.00	27.5	28.4	0.9	(pale) blue ppt
2	8.00	2.00	27.4	28.9	1.5	(pale) blue ppt
3	7.00	3.00	27.3	29.4	2.1	(pale) blue ppt
4	6.00	4.00	27.2	29.4	2.2	(pale) blue ppt
5	5.00	5.00	27.1	29.7	2.6	(pale) blue ppt in deep blue solution
6	4.00	6.00	27.0	29.3	2.3	Deep blue solution
7	3.00	7.00	26.9	28.9	2.0	Deep blue solution
8	2.00	8.00	26.8	28.5	1.7	Deep blue solution
9	1.00	9.00	26.7	27.9	1.2	Deep blue solution

g

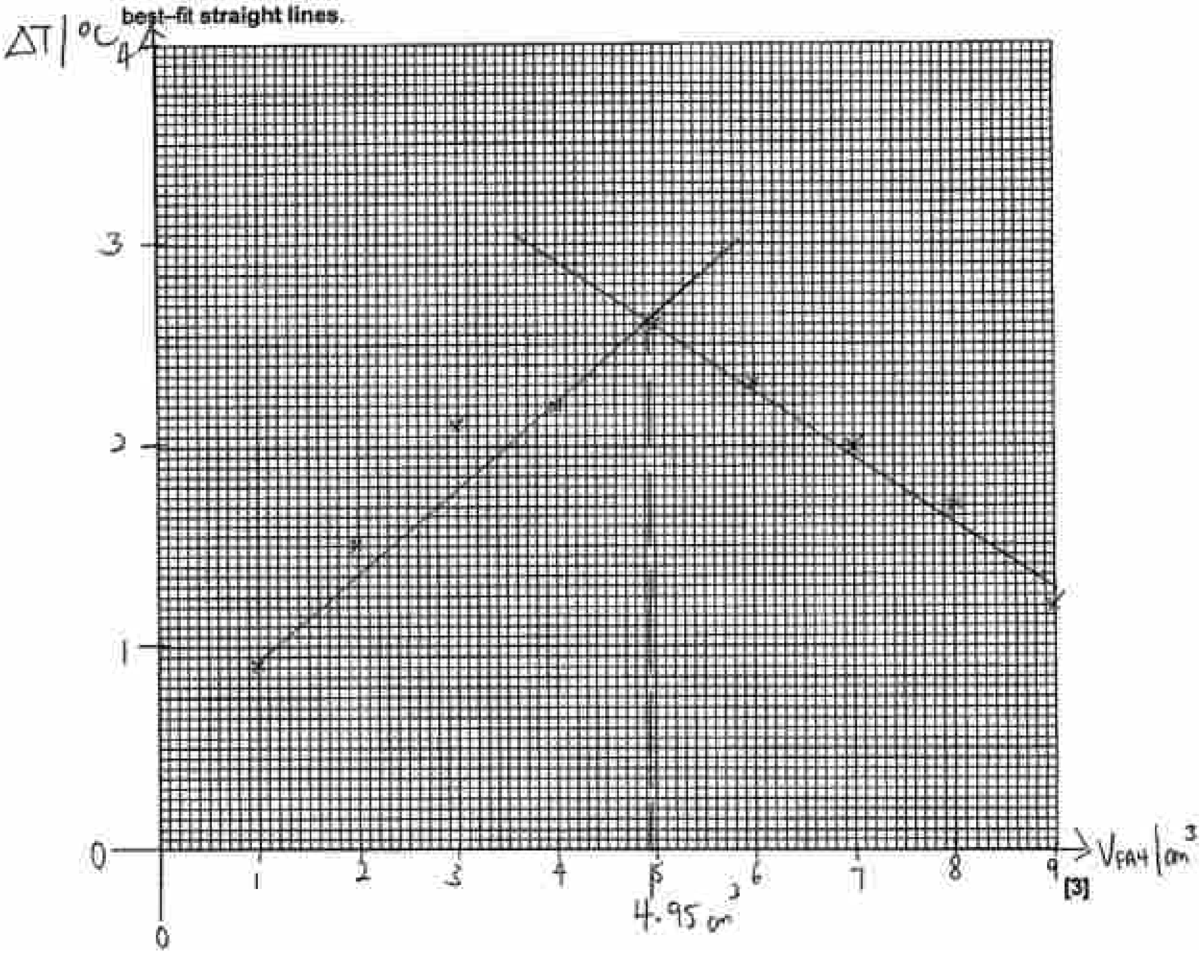
[5]

[1] for correct header (expt number not needed) with units
[1] for correct decreasing $V_{FA\ 3}$ and increasing $V_{FA\ 4}$ in 2 dp
[1] for 1 dp for T_{max} and ΔT; 1 dp / 3 - 4 sf for T_{initial}
[1] correctly calculated $T_{initial}$ and ΔT
[1] for observations changing from (pale) blue ppt [ONLY PURE BLUE, no greenish-blue] to (deep / dark) blue solution (doesn't matter where there's a change, as long as the trend is right; There should not be any ppt in expt 8 or 9)

(c) Plot a graph of temperature rise, ΔT, against volume of **FA 4**. Your plot should consist of **two** best-fit **straight lines**.

[3]

(c) Plot a graph of temperature rise, ΔT, against volume of **FA 4**. Your plot should consist of two best-fit straight lines.



[3]

[1] Axes labelled correctly with units, min and max points cover more than half the space in both directions, no awkward scale

[1] points plotted correctly to within half a small square (2 points before and 2 points after intersection)

[1] 2 lines of best fit with intersection

(d) **(i)** Show on your graph how the volume of **FA 4** that corresponds to the highest temperature rise can be determined.

[1] for extrapolating vertical line from x-axis to point of intersection / show coordinates at point of intersection + point correctly read to within ½ small square for volume of FA 4

Volume of **FA 4** with highest temperature rise = 4.95 cm^3

Hence, calculate the volume of **FA 3** that corresponds to this volume of **FA 4**.
Volume of **FA 3** = 10.00 – 4.95 = 5.05 cm^3

[1] for correct calculation of volume of FA 3

[1] for accuracy (see (c)(iv) 3.51 < n < 4.49)

Volume of **FA 3** = ...5.05 cm^3 **[3]**

(ii) Calculate the amount, in moles, of aqueous ammonia in the volume of **FA 4** with the highest temperature rise.

Amount of NH_3 = 4.95 /1000 x 2.0 = 9.90 x 10^{-3} mol **[1]**

Amount of $NH_3(aq)$ = ... **[1]**

(iii) Calculate the amount, in moles, of Cu^{2+} ions in the volume of **FA 3** that you have determined in **(i)**.

Amount of Cu^{2+} = 5.05 /1000 x 0.5 = 2.53 x 10^{-3} mol **[1]**

Amount of $Cu^{2+}(aq)$ = ... **[1]**

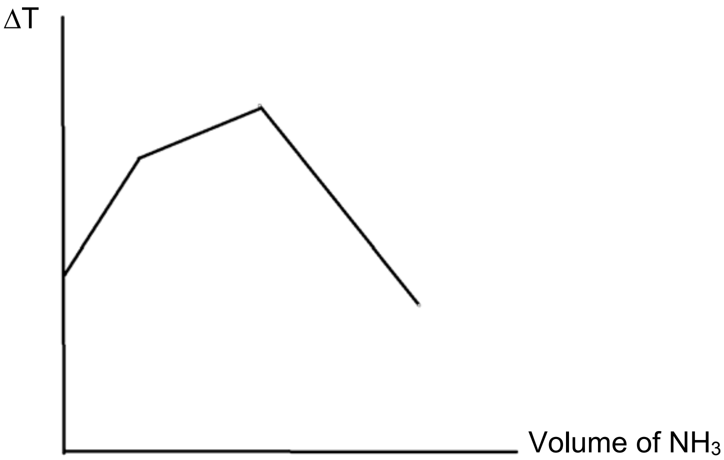
(iv) Calculate the number of moles of NH_3 bonded with one mole of Cu^{2+} ions in the solution and hence, deduce the value of n in the formula $[Cu(NH_3)_n]^{2+}$.

Amount of NH_3 = 9.90 x 10^{-3} mol
NH_3 : Cu^{2+} = 9.90 x 10^{-3} : 2.53 x 10^{-3} = 3.91 : 1
n = 4 **[1]**
Do not award if n is not a whole number.

[1]

n = ...

(e) The graph of ΔT against volume of NH_3 should theoretically look like the one below, with a combination of two straight lines with different positive gradients before the change in temperature starts to decrease.



With reference to the observations that you have recorded in the table on page 8, explain, with the aid of two relevant equations, why the graph is a combination of two straight lines with different positive gradients.

There were **two reactions** which produces different amount of heat / different enthalpy change of reaction. **[1]**

$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$
OR $Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$ **[1]**

$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$ **[1]**
OR $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$ OR $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$

Accept if students use their calculated n value.

.. **[3]**

(f) Suggest an improvement that you will make to this experiment to improve the accuracy of the results obtained.

Use a rubber bung with a hole (for the thermometer to be inserted) to cover the boiling tube immediately after the two reagents are mixed so as to prevent heat loss to surrounding. **[1]**
OR
Dry the boiling tube before each experiment so that the residual water will not add on to the total volume of solution and cause a lower temperature rise. **[1]**
OR
Mix the solutions in a Styrofoam cup (with a lid) to prevent heat loss to the surrounding. **[1]**

… **[1]**

Planning

(g) Chromium cations can also form complexes. A student was given a solid which has a formula of either $[Cr(H_2O)_5Cl]Cl_2$ or $[Cr(H_2O)_4Cl_2]Cl$. The relative formula mass of the compound is 248.5.

When dissolved in water, the chloride ions not involved in the complex ion would be liberated into the solution.

$$[Cr(H_2O)_5Cl]Cl_2(s) \rightarrow [Cr(H_2O)_5Cl]^{2+}(aq) + 2Cl^-(aq)$$

$$[Cr(H_2O)_4Cl_2]Cl(s) \rightarrow [Cr(H_2O)_4Cl_2]^+(aq) + Cl^-(aq)$$

To determine the formula of the solid given, a student prepared a 250 cm^3 of standard solution using 29.80 g of the given solid. He then determined the amount of free chloride ions by titrating 25.0 cm^3 of the standard solution against 0.3 mol dm^{-3} silver(I) nitrate solution while using some potassium chromate(VI) as an indicator. When silver(I) nitrate solution was added, a white precipitate of AgCl was formed.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

When all the free chloride ions had precipitated, a red-brown precipitate of silver chromate(VI) was formed to signify that the end-point had been reached.

(i) The teacher commented that the student should have reduced the mass of solid used by half for the preparation of standard solution.
Explain, with the aid of suitable calculations, why 29.80 g is not a suitable mass to be used. **[2]**

Amount of solid in 250 cm^3 = 29.80 / 248.5 = 0.1199 mol

If solid has formula $[Cr(H_2O)_5Cl]Cl_2$,

Amount of Cl^- in 25.0 cm^3 = 0.1199 x 25.0/250 x 2 = 0.02398 mol

Amount of $AgNO_3$ needed = (0.02398 / 0.3) x 1000 = 79.9 cm^3 **[1]**

Since the volume required is more than a burette full or > 50.00 cm^3, the mass is not suitable. **[1]**

(g) **(ii)** You are to describe how the student should prepare the standard solution by using his teacher's proposal.

In your answer, include

- the procedures involved in the preparation of the standard solution,
- the apparatus and equipment used to prepare the standard solution. **[2]**

……………………………………………………………………………………………………

Procedure [2]

Using a **weighing balance**, weigh accurately about 14.90 of the unknown solid.

Tip/transfer the solid into a **small beaker and reweigh the emptied weighing bottle**.

Add some **deionised water to dissolve the solid**.

Transfer the solution into a **250 cm^3 volumetric flask** carefully and **top up to the mark using deionised water**.

Stopper and shake well to obtain a homogeneous solution.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

[Total: 23]

3 Identifying cations in an unknown sample

(a) You are given **FA 5**, which is an aqueous solution containing two cations and one anion. One of the cations is Cu^{2+}. The other cation can be found from the list in the **Qualitative Analysis Notes** provided on page 16.

Perform the tests described in Table 3.1. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

Table 3.1

	Tests	**Observations**
1.	To 1 cm depth of **FA 5**, add 2 cm depth of **FA 1** (from question 1).	Green solution turned brown which eventually turned yellow-green. **Effervescence / Bubbling / Gas** **[1/2]** is observed. The **gas formed white ppt with $Ca(OH)_2(aq)$**. **[1/2]** The gas is CO_2.
2.	Add about 3 cm^3 of dilute aqueous ammonia to 1 cm^3 of **FA 5.** Filter the mixture and note the appearance of both the filtrate and residue. Add dilute sulfuric acid dropwise to the filtrate till in excess.	Reddish-brown ppt is formed. The solution turned from (dark) green to dark blue. The **residue is brown (can accept reddish-brown)** **[1/2]** and the **filtrate is (deep / dark) blue**. **[1/2]** **(Light) blue ppt** **[1/2]** is formed upon dropwise addition of H_2SO_4. **Ppt dissolves to form a very light blue / colourless solution** in excess H_2SO_4. **[1/2]**
3.	Add a spatula of solid potassium iodide to 3 cm^3 of **FA 5.** Filter the mixture and note the appearance of the filtrate. Add 1 cm^3 of hexane to the filtrate and shake well.	The **filtrate is green / yellow** **[1/2]**, residue contains black and off-white ppt. 2 immiscible layers are formed. The **top layer is pink / violet / purple in colour** **[1]** **and the bottom layer is green / yellow**. **[1/2]**

[5]

(b) Consider your observations in Table 3.1.

(i) State the other cation which is present in **FA 5**.

………………………………………………………………………………………………….……. **[1]**

Fe^{3+} **[1]**

Do not accept H^+

(ii) **FA 5** turns Universal Indicator paper red. With reference to this and your observations in test 1, write an ionic equation to represent the reaction between **FA 1** and **FA 5**.

……..……………………………………………………………………………………………….... **[1]**

$2\,H^+\,(aq) + CO_3^{2-}\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$ **[1]** OR

$H^+\,(aq) + HCO_3^-\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$ **[1] (no need state symbols)**

(iii) With reference to test 3, suggest the identity of the species which was responsible for the observations seen when hexane was added to the filtrate. Hence, suggest the property of **FA 5**.

……..……………………………………………………………………………………………….... **[2]**

I_2 **[1]**

FA 5 is oxidising / can be reduced. **[1]**

Planning

(c) **FA 5** also contains an anion. To determine the identity, a student heated **FA 5** with A*l* and NaOH(aq). A gas was evolved and it turned moist red litmus paper blue.

(i) Based on the observations given, state the possible identities of the anions.

……..……………………………………………………………………………………………….... **[1]**

NO_3^- and NO_2^- **[1]**

(ii) You are provided with the reagents NaOH(aq), NH_3(aq), HNO_3(aq) and $AgNO_3$(aq).

Suggest a test to confirm the identity of the anion in **FA 5**. State the expected observations.

DO NOT carry out the test.

Test: ……..………………………………………………………………………………………......

………

Expected observation for each of the possible anions in **(i)**.

………

……… **[2]**

Add HNO_3 (aq) (dropwise) to **FA 5**. **[1]**

If brown gas is observed, NO_2^- is present. **[1]**

If no brown gas is seen, NO_3^- is present.

[Total: 12]

~ END OF PAPER ~

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

Cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

Halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 SAJC Prelim Practical Exam Preparation List

Title	**Q1 – Determination of percentage by mass of sodium carbonate in a mixture of sodium carbonate and sodium hydrogen carbonate**		
Label Code	**Chemicals**	**Preparation**	**Per Student**
FA 1	0.0256 mol dm^{-3} $NaHCO_3$ + 0.0482 mol dm^{-3} Na_2CO_3	Dissolve 2.15 g $NaHCO_3$ and 5.11 g Na_2CO_3 in 1 dm^3	200 cm^3 (in capped plastic container)
FA 2	0.10 mol dm^{-3} of hydrochloric acid, HCl		200 cm^3 (in capped plastic container)
Thymolpthalein indicator	Thymolpthalein	Dissolve 0.8 g of thymolpthalein powder in 500 ml of 96% ethanol and top up to 1 dm^3	1 bottle per candidate
Screened methyl orange indicator	Screened methyl orange		1 bottle per candidate
Apparatus **(per student)**	**a)** **FA 1** and **FA 2** in labelled capped plastic containers **b)** Filter funnel **c)** 25.0 cm^3 pipette **d)** Burette x 1 **e)** Conical flask x 3 **f)** Dropping pipettes × 2 **g)** White tile **h)** Retort stand with clamp **j)** Distilled water bottle		

Title	**Q2 Determination of n in the complex ion formula $[Cu(NH_3)_n]^{2+}$**		
Label Code	**Chemicals**	**Preparation**	**Per Student**
FA 3	$CuSO_4$ solution	0.5 mol dm^{-3}	80 cm^3 (in capped plastic container)
FA 4	NH_3 solution	2.0 mol dm^{-3}	80 cm^3 (in capped plastic container)
Apparatus **(per student)**	**a)** 2 boiling tubes **b)** 2 50.00 cm^3 burettes **c)** 1 thermometer **d)** 1 glass funnel **e)** Paper towels		

Title	**Q3 dentifying cations in an unknown sample**		
Label Code	**Chemicals**	**Preparation**	**Per Student**
FA 3	$CuSO_4$ + $Fe_2(SO_4)_3$ solution	1.5 mol dm^{-3} $CuSO_4$ 0.5 mol dm^{-3} $Fe_2(SO_4)_3$ Filter to remove the undissolved $CuSO_4$.	30 cm^3 (in capped plastic container)
FA 1	Mixture of Na_2CO_3 and $NaHCO_3$	See Q1	See Q1
Potassium iodide	Solid KI		5 g
Hexane	Hexane		10 cm^3
Aqueous ammonia	NH_3 (aq)	Std. preparation Ammonia needs to be made fresh.	Bench reagent
Aqueous sodium hydroxide	NaOH (aq)	Std. preparation	Bench reagent
Sulfuric acid	H_2SO_4 (aq)	Std. preparation	Bench reagent
Nitric acid	HNO_3 (aq)	Std. preparation	Bench reagent
Hydrochloric acid	HCl (aq)	Std. preparation	Bench reagent
Barium nitrate	$Ba(NO_3)_2$ (aq)	Std. preparation	Bench reagent
Silver nitrate	$AgNO_3$ (aq)	Std. preparation	Bench reagent
Potassium manganate(VII)	$KMnO_4$ (aq)	Std. preparation	Bench reagent

Limewater $Ca(OH)_2$	$Ca(OH)_2$	Std. preparation	Bench reagent
Apparatus **(per student)**	**a)** 1 × glass rod; **b)** 1 × white tile; **c)** 1 × glass funnel; **d)** 4 × dropping pipettes; **e)** 1 × wash bottle containing deionised water; **f)** 6 x test tubes **g)** 2 x boiling tubes **h)** 1 x test tube rack **i)** 1 x test tube brush **j)** 1 x tongs **k)** 1 x Bunsen burner **l)** 1 x delivery tube **m)** 2 x wooden splints **n)** 1 x goggles **o)** 1 x marker pen **p)** Filter paper **q)** Filter Paper/ Litmus Box **r)** 1 x Lighter **s)** Paper towels		

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name	
Class	

CHEMISTRY **9729/01**

JC2 Preliminary Examination 20 September 2018
Paper 1 Multiple Choice 1 hour
Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **30** questions in this paper. Answer **all** questions.
For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

This document consists of **15** printed pages and **1** blank page.

Answer all questions

1 One mole of sulfuric acid is used to make an aqueous solution. The solution contains H_2SO_4 molecules, H^+ ions, SO_4^{2-} ions and HSO_4^- ions.

Which statements are correct?

(1) The solution contains 6.02×10^{23} sulfur atoms.

(2) The solution contains an exactly equal number of H^+ ions and HSO_4^- ions.

(3) One mole of SO_4^{2-} ions contains two moles of electrons

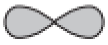
A 1 only

B 1 and 2 only

C 2 and 3 only

D 1 and 3 only

2 The table refers to the electron distribution in the second shell of an atom with eight protons. Which row is correct for this atom?

	Orbital shape 		Orbital shape 	
	Orbital type	Number of electrons	Orbital type	Number of electrons
A	p	2	s	4
B	p	4	s	2
C	s	2	p	4
D	s	4	p	2

3 50 cm^3 of a 0.10 mol dm^{-3} solution of a metallic salt was found to react exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

A +1

B +2

C +4

D +5

4 A 2 g sample of hydrogen at temperature T and of volume V exerts a pressure *p*.

Deuterium, $^{2}_{1}H$ is an isotope of hydrogen.

Which of the following would also exert a pressure of *p* at the same temperature T?

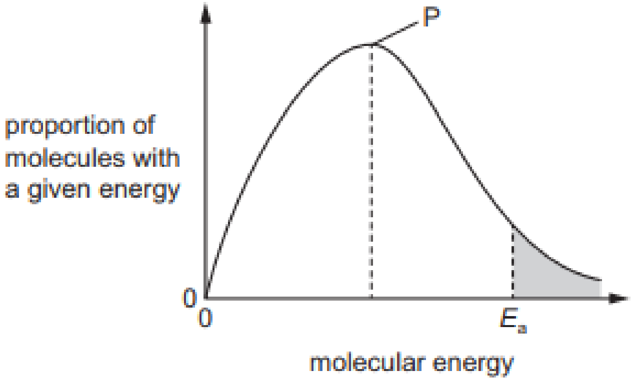
A A mixture of 2 g of hydrogen and 2 g of deuterium of total volume 2V

B A mixture of 1 g of hydrogen and 2 g of deuterium of total volume 2V

C A mixture of 1 g of hydrogen and 2 g of deuterium of total volume V

D A mixture of 1 g of hydrogen and 1 g of deuterium of total volume V

5 The diagram shows the Boltzmann distribution of energies in a gas. The gas can take part in a reaction with an activation energy, E_a.



Which statement is correct?

A If temperature is increased, peak P will be lower and E_a will move to the right.

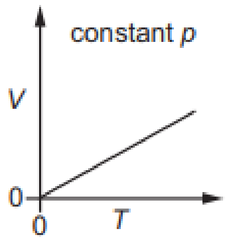
B If temperature is increased, peak P will be higher and E_a will not move

C If temperature is decreased, peak P will be the same and E_a will move to the left.

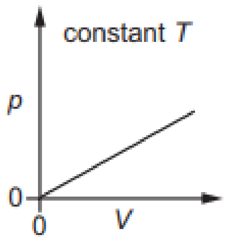
D If temperature is decreased, peak P will be higher and E_a will not move.

6 Which diagram correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K.)

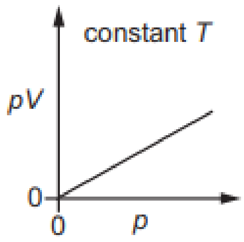
A



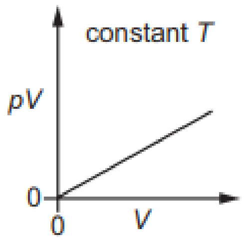
B



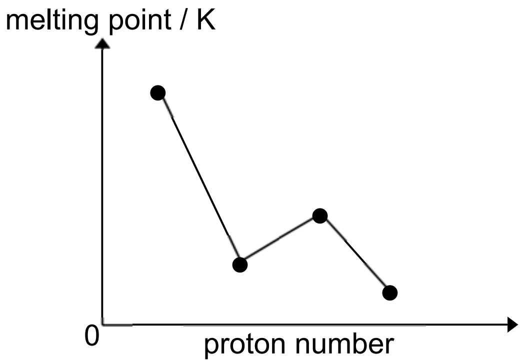
C



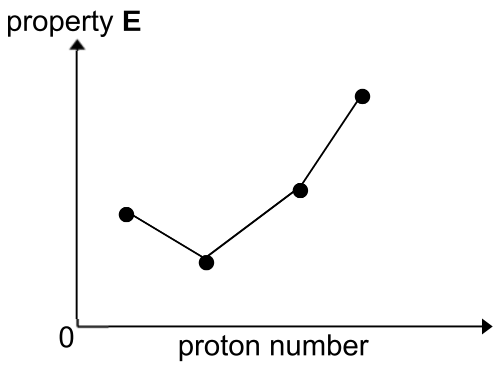
D

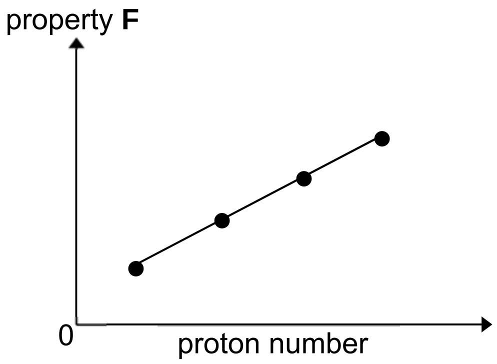


7 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





What are properties **E** and **F**?

	property **E**	property **F**
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	nuclear charge
D	electrical conductivity	atomic radius

8 When 60 cm^3 of 0.1 mol dm^{-3} of sulfuric acid and 40 cm^3 of 0.2 mol dm^{-3} sodium hydroxide were mixed in a styrofoam cup, the temperature rose by 6.5 ^{o}C.

Calculate the standard enthalpy change of neutralisation. Assume that the specific heat capacity of the solution is 4.2 $Jg^{-1}K^{-1}$.

A + 34.1 kJ mol^{-1}

B + 45.5 kJ mol^{-1}

C - 34.1 kJ mol^{-1}

D - 45.5 kJ mol^{-1}

9 In which reactions does NH_3 behave as a Brønsted-Lowry acid?

(1) $HSO_4^- + NH_3 \rightarrow SO_4^{2-} + NH_4^+$
(2) $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]$
(3) $2NH_3 \rightarrow NH_2^- + NH_4^+$

A 1 and 2 only
B 1 and 3 only
C 1 only
D 3 only

10 A current of 0.2 ampere passing for 5 hours through a solution of gold ions deposits a mass of 2.45 g of gold on the cathode. Which of these expressions gives the charge on a gold ion?

A $$\frac{2.45 \times 0.2 \times 5 \times 60 \times 60}{197 \times 96500}$$

B $$\frac{0.2 \times 5 \times 60 \times 60 \times 197}{96500 \times 2.45}$$

C $$\frac{2.45 \times 96500}{197 \times 0.2 \times 5 \times 60 \times 60}$$

D $$\frac{197 \times 0.2 \times 5 \times 60 \times 96500}{2.45}$$

11 Pure nitrosyl chloride, NOC*l* gas, was heated at 320°C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas had dissociated according to the equation below and the total pressure was p atm.

$$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$

What is value of the equilibrium constant, K_p?

A $\frac{17.9}{p}$ **B** $\frac{41.7}{p}$ **C** 0.0120p **D** 0.0130p

12 Calculate the resultant pH of the solution when 10 cm^3 of hydrochloric acid with a concentration of 0.015 mol dm^{-3} was added to a 25 cm^3 sample of ammonia with a concentration of 0.25 mol dm^{-3}.

(K_b of ammonia = 1.778 x 10^{-5} mol dm^{-3})

A 10.9

B 8.25

C 7.64

D 9.25

13 Hydrogen can be made from steam according to the following equation:

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

The Gibbs free energy change of reaction at two different temperature are shown

ΔG_1 = +78 kJ mol^{-1} at 378 K
ΔG_2 = −58 kJ mol^{-1} at 1300 K

Which row of the table gives the correct sign of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	−	−
B	−	+
C	+	−
D	+	+

14 An experiment was carried out to investigate the initial rate of reaction between potassium peroxodisulphate, $K_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial volumes of the $K_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

Volume of $K_2S_2O_8$ / cm^3	Volume KI / cm^3	Volume of water /cm^3	time taken to darken / s
10	20	10	35
5	20	15	70
10	8	22	88
20	40	20	***y***

Select the correct option for the following reaction.

	Order with respect to $K_2S_2O_8$	Order with respect to KI	**y** / s
A	1	1	70.0
B	1	2	17.5
C	1	1	35.0
D	2	1	17.5

15 The enzyme maltase speeds up the reaction between maltose and water.

$$\text{maltose + water} \xrightarrow{\text{maltase}} \text{glucose}$$

Maltase shows **specificity**.

Which statement describes the **specificity** of maltase?

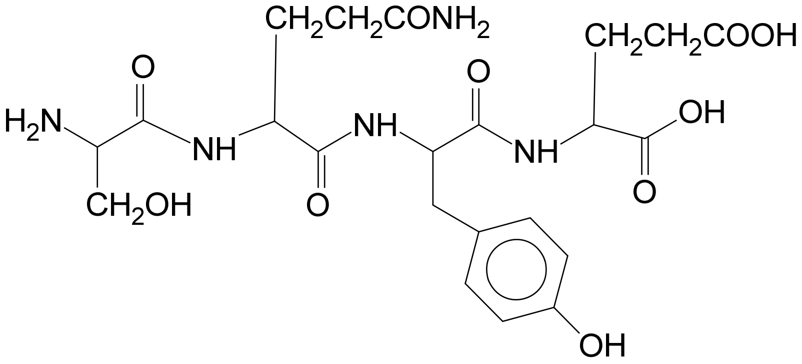
A Maltase is a biological catalyst and it is a type of protein.

B Maltase is most effective between pH 6.1 and pH 6.8.

C Maltase lowers the activation energies of the reactions it catalyses.

D Maltase only speeds up a small number of chemical reactions.

16 The diagram shows the structure of the tetrapeptide, **J**.



Which statements are correct?

(1) When 1 mol of **J** reacts with hot NaOH(aq) until no further reaction occurs, 8 mol of NaOH will react.

(2) When 1 mol of **J** reacts with hot HC*l*(aq) until no further reaction occurs, 5 mol of HC*l* will react.

(3) When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react forming ester or amide.

(4) When 1 mol of **J** reacts with Na(s), 4 mol of hydrogen gas will be given out.

A 1 and 2 only

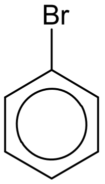
B 2 and 3 only

C 1, 2 and 4 only

D 3 and 4 only

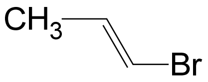
17 Which of these will produce the most silver bromide precipitate when a 1 g sample reacts with excess hot sodium hydroxide, followed by silver nitrate solution?

A



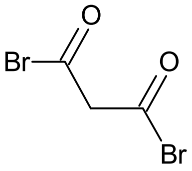
(M_r: 156.9)

B



(M_r: 120.9)

C



(M_r: 229.8)

D CH_3Br (M_r: 94.9)

18 Identify the final product **L** in this sequence of reactions.

$$CH_2CHCOCH_2CHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \textbf{K} \xrightarrow[\text{heat}]{K_2Cr_2O_7/\ H^+} \textbf{L}$$

A $CH_2CHCOCH_2COOH$

B $CH_3CH_2COCH_2COOH$

C $CH_2(OH)CH(OH)COCH_2CH_2OH$

D $CH_2(OH)CH(OH)CH(OH)CH_2CH_2OH$

19 An alcohol **M** with molecular formula $C_4H_{10}O$ is oxidised by acidified potassium dichromate(VI) under certain conditions to give **N**.

- **N** does not produce a yellow precipitate with aqueous alkaline iodine
- **N** gives a reddish brown precipitate when reacted with Fehling's solution

How many isomers of alcohol **M** could result in the observations for **N**?

A 1

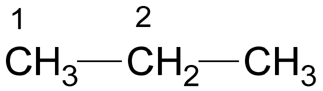
B 2

C 3

D 4

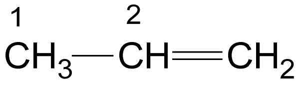
20 Which of the following compounds has the shortest C1-C2 bond length?

A



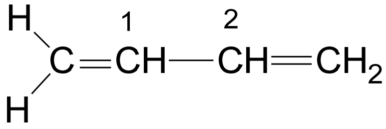
$\overset{1}{CH_3}-\overset{2}{CH_2}-CH_3$

B



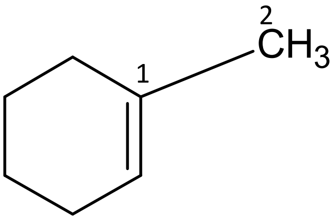
$\overset{1}{CH_3}-\overset{2}{CH}=CH_2$

C



$H_2C=\overset{1}{CH}-\overset{2}{CH}=CH_2$

D



21 Maleic acid is used in the food industry and for stabilising drugs. It is the cis-isomer of butenedioic acid and has the structural formula $HO_2CCH{=}CHCO_2H$.

What is the product formed from the reaction of maleic acid with cold, dilute, acidified manganate(VII) ions?

A $HO_2CCH(OH)CH(OH)CO_2H$

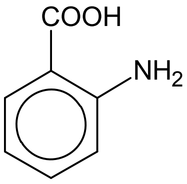
B HO_2CCO_2H

C $HO_2CCH_2CH(OH)CO_2H$

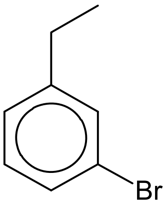
D $HO_2CCOCOCO_2H$

22 Which one of the following compounds **cannot** be synthesised from ethylbenzene?

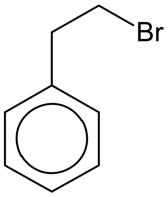
A



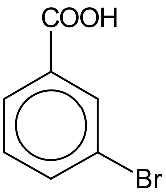
B



C



D

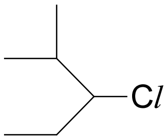


23 Structural isomerism and stereoisomerism should be considered when answering this question.

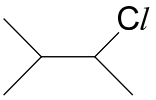
A colourless liquid, $C_5H_{11}Cl$, exists as a mixture of two optical isomers.

When heated with sodium hydroxide in ethanol, a mixture of only **two** alkenes is formed. What could the colourless liquid be?

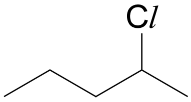
A



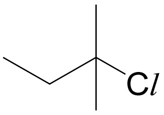
C



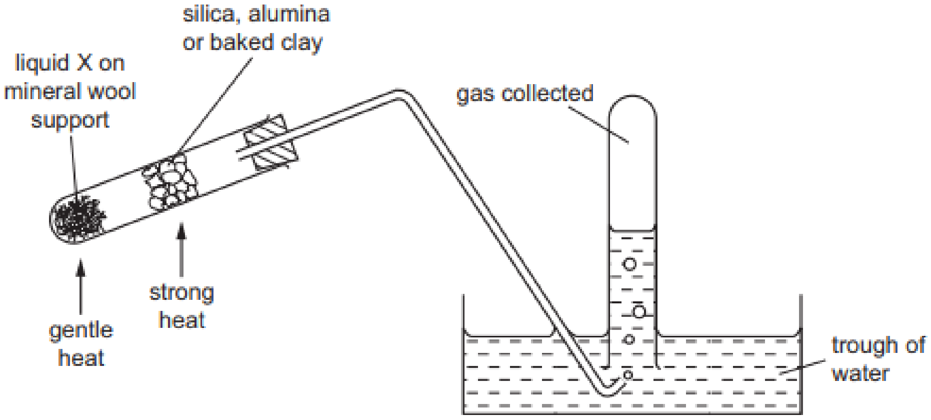
B



D



24 The diagram shows an experimental set-up which can be used in several different experiments.



Which processes could be demonstrated by using the above apparatus?

(1) oxidation of ethanol (liquid X)
(2) dehydration of ethanol (liquid X)
(3) cracking of paraffin (liquid X)

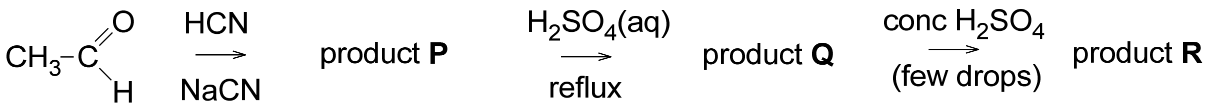
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 3 only

25 Ethanal, CH_3CHO, is used to make product **R** in a three-stage synthesis.



Two molecules of **Q** react to give one molecule of **R** plus two molecules of water.

R does not react with sodium.

What is the molecular formula and empirical formula of **R**?

	Molecular formula	Empirical formula
A	$C_3H_4O_2$	$C_3H_4O_2$
B	$C_6H_8O_4$	$C_3H_4O_2$
C	$C_3H_5O_2$	$C_3H_5O_2$
D	$C_6H_{10}O_5$	$C_6H_{10}O_5$

26 Chlorofluoroalkanes have been used as the refrigerant in refrigerators but care has to be taken in disposing of old refrigerators.

Which statements about chlorofluoroalkanes are correct?

(1) C–C*l* bonds more readily undergo homolytic fission than C–F bonds.

(2) Care is taken in the disposal of old refrigerators because of possible ozone depletion.

(3) $C_2H_4C\mathit{l}F$ is more volatile than C_2H_6.

A 2 only

B 1 and 2 only

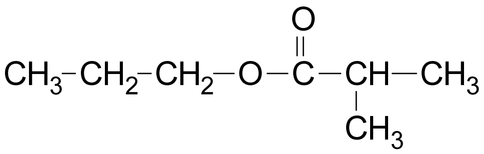
C 2 and 3 only

D 1, 2 and 3

27 Ethyl propanoate is refluxed with aqueous sodium hydroxide. The alcohol produced is then reacted with methyl propanoic acid to make a second ester.

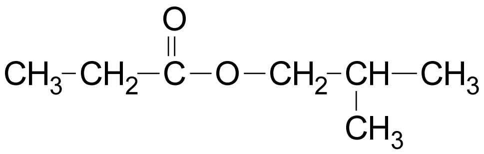
What is the structural formula of this second ester?

A



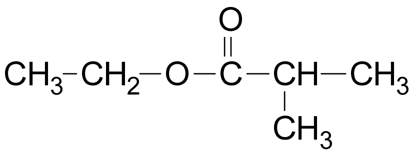
$CH_3-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

B



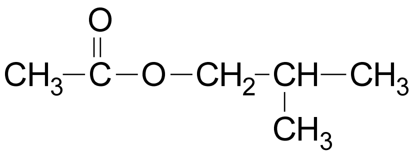
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

C



$CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

D



$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

28 Ethanedioic acid has the formula HO_2CCO_2H.

What is the formula of aluminium ethanedioate?

A $Al C_2O_4$

B $Al(C_2O_4)_3$

C $Al_2C_2O_4$

D $Al_2(C_2O_4)_3$

29 Which of the following processes lead to an increase in entropy?

(1) Diffusion of air fresher in the lecture theatre.
(2) Combustion of a piece of charcoal to form CO_2 (g) and H_2O (g).
(3) Desalination of sea water by reverse osmosis (solvent passes from a dilute solution to a concentrated solution).

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

30 How many structural isomers with the molecular formula $C_5H_{10}O_2$ give infra-red absorptions both at approximately 1300 cm^{-1} and at approximately 1740 cm^{-1}?

A 3

B 5

C 7

D 9

END OF PAPER 1

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SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

Candidate Name

Class

CHEMISTRY 9729/01

JC2 Preliminary Examination 20 September 2018
Paper 1 Multiple Choice 1 hour
Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **30** questions in this paper. Answer **all** questions.
For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the one you consider correct and record your choice using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

This document consists of ___ printed pages and __ blank page.

Answer all questions

1 One mole of sulfuric acid is used to make an aqueous solution. The solution contains H_2SO_4 molecules, H^+ ions, SO_4^{2-} ions and HSO_4^- ions.

Which statements are correct?

(1) The solution contains 6.02×10^{23} sulfur atoms.

(2) The solution contains an exactly equal number of H^+ ions and HSO_4^- ions.

(3) One mole of SO_4^{2-} ions contains two moles of electrons

A	1 only
B	1 and 2 only
C	2 and 3 only
D	1 and 3 only

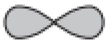
Answer: **A**

For statement 1 is correct: 1 mol of H_2SO_4 has 1 mol of S. The solution contains 6.02×10^{23} S atoms

For statement 2 is wrong: From the question, one mole of H_2SO_4 contains H_2SO_4 molecules, H^+, SO_4^{2-} and HSO_4^-. This means the amt of H^+ and HSO_4^- is not equal as some H_2SO_4 may have dissociate into SO_4^{2-}.

For statement 3 is wrong: One mole of SO_4^{2-} has more than 2 mol of electrons. Do not be tricked by the charge of negative two

2 The table refers to the electron distribution in the second shell of an atom with eight protons. Which row is correct for this atom?

	Orbital shape 		Orbital shape 	
	Orbital type	Number of electrons	Orbital type	Number of electrons
A	p	2	s	4
B	p	4	s	2
C	s	2	p	4
D	s	4	p	2

Answer: **B**

Second shell of an atom with eight protons: oxygen ➔ electronic configuration: $1s^2 2s^2 2p^4$

3 50 cm^3 of a 0.10 mol dm^{-3} solution of a metallic salt was found to react exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows:

$$SO_3^{2-}(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

A	+1
B	+2
C	+4
D	+5

Answer: **B**

Amount of sulphite ions = $\frac{25}{1000} \times 0.10$ = 0.0025 mol

Amount of metallic salt = $\frac{50}{1000} \times 0.10$ = 0.005 mol

Let x be the new oxidation no of metal in salt.

[R]: $M^{3+} + (3-x)e \rightarrow M^x$

Since moles of electrons gained = moles of electrons lost in a redox reaction,

$$\frac{3-x}{2} = \frac{0.0025}{0.005}$$

x = +2

4	A 2 g sample of hydrogen at temperature T and of volume V exerts a pressure *p*. Deuterium, $^{2}_{1}H$ is an isotope of hydrogen. Which of the following would also exert a pressure of *p* at the same temperature T?	
	A	A mixture of 2 g of hydrogen and 2 g of deuterium of total volume 2V
	B	A mixture of 1 g of hydrogen and 2 g of deuterium of total volume 2V
	C	A mixture of 1 g of hydrogen and 2 g of deuterium of total volume V
	D	A mixture of 1 g of hydrogen and 1 g of deuterium of total volume V

Answer: **C**

P (of sample of 2 g of hydrogen) V = nRT

P (of sample of 2 g of hydrogen) $= \frac{nRT}{V}$

$$= \frac{\frac{2}{2}RT}{V}$$

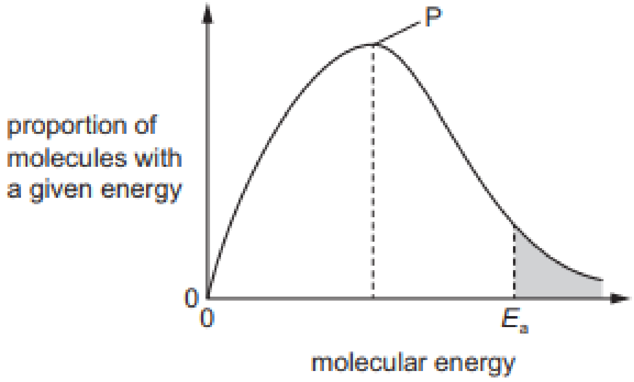
$$= \frac{RT}{V}$$

For option C:

P (of mixture) $= \frac{\frac{1}{2}RT + \frac{2}{4}RT}{V}$

$= \frac{RT}{V}$ (same pressure as the sample of 2 g of hydrogen)

5 The diagram shows the Boltzmann distribution of energies in a gas. The gas can take part in a reaction with an activation energy, E_a.



Which statement is correct?

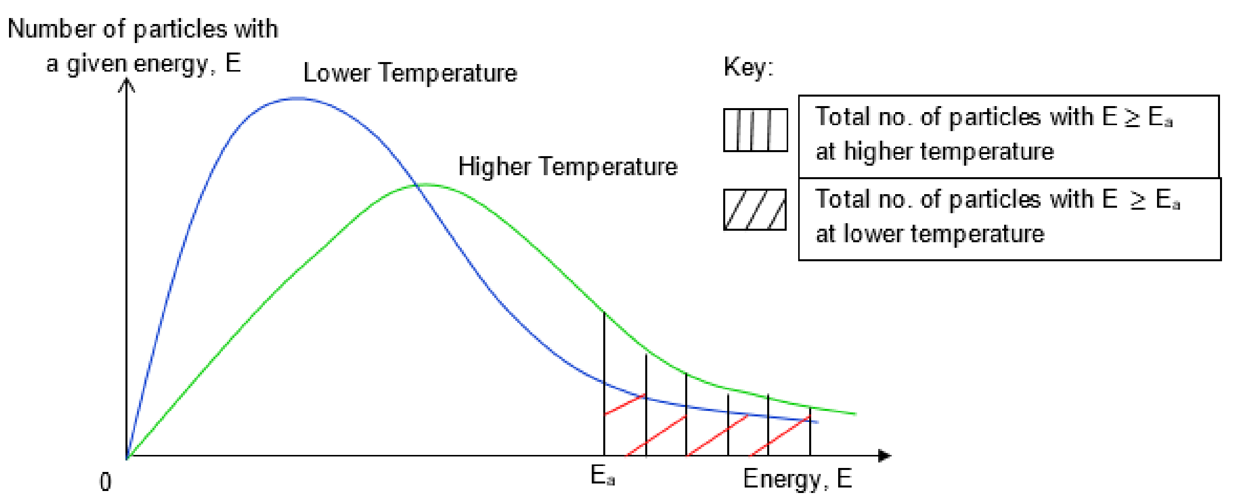
A If temperature is increased, peak P will be lower and E_a will move to the right.

B If temperature is increased, peak P will be higher and E_a will not move

C If temperature is decreased, peak P will be the same and E_a will move to the left.

D If temperature is decreased, peak P will be higher and E_a will not move.

Answer: **D**

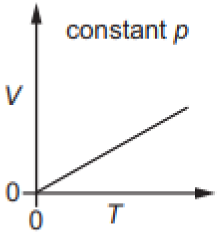


Option A and C are wrong as E_a will not shift when temperature is increased or decreased

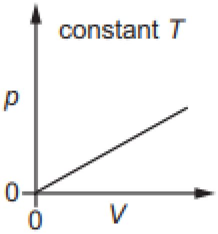
Option B is wrong. When temperature is increased, peak P will shift lower not higher.

6 Which diagram correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K.)

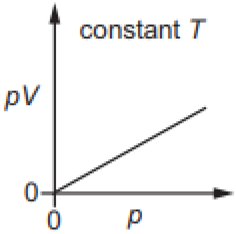
A



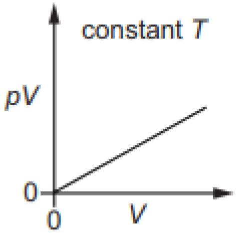
B



C



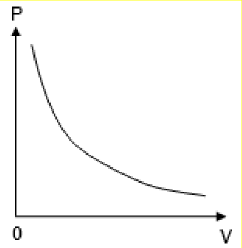
D



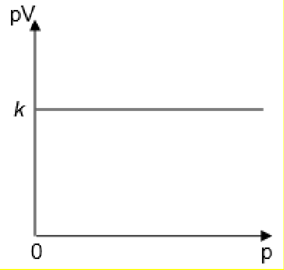
Answer: A

Using $pV = nRT$

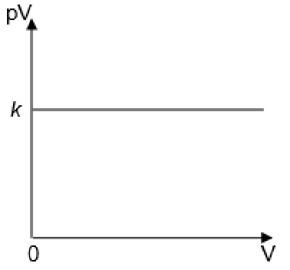
For B the correct graph is as shown



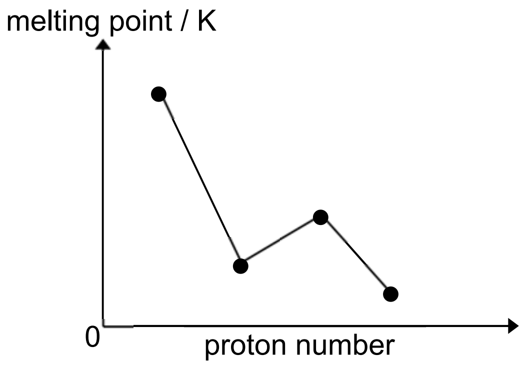
For C the correct graph is as shown



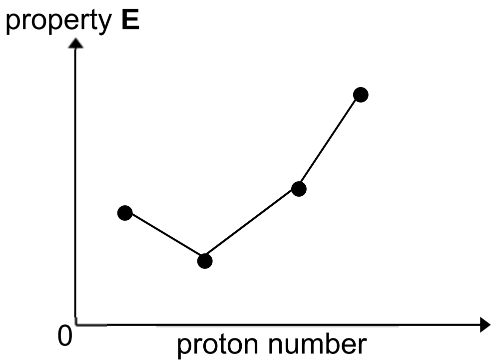
Similarly for D the correct graph is as shown

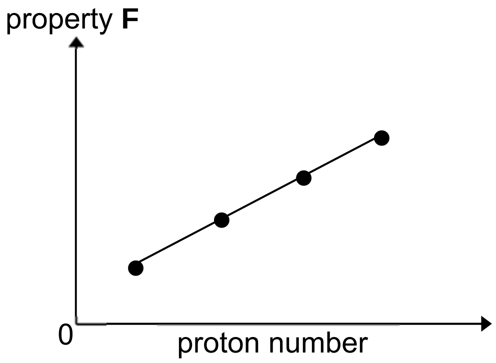


7 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





What are properties **E** and **F**?

	property **E**	property **F**
A	third ionisation energy	electronegativity
B	number of valence electrons	boiling point
C	ionic radius	nuclear charge
D	electrical conductivity	atomic radius

Answer: **A**

From the melting point data, student should be able to appreciate the highest m.p should be Si and since they are consecutive elements in third period, the next 3 points will be P, S and P.

Thus, only option A is valid.

8 When 60 cm^3 of 0.1 mol dm^{-3} of sulfuric acid and 40 cm^3 of 0.2 mol dm^{-3} sodium hydroxide were mixed in a styrofoam cup, the temperature rose by 6.5 ^oC.

Calculate the standard enthalpy change of neutralisation. Assume that the specific heat capacity of the solution is 4.2 $Jg^{-1}K^{-1}$.

A	+ 34.1 kJ mol^{-1}
B	+ 45.5 kJ mol^{-1}
C	- 34.1 kJ mol^{-1}
D	- 45.5 kJ mol^{-1}

Answer: C

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Amount of sulfuric acid = $\frac{60}{1000} \times 0.1 = 0.006$ mol

Amount of sodium hydroxide = $\frac{40}{1000} \times 0.2 = 0.008$ mol (limiting reactant)

Amount of sodium hydroxide = amount of water = 0.008 mol

$\Delta H_{neutralisation} = -\frac{(100)(4.2)(6.5)}{0.008} = -34.1$ kJ mol^{-1}

9 In which reactions does NH_3 behave as a Brønsted-Lowry acid?

(1) $HSO_4^- + NH_3 \rightarrow SO_4^{2-} + NH_4^+$

(2) $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]$

(3) $2NH_3 \rightarrow NH_2^- + NH_4^+$

A	1 and 2 only
B	1 and 3 only
C	1 only
D	3 only

Answer: D

For reaction 1, ammonia is functioning as a Brønsted-Lowry base as it received a proton from HSO_4^-

For reaction 2, ammonia is functioning as a Lewis base because it can share its lone pair of electrons with Ag^+.

For reaction 3, ammonia is functioning as both Brønsted-Lowry acid as well as Brønsted-Lowry base.

10	A current of 0.2 ampere passing for 5 hours through a solution of gold ions deposits a mass of 2.45 g of gold on the cathode. Which of these expressions gives the charge on a gold ion?	
	A	$\frac{2.45 \times 0.2 \times 5 \times 60 \times 60}{197 \times 96500}$
	B	$\frac{0.2 \times 5 \times 60 \times 60 \times 197}{96500 \times 2.45}$
	C	$\frac{2.45 \times 96500}{197 \times 0.2 \times 5 \times 60 \times 60}$
	D	$\frac{197 \times 0.2 \times 5 \times 60 \times 96500}{2.45}$

Answer: B

Q = I x t
= 0.2 x 5 x 60 x 60

$$\text{Amt} = \frac{I \times t}{nF}$$

$$n = \frac{I \times t}{\text{amt} \times F} = \frac{0.2 \times 5 \times 60 \times 60}{\frac{2.45}{197} \times 96500} = \frac{0.2 \times 5 \times 60 \times 60 \times 197}{2.45 \times 96500}$$

11 Pure nitrosyl chloride, NOC*l* gas, was heated at 320°C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas had dissociated according to the equation below and the total pressure was P atm.

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$$

What is value of the equilibrium constant, K_p?

A	$\frac{17.9}{p}$	**B**	$\frac{41.7}{p}$	**C**	0.0120p	**D**	0.0130p

Answer: **C**

	$2NOCl\ (g) \rightleftharpoons$	$2NO\ (g)$ +	$Cl_2\ (g)$
Initial partial pressure/atm	**x**	0	**0**
Change in partial pressure / atm	-0.3x	+0.3x	+0.15x
Equilibrium partial pressure / atm	0.7x	0.3x	0.15x

0.7x + 0.3x + 0.15x = p
x = 0.8696p

$K_p = \frac{(0.2609p)(0.1304p)^2}{(0.6087p)^2}$
= 0.01197
= 0.0120p

12	Calculate the resultant pH of the solution when 10 cm^3 of hydrochloric acid with a concentration of 0.015 mol dm^{-3} was added to a 25 cm^3 sample of ammonia with a concentration of 0.25 mol dm^{-3}. (K_b of ammonia = 1.778×10^{-5} mol dm^{-3})	
	A	10.9
	B	8.25
	C	7.64
	D	9.25

Answer: **A**

$HCl + NH_3 \rightarrow NH_4Cl$

Amt HCl given = 10/1000 x 0.015 = 0.00015 mol

Amt NH_3 given = 25/1000 x 0.25 = 0.00625 mol

All the HCl added will be neutralised by the excess NH_3 forming the NH_4^+ thus

$[HCl \equiv NH_4^+]$

Amt NH_4^+ present = 0.00015 mol

Amt of NH_3 remaining = 0.00625 – 0.00015
= 0.0061 mol

Thus, present of a basic buffer

$$pOH = pK_b + \lg([NH_4^+] / [NH_3])$$
$$= -\lg(1.778 \times 10^{-5}) + \lg$$
$$= 3.14$$

pH = 14 – 3.14 = 10.9

13 Hydrogen can be made from steam according to the following equation:

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

The Gibbs free energy change of reaction at two different temperature are shown

$\Delta G_1 = +78$ kJ mol^{-1} at 378 K
$\Delta G_2 = -58$ kJ mol^{-1} at 1300 K

Which row of the table gives the correct sign of ΔH and ΔS for this reaction?

	ΔH	ΔS
A	−	−
B	−	+
C	+	−
D	+	+

Answer: D

Δn of gas = 2-1 = +1
ΔS is positive.
ΔG = ΔH – TΔS
As temperature increases to 1300 K, ΔG is negative and reaction is spontaneous.

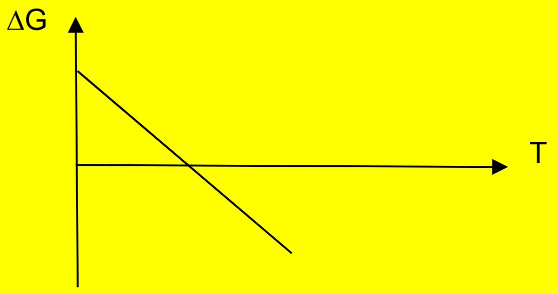
When the temperature is lower at 378 K, ΔG is positive and reaction is non-spontaneous.

Since ΔS is positive, this indicate that ΔH is positive as only low temperature can allow ΔG to become positive.

Alternatively, using ΔG = ΔH – TΔS where

- ΔG (y-axis)
- ΔH (y intercept)
- T (x-axis)
- - ΔS (gradient)

Since ΔS is positive (which leads to a negative gradient) and ΔG changes from positive to negative with increasing temperature, ΔH is positive.



14 An experiment was carried out to investigate the initial rate of reaction between potassium peroxodisulphate, $K_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial volumes of the $K_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

Volume of $K_2S_2O_8$ / cm^3	Volume KI / cm^3	Volume of water /cm^3	time taken to darken / s
10	20	10	35
5	20	15	70
10	8	22	88
20	40	20	***y***

Select the correct option for the following reaction.

	Order with respect to $K_2S_2O_8$	Order with respect to KI	**y** / s	
A	1	1	70.0	
B	1	2	17.5	
C	1	1	35.0	
D	2	1	17.5	

Answer: **C**
From the first two expt, order wrt $K_2S_2O_8$ is one.
From the 1st and 3rd expt, order wrt is KI one.
In the 4th expt, the concentration of $K_2S_2O_8$ and KI are both doubled from experiment one respectively. However, since total volume is doubled too, the concentrations of expt 4 are exaxtly the same as expt one. So the time taken for the solution to darken is the same.

15 The enzyme maltase speeds up the reaction between maltose and water.

$$\text{maltose + water} \xrightarrow{\text{maltase}} \text{glucose}$$

Maltase shows **specificity**.

Which statement describes the **specificity** of maltase?

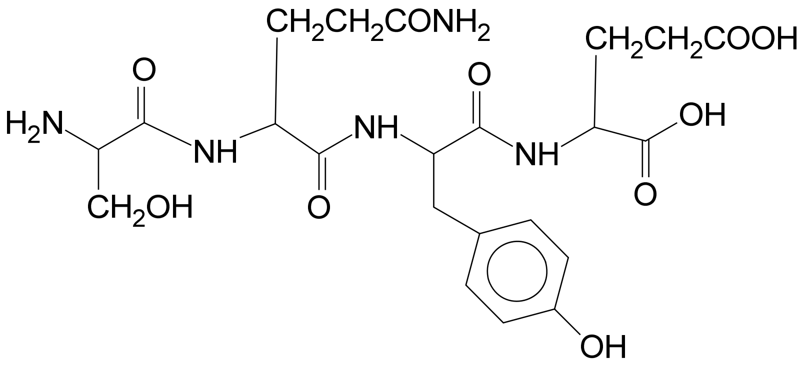
A	Maltase is a biological catalyst and it is a type of protein.
B	Maltase is most effective between pH 6.1 and pH 6.8.
C	Maltase lowers the activation energies of the reactions it catalyses.
D	Maltase only speeds up a small number of chemical reactions.

Answer: **D**
Being a biological catalyst and a type of protein does not define the term **specificity.** Thus option A is out

Effectiveness over a pH range does not define the term **specificity**. This make option B wrong.

Lowering activation energy does not define the term **specificity**. In fact all catalyst or enzyme lower E_a. Option C is thus wrong.

16 The diagram shows the structure of the tetrapeptide, **J**.



Which statements are correct?

(1) When 1 mol of **J** reacts with hot NaOH(aq) until no further reaction occurs, 8 mol of NaOH will react.

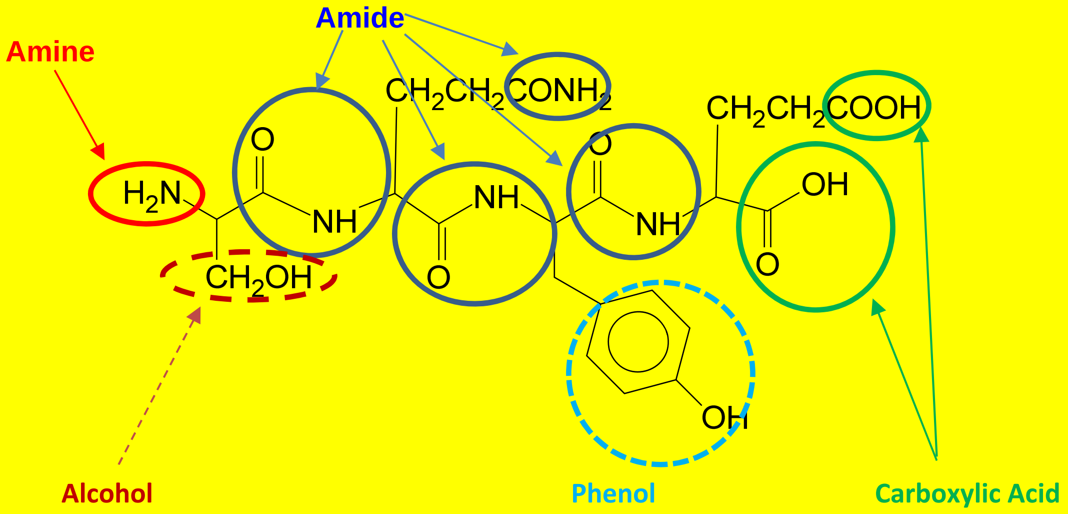
(2) When 1 mol of **J** reacts with hot HC*l*(aq) until no further reaction occurs, 5 mol of HCl will react.

(3) When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react forming ester or amide.

(4) When 1 mol of **J** reacts with Na(s), 4 mol of hydrogen gas will be given out.

A	1 and 2 only
B	2 and 3 only
C	1, 2 and 4 only
D	3 and 4 only

Answer: **B**

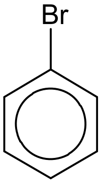
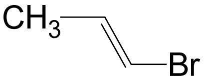
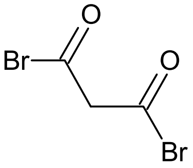


Hence, 1 mol of **J** will react with 7 mol of NaOH (aq) (Basic hydrolysis of amides, neutralisation of carboxylic acid and phenols).

1 mol of **J** will react with 5 mol of HCl (aq) (Acidic hydrolysis of amides, neutralisation of amine).

When 1 mol of **J** reacts with ethanoyl chloride, 3 mol of ethanoyl chloride will react (alcohol, phenol and amine)

When 1 mol of **J** reacts with Na(s), 2 mol of hydrogen gas will be given out. (Phenol, alcohol and carboxylic acid)

17	Which of these will produce the most silver bromide precipitate when a 1 g sample reacts with excess hot sodium hydroxide, followed by silver nitrate solution?	
	A	 (M_r: 156.9)
	B	 (M_r: 120.9)
	C	 (M_r: 229.8)
	D	CH_3Br (M_r: 94.9)

Answer: **D**

Both A and B are resistant to nucleophilic substitution due to the double bond character between C and Br.

Amt of C in 1g = $\frac{1}{229.8}$ = 0.00435 Hence amt of AgBr formed = 0.0087 mol	Amt of D in 1g = $\frac{1}{94.9}$ = 0.0105 Hence amt of AgBr formed = 0.0105

18 Identify the final product **L** in this sequence of reactions.

$$CH_2CHCOCH_2CHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \textbf{K} \xrightarrow[\text{heat}]{K_2Cr_2O_7/\ H^+} \textbf{L}$$

A $CH_2CHCOCH_2COOH$

B $CH_3CH_2COCH_2COOH$

C $CH_2(OH)CH(OH)COCH_2CH_2OH$

D $CH_2(OH)CH(OH)CH(OH)CH_2CH_2OH$

Answer: **A**

$$\begin{tikzcd} CH_2{=}CHCOCH_2CH{=}O \arrow[r, "NaBH_4 \text{ in } CH_3OH"', "\text{then } H_2O"] & CH_2{=}CHCH(OH)CH_2CH_2OH \arrow[d, "K_2Cr_2O_7/\ H^+", "\text{heat}"'] \\ & CH_3CH_2COCH_2COOH \end{tikzcd}$$

19 An alcohol **M** with molecular formula $C_4H_{10}O$ is oxidised by acidified potassium dichromate(VI) under certain conditions to give **N**.

- **N** does not produce a yellow precipitate with aqueous alkaline iodine
- **N** gives a reddish brown precipitate when reacted with Fehling's solution

How many isomers of alcohol **M** could result in the observations for **N**?

A 1

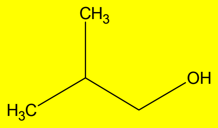
B 2

C 3

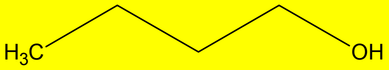
D 4

Answer: **B**

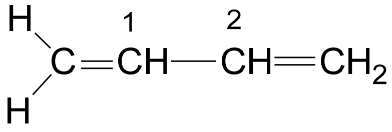
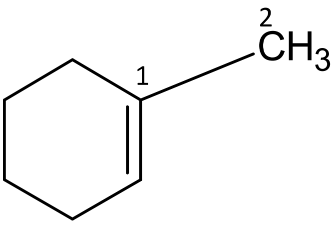
Since product **N** gives a reddish brown precipitate when reacted with Fehling's solution, an aldehyde functional group is present. Since aldehydes are formed from controlled oxidation of primary alcohol, the possible structures of primary alcohol from $C_4H_{10}O$ are:



and



Therefore, there are 2 isomers.

20	Which of the following compounds has the shortest C1-C2 bond length?	
	A	$\overset{1}{CH_3}-\overset{2}{CH_2}-CH_3$
	B	$\overset{1}{CH_3}-\overset{2}{CH}=CH_2$
	C	
	D	

Answer: C

Percentage of s character of hybridised orbitals are in order sp > sp^2 > sp^3. The higher the percentage of s character, the shorter the bond formed as the hybridised orbital will be more spherical.

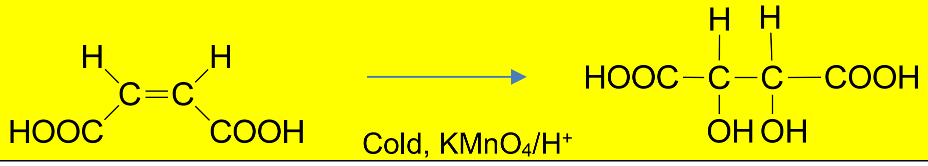
Option A has sp^3-sp^3 overlap.

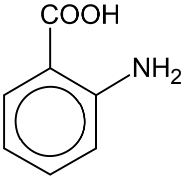
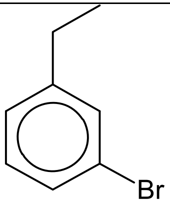
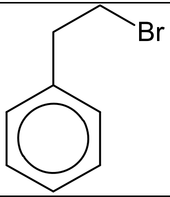
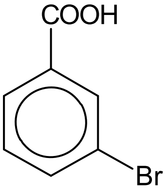
Option B and D has sp^3-sp^2.

Option C has sp^2-sp^2 overlap.

21	Maleic acid is used in the food industry and for stabilising drugs. It is the cis-isomer of butenedioic acid and has the structural formula $HO_2CCH{=}CHCO_2H$. What is the product formed from the reaction of maleic acid with cold, dilute, acidified manganate(VII) ions?	
	A	$HO_2CCH(OH)CH(OH)CO_2H$
	B	HO_2CCO_2H
	C	$HO_2CCH_2CH(OH)CO_2H$
	D	$HO_2CCOCOCO_2H$

Answer: **A**

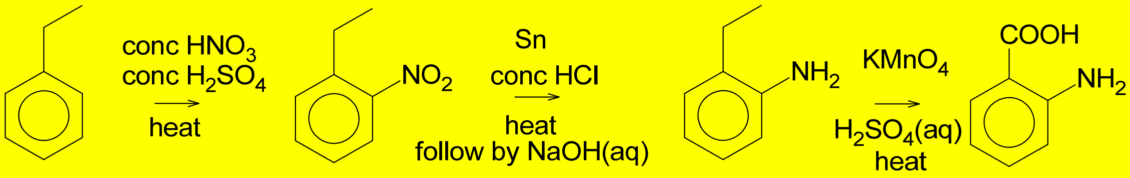


22	Which one of the following compounds **cannot** be synthesised from ethylbenzene?			
	A		**B**	
	C		**D**	

Answer: **B**

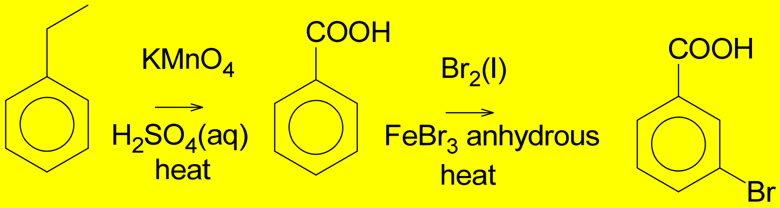
Ethyl group is 2,4 directing. Thus option B is wrong

Option A is correct



Option B is correct. Side chain free radical substitution has occurred.

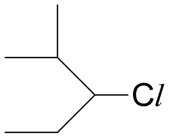
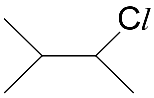
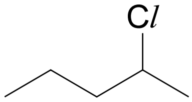
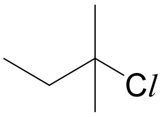
Option D is correct



23 Structural isomerism and stereoisomerism should be considered when answering this question.

A colourless liquid, $C_5H_{11}Cl$, exists as a mixture of two optical isomers.

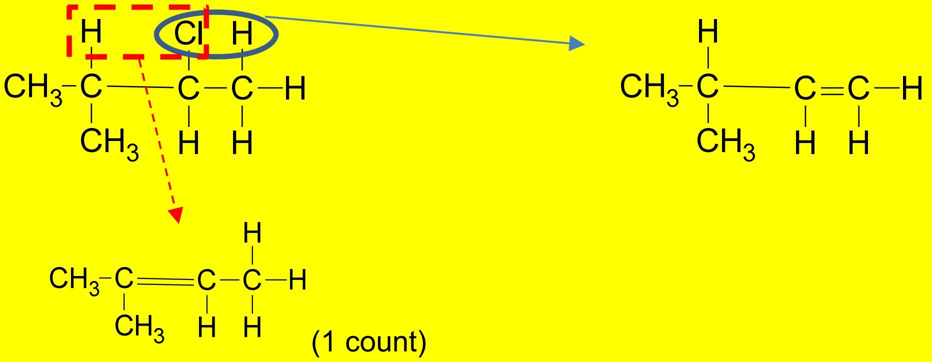
When heated with sodium hydroxide in ethanol, a mixture of only **two** alkenes is formed. What could the colourless liquid be?

A		**C**	
B		**D**	

Answer: **C**

Option A is wrong as it has one more carbon and thus does not match the molecular formula. Option D is out as they do not have chiral carbon to allow presence of two optical isomers.

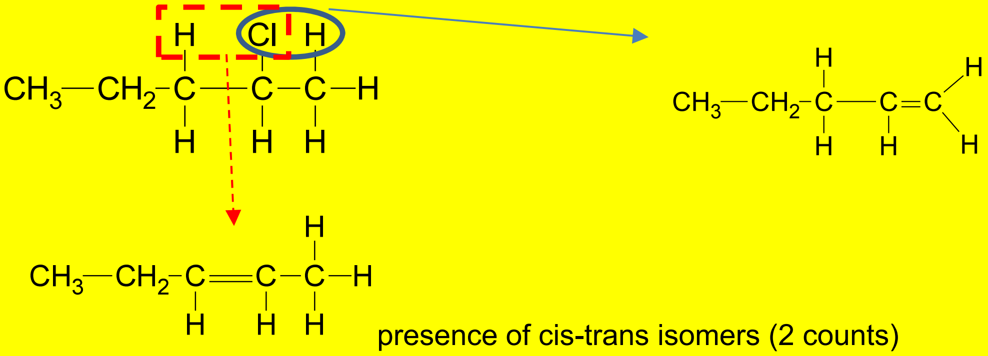
Option C is correct



(1 count)

(1 count)

Option B is wrong as during the elimination process (hot sodium hydroxide in ethanol) a mixture of three alkenes were obtained

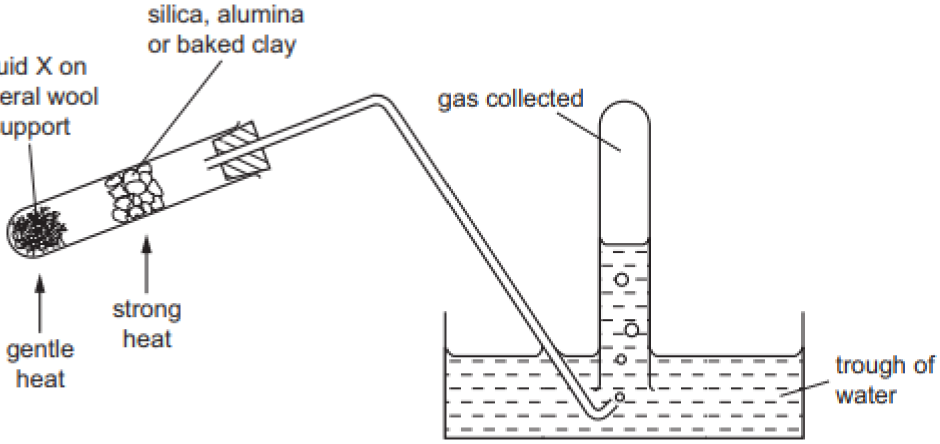


(1 count)

presence of cis-trans isomers (2 counts)

Thus, Option B structure will result in a mixture of 3 alkenes.

24 The diagram shows an experimental set-up which can be used in several different experiments.



Which processes could be demonstrated by using the above apparatus?

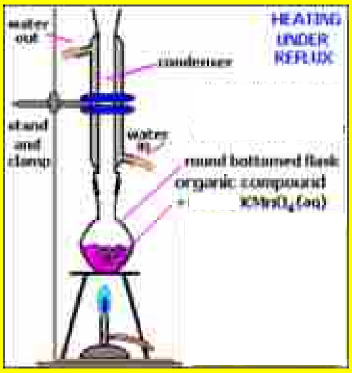
(1) oxidation of ethanol (liquid X)

(2) dehydration of ethanol (liquid X)

(3) cracking of paraffin (liquid X)

A	1, 2 and 3
B	1 and 2 only
C	2 and 3 only
D	3 only

Answer: C

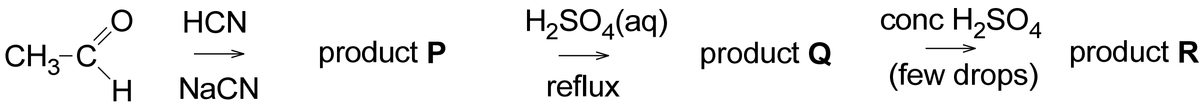


Oxidation of ethanol usually require a reflux set up

From lecture notes:

- Catalytic cracking is used to produce petrol (C_5 to C_{10}) and aromatic hydrocarbons.
- Catalyst: **zeolites** (mixture of Al_2O_3 and SiO_2).
- Temperature: **450 - 550°C** (Notice that lower temperatures are used)

25 Ethanal, CH_3CHO, is used to make product **R** in a three-stage synthesis.



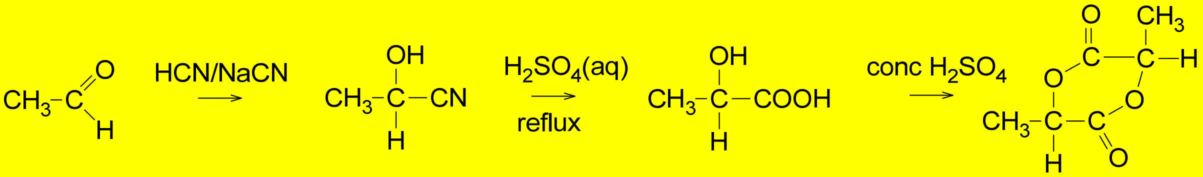
Two molecules of **Q** react to give one molecule of **R** plus two molecules of water.

R does not react with sodium.

What is the molecular formula and empirical formula of **R**?

	Molecular formula	Empirical formula
A	$C_3H_4O_2$	$C_3H_4O_2$
B	$C_6H_8O_4$	$C_3H_4O_2$
C	$C_3H_5O_2$	$C_3H_5O_2$
D	$C_6H_{10}O_5$	$C_6H_{10}O_5$

Answer: **B**



Molecular formula is $C_6H_8O_4$

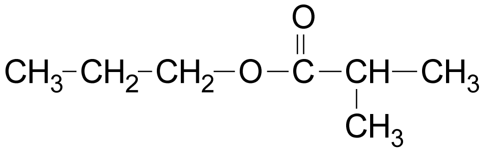
Empirical formula of product R is $C_3H_4O_2$

26	Chlorofluoroalkanes have been used as the refrigerant in refrigerators but care has to be taken in disposing of old refrigerators. Which statements about chlorofluoroalkanes are correct? (1) C–C*l* bonds more readily undergo homolytic fission than C–F bonds. (2) Care is taken in the disposal of old refrigerators because of possible ozone depletion. (3) C_2H_4ClF is more volatile than C_2H_6.	
	A	2 only
	B	1 and 2 only
	C	2 and 3 only
	D	1, 2 and 3
	Answer: B C-C*l* bonds are weaker than C-F bonds thus C-C*l* bonds require less energy to break when undergoing homolytic fission. Thus statement 1 is correct. Presence of Chlorofluoroalkanes will result in ozone depletion. Statement 2 is right. Statement 3 is wrong as C_2H_4ClF is polar and there are presence of stronger intermolecular permanent dipole-permanent dipole interaction as compared to the weaker instantaneous dipole-induced dipole interaction present in the non-polar molecule of C_2H_6.	

27 Ethyl propanoate is refluxed with aqueous sodium hydroxide. The alcohol produced is then reacted with methyl propanoic acid to make a second ester.

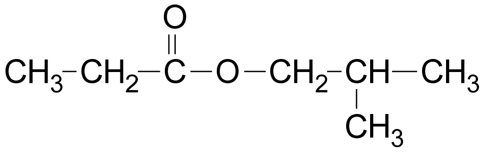
What is the structural formula of this second ester?

A



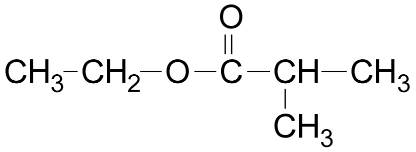
$CH_3-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

B



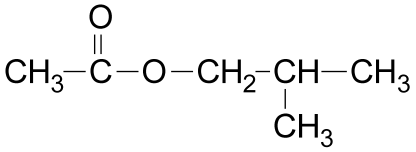
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

C



$CH_3-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

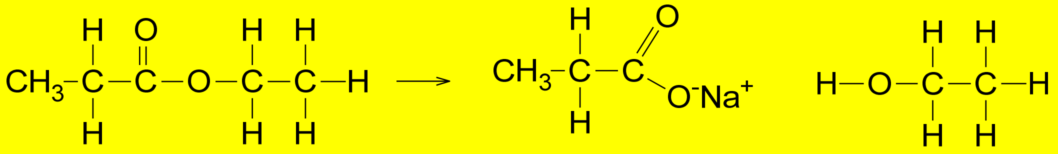
D



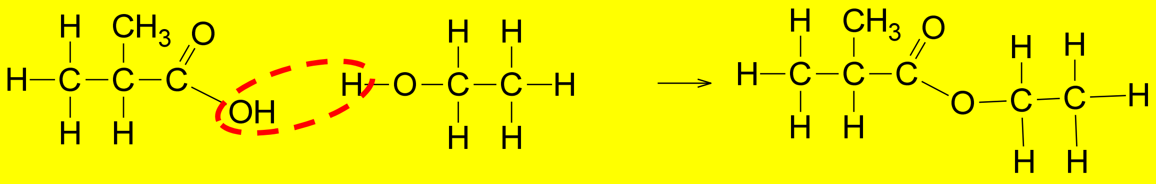
$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

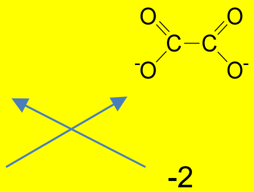
Answer: **C**

During the basic hydrolysis of ethyl propanoate with NaOH (aq)



Ethanol is produced



28	Ethanedioic acid has the formula HO_2CCO_2H. What is the formula of aluminium ethanedioate?	
	A	AlC_2O_4
	B	$Al(C_2O_4)_3$
	C	$Al_2C_2O_4$
	D	$Al_2(C_2O_4)_3$
Answer: **D** Species: Al^{3+}  Charge: +3 -2 Formula $Al_2(C_2O_4)_3$		

29	Which of the following processes lead to an increase in entropy? (1) Diffusion of air fresher in the lecture theatre. (2) Combustion of a piece of charcoal to form CO_2 (g) and H_2O (g). (3) Desalination of sea water by reverse osmosis (solvent passes from a dilute solution to a concentrated solution).	
	A	1 only
	B	1 and 2 only
	C	2 and 3 only
	D	1, 2 and 3
	Answer: **B** For option 3, there is an increase in orderliness as the solvent passes from a more concentrated solution to a more diluted solution. Hence, entropy will decrease.	

30 How many structural isomers with the molecular formula $C_5H_{10}O_2$ give infra-red absorptions both at approximately 1300 cm^{-1} and at approximately 1740 cm^{-1}?

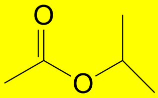
A 3

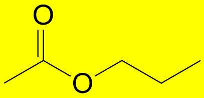
B 5

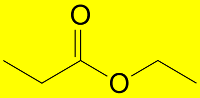
C 7

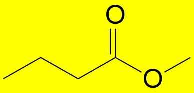
D 9

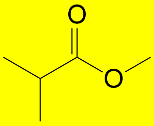
Answer: **B**
Infra-red absorption of 1300 cm^{-1}: carboxylic acid and ester
Infra-red absorption of 1740 cm^{-1}: ketone, aldehyde and ester
Thus, it has to be an ester since both conditions **MUST** be met.











END OF PAPER 1

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY **9729/02**

JC2 Preliminary Examination **12 September 2018**

Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part questions.

For Examiner's Use	
1	/9
2	/9
3	/22
4	/13
5	/13
6	/9
TOTAL	**/ 75**

This document consists of **19** printed pages and **1** blank page.

1 Elements in Period 3 exhibit a variety of physical and chemical properties.

(a) An element in Period 3 has a high melting point but low electrical conductivity. Identify this element and explain why it has a high melting point using concepts of structure and bonding.

....

....

....

[1]

(b) Two chlorides of Period 3 elements exist as liquids at room temperature. These two chlorides react with water to give white fumes, but only one of them gives a white solid.

(i) Using concepts of structure and bonding, explain why these two chlorides have low boiling points and exist as liquid at room temperature.

....

....

....

[1]

(ii) Write chemical equations, with state symbols, for each of these chlorides reacting with water.

....

....

[2]

(c) Period 3 elements also form oxides which reacts with water. Na_2O and SO_2 are two such oxides.

(i) Write chemical equations, with state symbols, when each of these oxides react with water.

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

(ii) SO_2 is used as a food preservative. Suggest the property of SO_2 which enables it to function this way.

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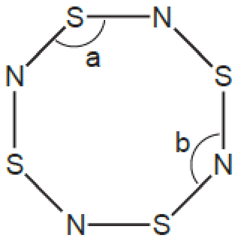
[1]

(d) Sulfur forms the compound S_4N_4 with nitrogen. The structure of S_4N_4 is shown below. Assume all bonds shown are single bonds.



Determine the number of lone pairs of electrons around a sulfur atom and a nitrogen atom in S_4N_4.

(i) Nitrogen atom: …………….. Sulfur atom: ………………..

[1]

(ii) Which bond angle, ***a*** or ***b***, will be smaller? Explain your answer.

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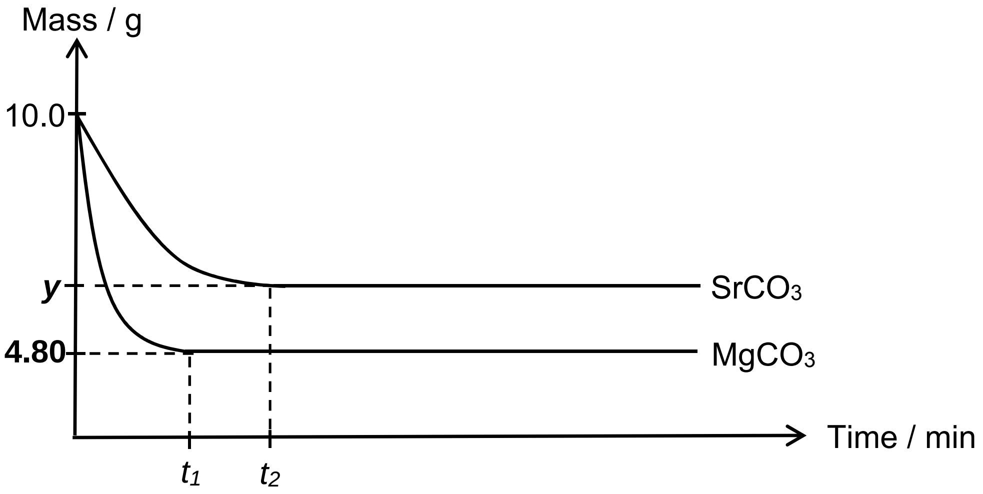
[1]

[Total: 9]

2 The following graph shows the change in mass with time for the decomposition of 10.0 g of magnesium carbonate and 10.0 g of strontium carbonate under the same conditions:



(a) **(i)** Calculate the value of ***y***.

[2]

(ii) Explain why the value of t_2 is larger than t_1.

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[3]

(b) There are three bottles labelled **A**, **B** and **C** in the laboratory. Each bottle contains one of the following reagents: aqueous Cl_2, KI solution and KBr solution.

The following tests were carried out and the results were summarised in the table below.

Experiment	Procedure	Observations
1	mixing reagent in bottle **A** with reagent in bottle **B**	mixture remains colourless
2	mixing reagent in bottle **A** with reagent in bottle **C**	mixture turns brown
3	mixing reagent in bottle **B** with reagent in bottle **C**	mixture turns brown

(i) Which bottle contains aqueous Cl_2?
With the aid of a balanced equation, explain your answer.

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[2]

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

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[1]

(c) Using relevant data from the *Data Booklet*, comment on the thermal stability of hydrogen bromide and hydrogen chloride.

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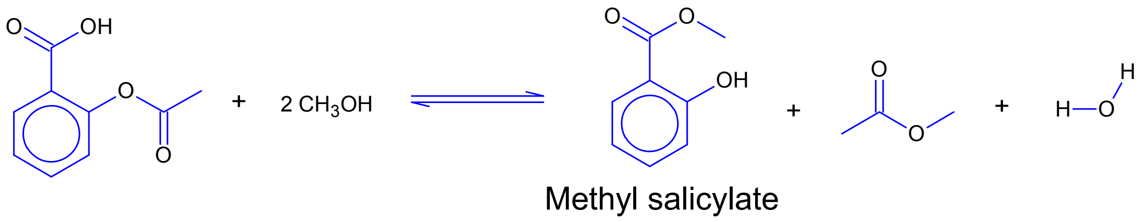
[1]

[Total:9]

3 Methyl salicylate, commonly known as oil of Wintergreen is used as a flavouring agent in candy. When methyl salicylate is applied to the skin, it causes a mild burning sensation which serves as a counter-irritant for sore muscles. It can be synthesise from aspirin. The reaction is as follows.



Reagent	**Density / g cm^{-3}**	**M$_r$**	**Solubility in water**
Acetylsalicylate acid (Aspirin)	[redacted]	180.0	insoluble
Sulfuric acid	1.84	98.0	soluble
Methanol	0.792	32.0	soluble
Methyl salicylate	1.17	152.1	insoluble
Water	1.00	18.0	[redacted]

Preparation of impure methyl salicylate

1. Weigh approximately 20 g of acetylsalicylate acid into a round-bottom flask. Add 30 cm^3 of methanol and stir until all the acetylsalicylate acid has dissolved.

2. Place 25 cm^3 of concentrated sulfuric acid in the tap funnel and then add the acid dropwise into the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.

3. When all of the acid have been added, replace the tap funnel with a reflux condenser and gently boil the mixture for an hour.

4. Remove the condenser and boil off about 50% of the volume.

(a) **(i)** By using the amounts given above, prove that methanol is in excess and suggest why it is done to increase yield.

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[2]

(b) When concentrated sulfuric acid is added to the reaction mixture, cooling is necessary. Suggest the main cause of heat being produced at this stage.

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…………………………………………………………………………………………

[1]

(c) The reaction mixture was heated overnight. Why is this process necessary for the preparation of many covalent organic compounds?

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…………………………………………………………………………………………

[1]

The crude product formed requires purification as it contains many impurities.

Purification of impure methyl salicylate

5. Transfer the remaining mixture into a separatory funnel. Shake the mixture with 30 cm^3 of ice cool water and separate the aqueous layer from the methyl salicylate. Reject the aqueous layer.

6. Return the methyl salicylate to the funnel. Add 20 cm^3 of dilute sodium hydrogencarbonate in the separating funnel, inverting the flask and opening the tap at intervals to prevent build up of pressure.

7. Transfer the methyl salicylate into a conical flask and add some granular anhydrous calcium sulfate. Swirl the mixture until the liquid is clear.

6. Filter the methyl salicylate into a clean vial. Weigh the purified product.

(d) Volume of methyl salicylate produced is 10 cm^3. Calculate the percentage yield.

[2]

(e) The impure methyl salicylate was shaken with water (step 5) and the two layers are allowed to separate.

(i) By considering the structure and bonding of methyl salicylate, suggest why it is an immiscible with methanol.

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[2]

(ii) Suggest the organic compounds inside both layers. Explain your answer.

Top layer: …………………………….. Bottom layer: …………………………………

Explanation: ………………………………………………………………………..
[2]

(f) **(i)** It is important to open the tap at intervals to prevent build up of pressure in when dilute aqueous sodium hydrogencarbonate was added (step 6). Explain, with the aid of an equation why this is important.

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[2]

(g) **(i)** Draw the dot-and-cross diagram of calcium sulfate used in step 7.

[2]

(ii) Calcium sulfate is a desiccant to remove any water left in the methyl salicylate product. When the desiccant has dissolved, the anions and cations are each surrounded by a number of water molecules.

Draw simple diagrams to show how a water molecule can be attached to a calcium cation, and to a sulfate anion. Label each of your diagram to show the type of interaction involved.

Ca^{2+} cation	SO_4^{2-} anion

[2]

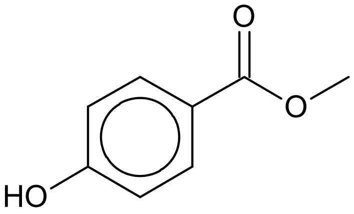
(iii) The lattice energy of calcium sulfate is − 2640 kJ mol^{-1}.

Use the following values of enthalpy change of hydration to construct an energy level diagram and use it to calculate the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for calcium sulfate.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	–1577
SO_4^{2-}	–1045

[3]

(h) Methyl 4–hydroxybenzoate is an isomer of methyl salicylate.



methyl 4–hydroxybenzoate

Predict and explain whether methyl 4–hydroxybenzoate or methyl salicylate would have a higher boiling point. [3]

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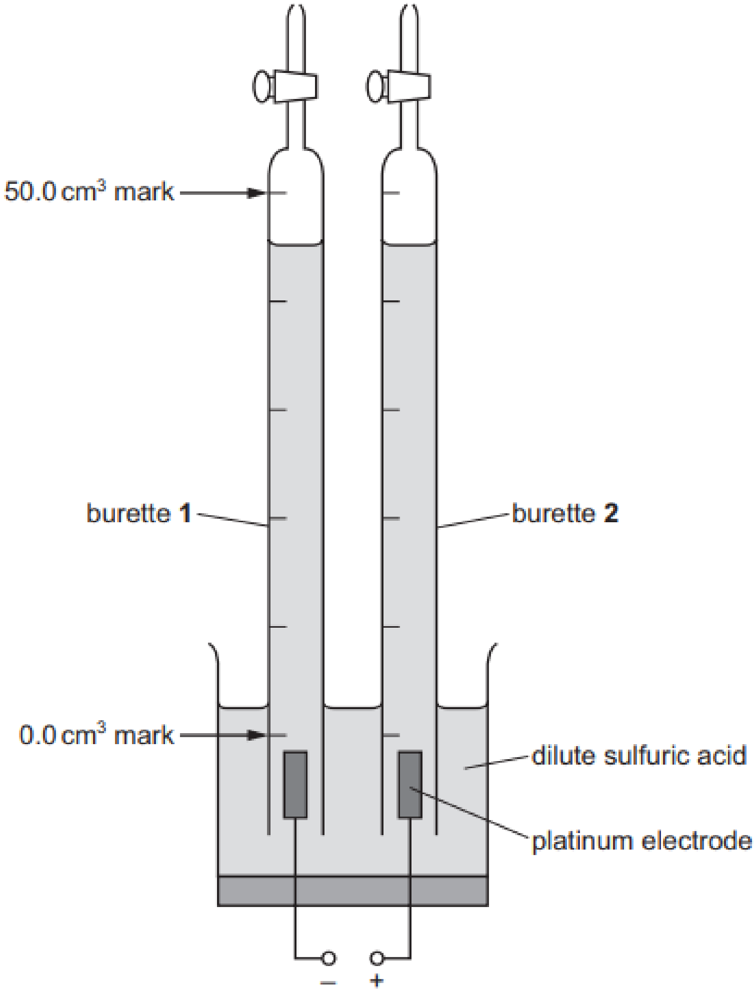
[3]

[Total: 22]

4 Dilute sulfuric acid, H_2SO_4(aq), can be electrolysed using platinum electrode and a direct current. Hydrogen gas is produced at the cathode and oxygen gas is formed at the anode. The two gases are collected separately in burettes filled with dilute sulfuric acid placed over each electrode.



Reaction at electrode in burette **1**: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Reaction at electrode in burette **2**: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-$

The production of hydrogen gas over time can be measured, and the data used to determine charge of one mole of electrons, known as the Faraday constant, *F*.

(a) (i) Student A performed the experiment and the volume of hydrogen gas produced during the electrolysis process were recorded in the table.

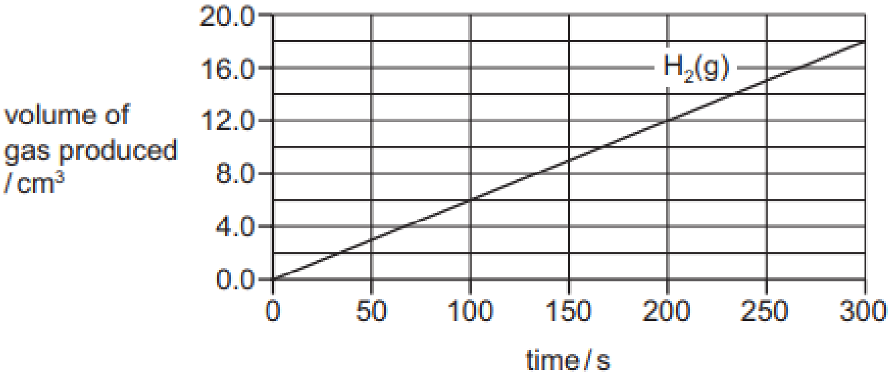
Process the results to calculate the volume of the hydrogen gas produced, in cm^3, and the charge passed, in coulombs, C.

The current was kept constant at 0.80A.

Time/s	Reading on burette **1**/cm^3	Volume of hydrogen gas produced /cm^3	Charge passed /C
0	46.20	0.00	
50	41.20		
100	36.20		
150	31.45		
200	25.80		
250	20.80		

[2]

(ii) Another student B, performed the experiment at room temperature and his graph showing the relationship between volume of $H_2(g)$ produced at the cathode and time was as shown below.



The gradient of the line of best fit gives the volume of hydrogen gas produced per coulomb.

Given that the gradient of the line to be 0.125 cm^3 C^{-1}, calculate the number of moles of hydrogen gas produced per coulomb.

[Molar volume of gas = 24.0 dm^3 at room temperature and pressure]

[1]

(iii) Using your answer from **(a)(ii)** and the half equation for the production of $H_2(g)$, calculate a numerical value for the Faraday constant (the charge of 1 mole of electrons).

[1]

(iv) Using the graph in **(a)(ii)**, draw a line on the graph to show the relationship between volume of $O_2(g)$ produced at the anode and time in this experiment.

[1]

(v) Explain why the volume of $O_2(g)$ measured in the experiment might be **less** than that shown by your drawn line. Assume that no gas is lost from leaks.

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…………………………………………………………………………………………

[1]

(b) A student suggested to replace the platinum electrodes with copper as it would be cheaper in the electrolysis of dilute sulfuric acid.

Quoting relevant data from the *Data Booklet*, suggest what effect, if any, the use of copper electrodes would have on the volume of gas produced at **each** electrode.

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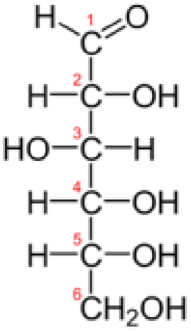
[3]

(c) Fehling's solution is a copper based chemical reagent used to differentiate between water soluble carbohydrate and ketone functional groups. This test was developed by German chemist Hermann von Fehling in 1849.

$RCHO + 2\ Cu(C_4H_4O_6)_2^{2-} + 5OH^- \rightarrow RCOO^- + Cu_2O + 4\ C_4H_4O_6^{2-} + 3H_2O$

Fehling's solution can be used to screen glucose in urine, thus detecting diabetes.



Glucose

(i) Suggest which carbon can be oxidised by Fehling's solution and draw the skeletal formula of the compound **D** which is the oxidised product of glucose after it has been acidified by dilute hydrochloric acid.

Carbon …………… Compound **D**:

[2]

(ii) Determine the change in oxidation number on the carbon mentioned in **(c)(i)** with respect to glucose and compound **D**.

[1]

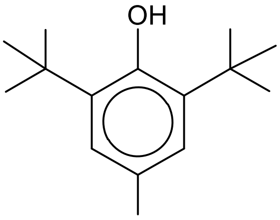
(iii) Hot concentrated sulfuric acid was added to compound **D**. Compound **E** which consists of a 6-atoms ring structure was formed.
Suggest the structure of compound **E**.

[1]

[Total: 13]

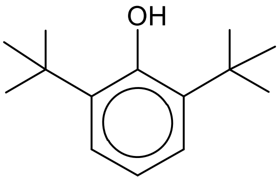
5 This question is about controversial food additives that are Generally Regarded As Safe (GRAS) by the American Food and Drug Administration (FDA), but are suspected to be harmful to humans when consumed.

(a) **(i)** Butylated hydroxytoluene (BHT) is useful for its antioxidant properties, to prevent oxidation in fluids (e.g. fuel, oil) and other foodstuffs where free radicals must be controlled.



Butylated hydroxytoluene (BHT)

Describe the mechanism for the synthesis of BHT using bromomethane and 2,6-di-tert-butylphenol shown below.



2,6-di-tert-butylphenol

[3]

(a) **(ii)** Propose a simple test-tube reaction to differentiate 2,6-di-tert-butylphenol and BHT. You are to clearly state the observation in your answer.

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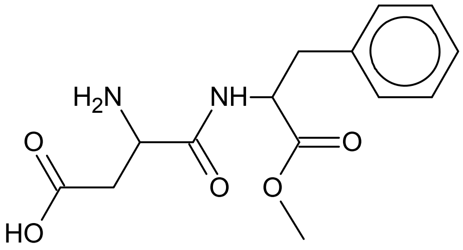
…………………………………………………………………………………… [2]

(b) Aspartame (APM) is an artificial non-carbohydrate sweetener used as a sugar substitute in some foods and beverages, which is especially useful for diabetic patients.



Aspartame (APM)

(i) Label all chiral carbons with an (*) in the diagram above and calculate the total number of possible stereoisomers of APM.

[2]

(ii) Draw all organic products formed when APM is reacted with a hot aqueous alkaline solution.

[3]

(c) Potassium bromate, $KBrO_3$, is typically used as a flour improver. It is a very strong oxidising agent, and allows for the baking of extremely white and fluffy bread, and it has the following half equation.

$$2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O \quad E^\ominus = +1.50\ V$$

(i) Suggest reagent and conditions for the oxidation of ethene to carbon dioxide.

…………………………………………………………………………………………..

[1]

(ii) Hot acidified bromate is also able to oxidise ethene into carbon dioxide. With reference to the *Data Booklet*, explain.

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[1]

(iii) Hence, suggest how the yield of the carbon dioxide produced would be affected due to the use of bromate as an oxidising agent.

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[1]

[Total: 13]

6 Compound **G** and **H** have molecular formula of C_4H_8 and C_3H_6 respectively, and do not exhibit cis-trans isomerism.

Both **G** and **H** can decolourise hot potassium manganate(VII) to give compounds **J** and **K** respectively, together with a gas that produces a white precipitate when bubbled through calcium hydroxide.

J produces an orange precipitate when warm with 2,4–dinitrophenylhydrazine, and **K** produces effervescence when sodium hydrogencarbonate is added.
J decolourises alkaline aqueous iodine but not **K**.

(a) Draw the structures of **G**, **H**, **J**, and **K**.

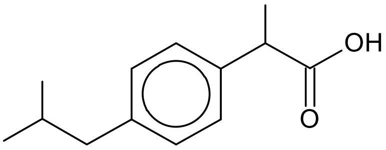
[4]

(b) Construct a balanced chemical equation on how **J** reacts with

- alkaline aqueous iodine,
- 2,4-DNPH.

[2]

(c) Ibuprofen is an oral or intravenous medication that is used for treating pain, fever, and inflammation. It typically begins working within an hour and it has the following structure.



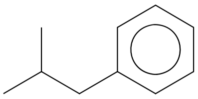
Ibuprofen

Compounds **G** and **H** from **(a)** are both prerequisites for the synthesis of Ibuprofen.

The reaction schema to obtain ibuprofen is described below.

(1) HBr gas is introduced to **G** to form **L**.

(2) **L** is reacted with benzene in the presence of anhydrous $FeBr_3$. Compound **M** is obtained.



Compound **M**

(3) Aqueous Br_2 is added to **H** to form **N**.

(4) **N** and **M** are reacted in the presence of anhydrous $FeBr_3$. Compound **P** with molecular formula $C_{13}H_{20}O$ is produced.

(5) Hot acidified potassium dichromate(VI) is then added to **P** to produce ibuprofen.

Using the structure of ibuprofen and the information provided, draw the structures of **L**, **N** and **P**.

[3]

[Total: 9]

END OF PAPER

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SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/02

JC2 Preliminary Examination **12 September 2018**
Paper 2 Structured Questions (Solutions) **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

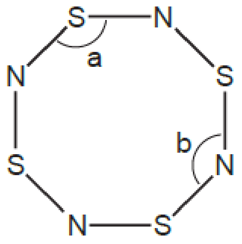
READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

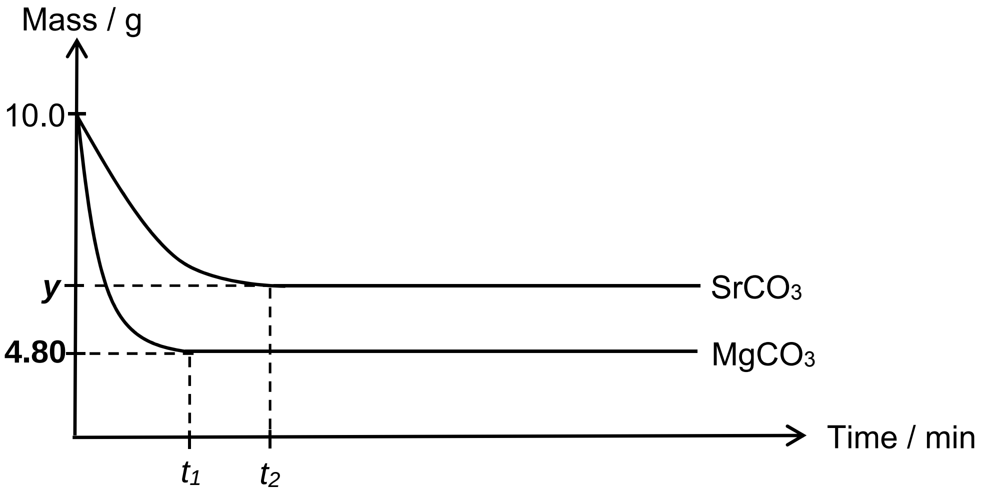
Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part questions.

For Examiner's Use	
1	/9
2	/9
3	/22
4	/13
5	/13
6	/9
TOTAL	**/ 75**

1	Elements in Period 3 exhibit a variety of physical and chemical properties.		
	(a)	An element in Period 3 has a high melting point but low electrical conductivity. Identify this element and explain why it has a high melting point using concepts of structure and bonding. [1]	
		Silicon has a **giant molecular structure** and **strong covalent bonds between the atoms in the molecule**. Hence it needs a large about of energy to overcome it. [1]	
	(b)	Two chlorides of Period 3 elements exist as liquids at room temperature. These two chlorides react with water to give white fumes, but only one of them gives a white solid.	
		(i)	Using concepts of structure and bonding, explain why these two chlorides have low boiling points and exist as liquid at room temperature. [1]
			Both have **simple molecular structure**. These compounds have low boiling points since **less heat energy** is required to overcome the **weak intermolecular forces of attraction**. [1]
		(ii)	Write chemical equations, with state symbols, for each of these chlorides reacting with water. [2]
			$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$ [1] $PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(g)$ [1] Do not accept PCl_5 as it is a solid
	(c)	Period 3 elements also form oxides which reacts with water. Na_2O and SO_2 are two such oxides.	
		(i)	Write chemical equations, with state symbols, when each of these oxides react with water. [2]
			$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ [1] $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$ [1]
		(ii)	SO_2 is used as a food preservative. Suggest the property of SO_2 which enables it to function this way. [1]
			It acts as a reducing agent/ antioxidant. [1] Note: Food may turn bad due to oxidation process. SO_2 will be oxidised in place of the food.
	(d)	Sulfur forms the compound S_4N_4 with nitrogen. The structure of S_4N_4 is shown below. Assume all bonds shown are single bonds. 	

		Determine the number of lone pairs of electrons around a sulfur atom and a nitrogen atom in S_4N_4.	
		(i)	Nitrogen atom Sulfur atom [1]
			Nitrogen atom: **1** lone pair Sulfur atom: **2** lone pairs [1]
		(ii)	Which bond angle, ***a*** or ***b***, will be smaller? Explain your answer. [1]
			Bond angle **a** will be **smaller**. **Lone-pair lone-pair repulsion is greater** than lone-pair single electron repulsion. [1]
			[Total: 9]

2	The following graph shows the change in mass with time for the decomposition of 10.0 g of magnesium carbonate and 10.0 g of strontium carbonate under the same conditions:  		
	(a)	**(i)**	Calculate the value of ***y***. [2]
			$SrCO_3(s) \rightarrow SrO(s) + CO_2(g)$ **y** is the mass of SrO that formed from the decomposition Amount of $SrCO_3$ = $\frac{10}{(87.6+12.0+16.0\times3)} = 0.06775\,mol$ [1] Amount of SrO formed = 0.06775 mol Mass of SrO, **y** = 0.06775 x (87.6 + 16.0) = 7.02 g [1]

(ii) Explain why the value of t_2 is larger than t_1.

[3]

- **Cationic radius of Sr^{2+} is larger than Mg^{2+}** while cationic charge is the same or **Charge density, and hence polarising power, of the Sr^{2+} is smaller**. **[1]**
- **Polarising effect on the anion by Sr^{2+} is smaller** **[1]** and the anion electron cloud is distorted to a smaller extent.
- More energy is required to overcome the C–O bond in $SrCO_3$.
- **Rate is slower and a longer time (t_2) is needed to decompose $SrCO_3$**.[1]

(b) There are three bottles labelled **A**, **B** and **C** in the laboratory. Each bottle contains one of the following reagents: aqueous Cl_2, KI solution and KBr solution.

The following tests were carried out and the results were summarised in the table below.

Experiment	Procedure	Observations
1	mixing reagent in bottle **A** with reagent in bottle **B**	mixture remains colourless
2	mixing reagent in bottle **A** with reagent in bottle **C**	mixture turns brown
3	mixing reagent in bottle **B** with reagent in bottle **C**	mixture turns brown

(i) Which bottle contains aqueous Cl_2? With the aid of a balanced equation, explain your answer.

[2]

Bottle **C** **[1]**

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$ where X = Br or I **[1]**

Down the group, reduction potential becomes **less positive**.

The halogens have **lower tendency to be reduced**.

Stronger oxidising agent higher in the Group oxidises (and hence displaces) the **halide ions in aqueous solution further down the Group** **[1]**

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

[1]

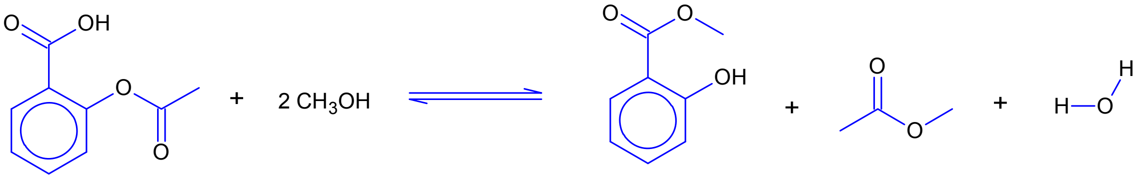
Knowing that bottle **A** and **B** is either KBr or KI, **add hexane to the two brown mixtures obtained, separately.**

If the organic layer is **purple, bottle contains KI**.

If the organic layer is **red–brown, bottle contains KBr.** **[1]**

	(c)	Using relevant data from the *Data Booklet*, comment on the thermal stability of hydrogen bromide and hydrogen chloride. [1]
		Bond energy of H-Br (366 kJ mol^{-1}) is lesser than bond energy of H-C*l* (431 kJ mol^{-1}) Less energy is required to overcome the weaker covalent bond in H-Br thus HBr will decompose at a lower temperature. **[1]**
		[Total:9]

3 Methyl salicylate, commonly known as oil of Wintergreen is used as a flavouring agent in candy. When methyl salicylate is applied to the skin, it causes a mild burning sensation which serves as a counter-irritant for sore muscles. It can be synthesise from aspirin. The reaction is as follows.



Methyl salicylate

Reagent	Density / g cm⁻³	Mr	Solubility in water
Acetylsalicylate acid (Aspirin)	[redacted]	180.0	insoluble
Sulfuric acid	1.84	98.0	soluble
Methanol	0.792	32.0	soluble
Methyl salicylate	1.17	152.1	insoluble
Water	1.00	18.0	[redacted]

Preparation of impure methyl salicylate

1. Weigh approximately 20 g of acetylsalicylate acid into a round-bottom flask. Add 30 cm^3 of methanol and stir until all the acetylsalicylate acid has dissolved.

2. Place 25 cm^3 of concentrated sulfuric acid in the tap funnel and then add the acid dropwise into the reagents in the flask. Keep the contents well shaken and cool occasionally in an ice-water bath.

3. When all of the acid have been added, replace the tap funnel with a reflux condenser and gently boil the mixture for an hour.

4. Remove the condenser and boil off about 50% of the volume.

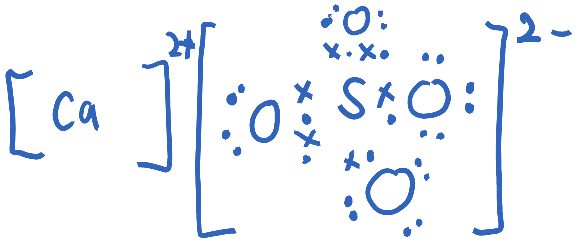
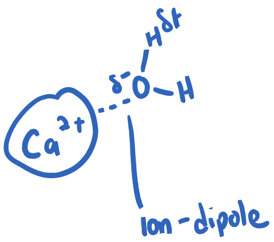
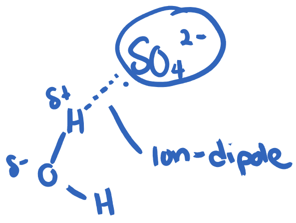
(a) **(i)** By using the amounts given above, prove that methanol is in excess and suggest why it is done to increase yield.

[2]

$n_{methanol}$ = (30 x 0.792) / 32 = 0.742 mol
$n_{aspirin}$ = 20/180 = 0.1111mol
$n_{methanol}$ = ½ aspirin
Hence methanol is in excess. [1]

		By LCP, increase the methanol concentration would cause the position of equilibrium to lie towards the forward reaction (right), [1] increasing the amount of methyl salicylate produced.
(b)		When concentrated sullfuric acid is added to the reaction mixture, cooling is necessary. Suggest the main cause of heat being produced at this stage. [1]
		Dilution of concentrated sulfuric acid produces heat. [1]
(c)		The reaction mixture was heated overnight. Why is this process necessary for the preparation of many covalent organic compounds? [1]
		Breaking strong covalent bonds [1] requires a large amount of energy to overcome.
		The crude product formed requires purification as it contains many impurities. Purification of impure methyl salicylate 5. Transfer the remaining mixture into a separatory funnel. Shake the mixture with 30 cm^3 of ice cool water and separate the aqueous layer from the methyl salicylate. Reject the aqueous layer. 6. Return the methyl salicylate to the funnel. Add 20 cm^3 of dilute sodium hydrogencarbonate in the separating funnel, inverting the flask and opening the tap at intervals to prevent build up of pressure. 7. Transfer the methyl salicylate into a conical flask and add some granular anhydrous calcium sulfate. Swirl the mixture until the liquid is clear. 6. Filter the methyl salicylate into a clean vial. Weigh the purified
(d)		Volume of methyl salicylate produced is 10 cm^3. Calculate the percentage yield.
		Aspirin is the limiting reaction $n_{\text{methyl salicylate}} = n_{\text{aspirin}}$ = 20/180 = 0.1111mol [1] Theortical yield (in Vol) = 0.1111 x 152.1 ÷ 1.17 = 14.44 cm^3 % yield = 10/14.44 = 69.2 % [1]
(e)	The impure methyl salicylate was shaken with water (step 5) and the two layers are allowed to separate.	

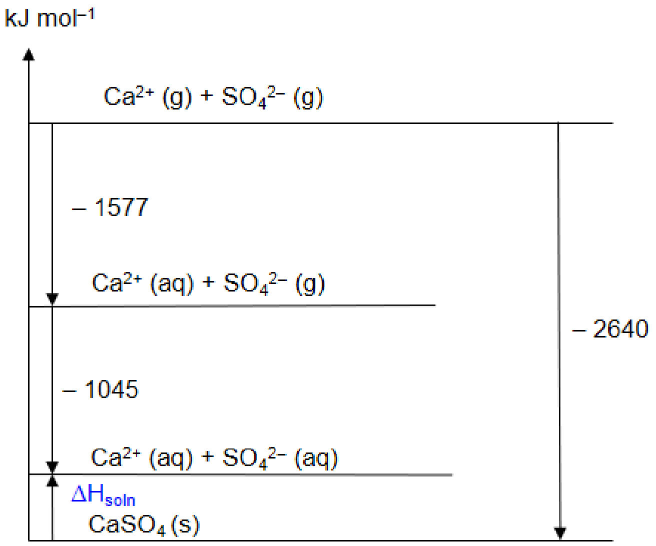
	(i)	By considering the structure and bonding of methyl salicylate, suggest why it is an immiscible with methanol. [2]
		The extensive intermolecular id-id interactions due to the hydrophobic benzene ring [1] is not strong enough to displace the stronger intermolecular hydrogen bonds. [1]
	(ii)	Suggest the organic compounds inside both layers. Explain your answer. [2]
		Top layer: methanol Bottom layer: methyl salicylate [1] for both Explanation: methyl salicylate is more dense than methanol [1] for reason

(f)	**(i)**	It is important to open the tap at intervals to prevent build up of pressure in when dilute aqueous sodium hydrogencarbonate was added (step 6). Explain, with the aid of an equation why this is important. [2]
		$H_2SO_4 + 2NaHCO_3 \rightarrow 2CO_2 + 2H_2O + Na_2SO_4$ [1] (x) but mark reason separately – $H_2SO_4 + NaHCO_3 \rightarrow CO_2 + H_2O + NaHSO_4$ H_2SO_4 + methyl salicylate → CO_2 **Gaseous CO_2** is produced which will **increase the pressure** in the separatory funnel. [1]
(g)	**(i)**	Draw the dot-and-cross diagram of calcium sulfate used in step 7. [2]
		 [1] [1]
	(ii)	Calcium sulfate is a desiccant to remove any water left in the methyl salicylate product. When the desiccant has dissolved, the anions and cations are each surrounded by a number of water molecules. Draw simple diagrams to show how a water molecule can be attached to a calcium cation, and to a sulfate anion. Label each of your diagram to show the type of interaction involved. [2]
		 Ca^{2+} cation [1]  SO_4^{2-} anion [1]

(iii) The lattice energy of calcium sulfate is — 2640 kJ mol^{-1}.
Use the following values of enthalpy change of hydration to construct an energy cycle and use it to calculate the enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, for calcium sulfate.

	$\Delta H_{hyd}^{\ominus}$ / kJ mol^{-1}
Ca^{2+}	–1577
SO_4^{2-}	–1045

[3]

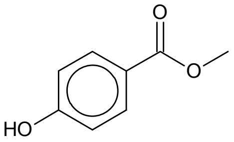


[2] energy level

$\Delta H_{sol}^{\ominus} = \Delta H_{hyd}^{\ominus}(Ca^{2+}) + \Delta H_{hyd}^{\ominus}(SO_4^{2-}) - \Delta H_{latt}^{\ominus}$

$= -1577 + (-1045) - (-2640) =$ **<u>+ 18.0 kJ mol^{-1}</u>** [1]

(h) Methyl 4–hydroxybenzoate is an isomer of methyl salicylate.



methyl 4–hydroxybenzoate

Predict and explain whether methyl 4–hydroxybenzoate or methyl salicylate would have a higher boiling point. [3]

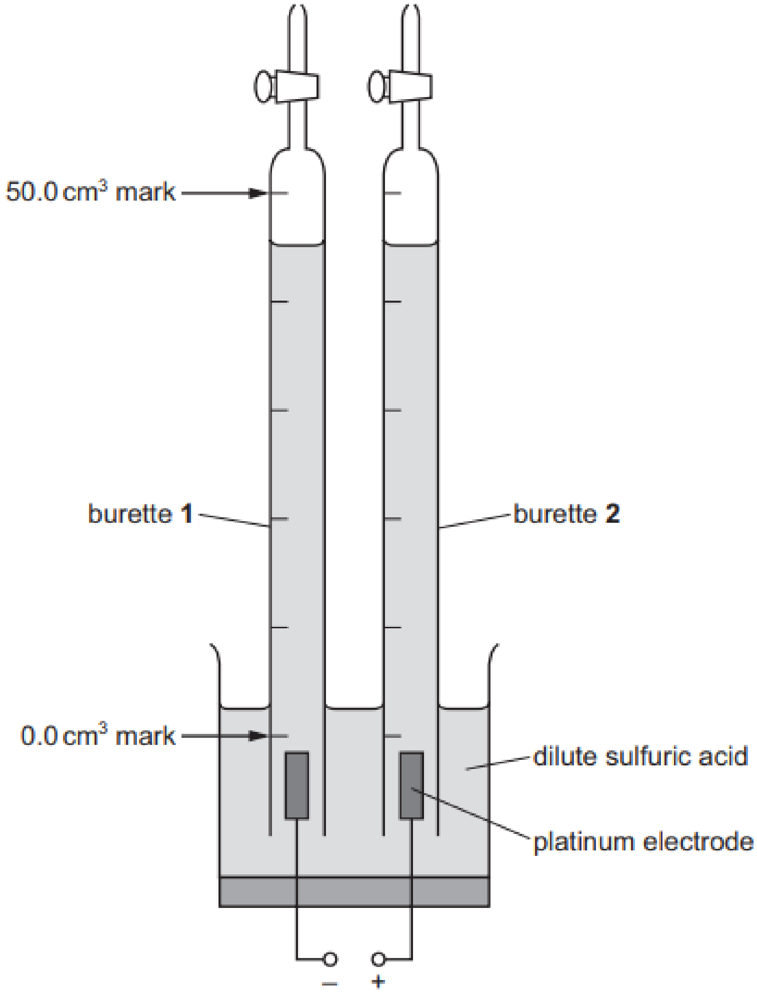
Both have simple molecular structure.
<u>Methyl 4–hydroxybenzoate would have a **higher boiling point**</u> [1] than methyl salicylate.

The **<u>close proximity</u>** of the two substituents on methyl salicylate allows for **<u>intramolecular hydrogen bonding</u>**[1] as compared to methyl 4–hydroxybenzoate which is far apart.

There will be **<u>less energy</u>** required to overcome the **<u>less extensive intermolecular hydrogen bonds</u>** [1] to overcome in methyl salicylate and thus it has a lower boiling point.

[Total: 22]

4 Dilute sulfuric acid, $H_2SO_4(aq)$, can be electrolysed using platinum electrode and a direct current. Hydrogen gas is produced at the cathode and oxygen gas is formed at the anode. The two gases are collected separately in burettes filled with dilute sulfuric acid placed over each electrode.



Reaction at electrode in burette **1**: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
Reaction at electrode in burette **2**: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-$

The production of hydrogen gas over time can be measured, and the data used to determine charge of one mole of electrons, known as the Faraday constant, *F*.

(a) **(i)** Student A performed the experiment and the volume of hydrogen gas produced during the electrolysis process were recorded in the table.

Process the results to calculate the volume of the hydrogen gas produced, in cm^3, and the charge passed, in coulombs, C.

The current was kept constant at 0.80A.

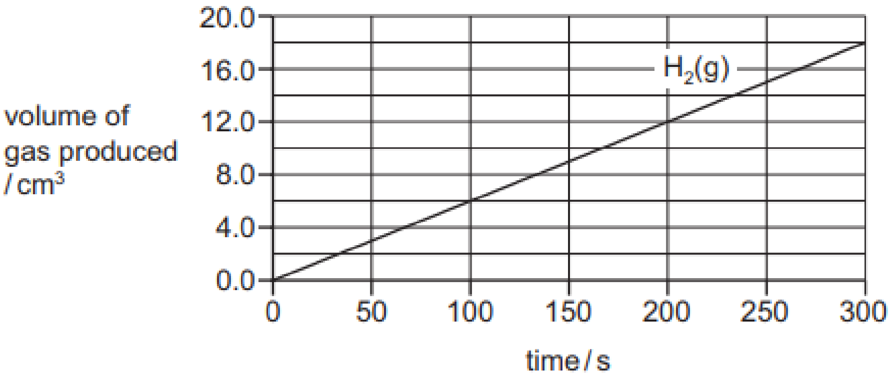
Time/s	Reading on burette **1**/cm^3	Volume of hydrogen gas produced /cm^3	Charge passed /C
0	46.20	0.00	0
50	41.20	5.00	40
100	36.20	10.00	80
150	31.45	14.75	120
200	25.80	20.40	160
250	20.80	25.40	200

[2]

[1]: Volume of H_2 correct and to 2 d.p

[1] charge correct

(ii) Another student B, performed the experiment at room temperature and his graph showing the relationship between volume of $H_2(g)$ produced at the cathode and time was as shown below.



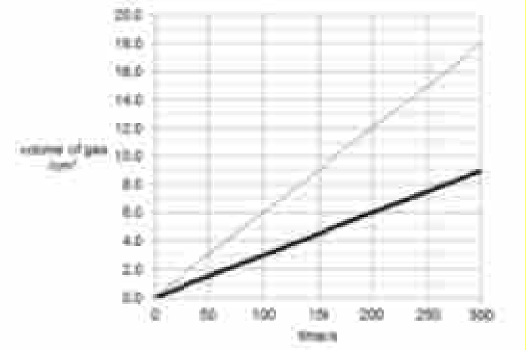
The gradient of the line of best fit gives the volume of hydrogen gas produced per coulomb.

Given that the gradient of the line to be 0.125 cm^3 C^{-1}, calculate the number of moles of hydrogen gas produced per coulomb.

[Molar volume of gas = 24.0 dm^3 at room temperature and pressure]

[1]

$\frac{0.125}{24000} = 5.208 \times 10^{-6}$ mol C^{-1} [1]

		(iii)	Using your answer from **(a)(ii)** and the half equation for the production of H_2(g), calculate a numerical value for the Faraday constant (the charge of 1 mole of electrons). [1]
			$1 \div \left(2 \times \frac{0.125}{24000}\right)$ = 96000 C mol^{-1} [1]
		(iv)	Using the graph in **(a)(ii)**, draw a line on the graph to show the relationship between volume of O_2(g) produced at the anode and time in this experiment. [1]
			 Straight line from origin to (300, 9.0) [1]
		(v)	Explain why the volume of O_2(g) measured in the experiment might be **less** than that shown by your drawn line. Assume that no gas is lost from leaks. [1]
			Oxygen is slightly soluble in water. [1] Or Oxygen gas is assumed to be ideal based on the fact of 24 dm^3 mentioned in the question.
	(b)	A student suggested to replace the platinum electrodes with copper as it would be cheaper in the electrolysis of dilute sulfuric acid. Quoting relevant data from the *Data Booklet*, suggest what effect, if any, the use of copper electrodes would have on the volume of gas produced at **each** electrode. [3]	
		Cu^{2+}/Cu +0.34 V $O_2/2H_2O$ +1.23 V H^+/H_2 0.00 V Cathode: No effect at cathode. [1] Anode: Copper anode will dissolve as it is a reactive electrode as Cu^{2+}/Cu has a more negative E^θ value [1 with data quoted] Less gas produced at anode when copper electrode is used. [1]	

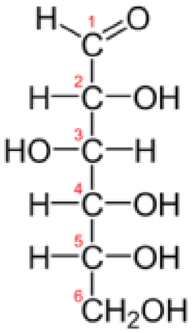
Reason: *not marking for this question but essential for understanding*.
At the anode: Cu^{2+}/Cu has more negative E^{θ}, hence Cu will be oxidised instead of H_2O
Anodic reaction when Cu electrode is used: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$
Anodic reaction when Pt electrode is used: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e$

At the cathode: Cathodic reaction for Pt and Cu electrode will be the same
$2H^+(aq) + 2e \rightarrow H_2(g)$.

(c) Fehling's solution is a copper based chemical reagent used to differentiate between water soluble carbohydrate and ketone functional groups. This test was developed by German chemist Hermann von Fehling in 1849.

$$RCHO + 2\,Cu(C_4H_4O_6)_2^{2-} + 5OH^- \rightarrow RCOO^- + Cu_2O + 4\,C_4H_4O_6^{2-} + 3H_2O$$

Fehling's solution can be used to screen glucose in urine, thus detecting diabetes.



Glucose

(i) Suggest which carbon can be oxidised by Fehling's solution and draw the skeletal formula of the compound **D** which is the oxidised product of glucose after it has been acidified by dilute hydrochloric acid.

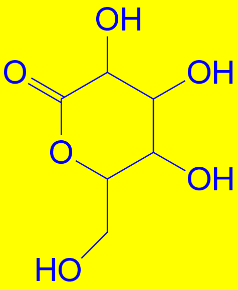
[2]

Carbon 1 [1]

Compound **D**: [1]

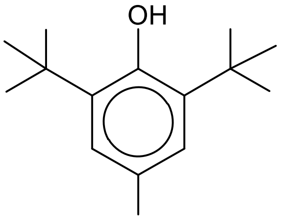
(ii) Determine the change in oxidation number on the carbon mentioned in **(c)(i)** with respect to glucose and compound **D**.

[1]

			Oxidation number of carbon 1 on glucose: +1 Oxidation number of carbon 1 on compound D +3 The oxidation number changes from +1 to +3 [1] Or The oxidation number increase by 2 Or +2
		(iii)	Hot concentrated sulfuric acid was added to compound **D**. Compound **E** which consists of a 6-atoms ring structure was formed. Suggest the structure of compound **E**. [1]
			 [1]
			[Total: 13]

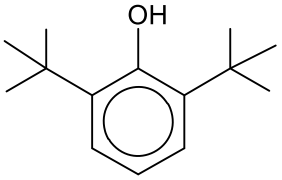
5 This question is about controversial food additives that are Generally Regarded As Safe (GRAS) by the American Food and Drug Administration (FDA), but are suspected to be harmful to humans when consumed.

(a) (i) Butylated hydroxytoluene (BHT) is useful for its antioxidant properties, to prevent oxidation in fluids (e.g. fuel, oil) and other foodstuffs where free radicals must be controlled.



Butylated hydroxytoluene (BHT)

Describe the mechanism for the synthesis of BHT using bromomethane and 2,6-di-tert-butylphenol shown below.



2,6-di-tert-butylphenol

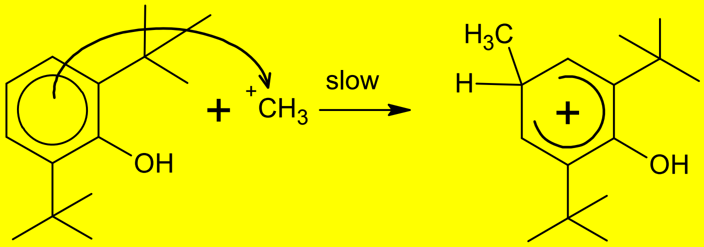
[3]

Electrophilic Substitution

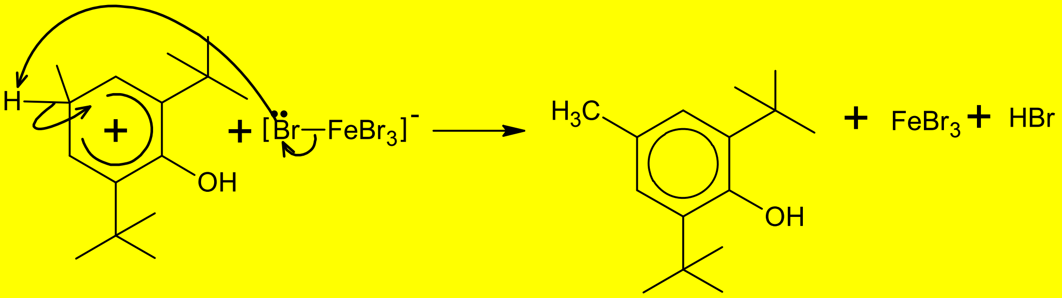
Step 1

$CH_3Br + FeBr_3 \longrightarrow {}^{+}CH_3 + [Br\text{–}FeBr_3]^{-}$ (it's in the lecture note ☺)

Step 2

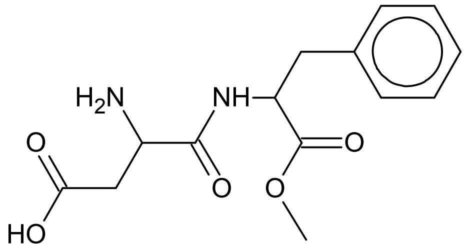
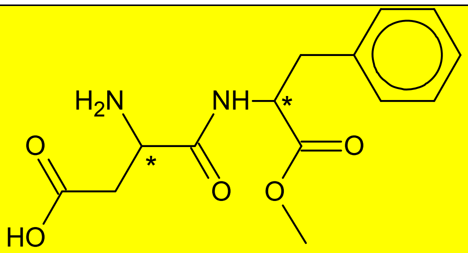
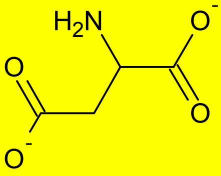
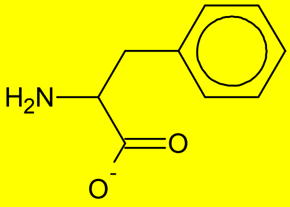


Step 3



If mis-draw the structure penalise one mark

[3m] each mistake minus 1m

	(a)	**(ii)**	Propose a simple test-tube reaction to differentiate 2,6-di-tert-butylphenol and BHT. You are to clearly state the observation in your answer. [2]
			Test: Add Br_2 (aq) [1] Observation: Orange Br_2 decolourises in 2,6-di-tert-butylphenol but not in BHT. [1]
	(b)	Aspartame (APM) is an artificial non-carbohydrate sweetener used as a sugar substitute in some foods and beverages, which is especially useful for diabetic patients.  Aspartame (APM)	
		(i)	Label all chiral carbons with an (*) in the diagram above and calculate the total number of possible stereoisomers of APM. [2]
			 [1] 2^2 = 4 isomers [1]
		(ii)	Draw all organic products formed when APM is reacted with a hot aqueous alkaline solution. [3]
			  H_3C-OH [1] for each correct structure

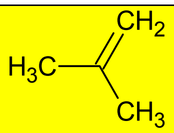
	(c)	Potassium bromate, $KBrO_3$, is typically used as a flour improver. It is a very strong oxidising agent, and allows for the baking of extremely white and fluffy bread, and it has the following half equation. $2BrO_3^- + 12H^+ + 10e \rightleftharpoons Br_2 + 6H_2O \quad E^\ominus = +1.50\text{ V}$	
		(i)	Suggest reagent and conditions for the oxidation of ethene to carbon dioxide.
			$KMnO_4$, H_2SO_4 (aq), Heat [1]
		(ii)	Hot acidified bromate is also able to oxidise ethene into carbon dioxide. With reference to the *Data Booklet*, explain. [1]
			$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \quad E = +1.52\text{ V}$ Since the **reduction potential of bromate is similar to that of manganate(VII)**, bromate would be a strong enough oxidising agent to oxidise ethene to carbon dioxide. [1]
		(iii)	Hence, suggest how the yield of the carbon dioxide produced would be affected due to the use of bromate as an oxidising agent. [1]
			The yield of CO_2 produced would be lower than expected as Br_2 would be produced which would then react with some ethene reactant present. [1]
			[Total: 13]

6 Compound **G** and **H** have molecular formula of C_4H_8 and C_3H_6 respectively, and do not exhibit cis-trans isomerism.

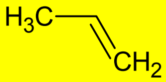
Both **G** and **H** can decolourise hot potassium manganate(VII) to give compounds **J** and **K** respectively, together with a gas that produces a white precipitate when bubbled through calcium hydroxide.

J produces an orange precipitate when warm with 2,4–dinitrophenylhydrazine, and **K** produces effervescence when sodium hydrogencarbonate is added.
J decolourises alkaline aqueous iodine but not **K**.

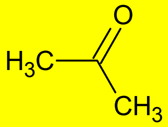
(a) Draw the structures of **G**, **H**, **J**, and **K**. [4]



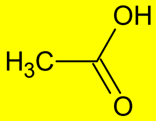
G



H



J



K

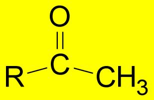
[1] for each correct structure

Statements for your information (not required by question)

✓ Both **G** and **H** has molecular formula with general formula C_nH_{2n}
- G and H are **alkenes**

✓Both **G** and **H** decolourises hot $KMnO_4$ to form **J** and **K** and CO_2
- **oxidation**
- G and H are **terminal alkenes**

✓ **J** produces orange ppt with 2,4–DNPH
- **condensation**
- **J** is a **ketone**

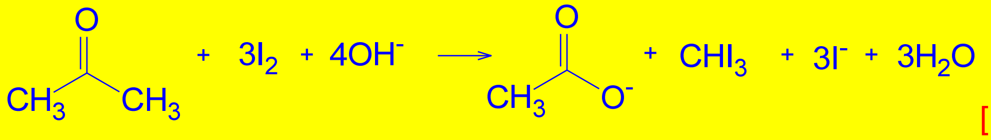
✓ **J** decolourises alkaline I_2
- **Oxidation**
- **J** has  $R-C(=O)-CH_3$

✓ **K** produces gas with $NaHCO_3$
- **neutralisation**
- **K** is a **carboxylic acid**

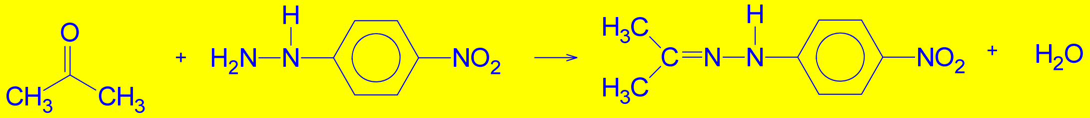
(b) Construct a balanced chemical equation on how **J** reacts with

- alkaline aqueous iodine,
- 2,4-DNPH.

[2]

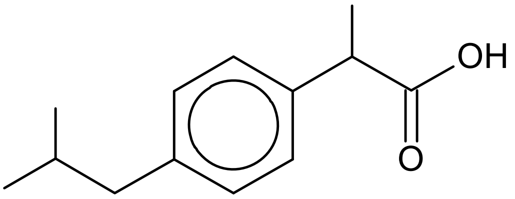


[1]



[1]

(c) Ibuprofen is an oral or intravenous medication that is used for treating pain, fever, and inflammation. It typically begins working within an hour and it has the following structure.



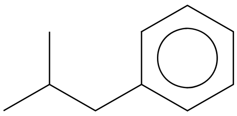
Ibuprofen

Compounds **G** and **H** from **(a)** are both prerequisites for the synthesis of Ibuprofen.

The reaction schema to obtain ibuprofen is described below.

(1) HBr gas is introduced to **G** to form **L**.

(2) **L** is reacted with benzene in the presence of anhydrous $FeBr_3$. Compound **M** is obtained.



Compound **M**

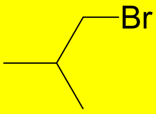
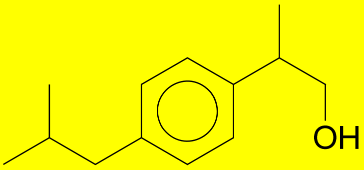
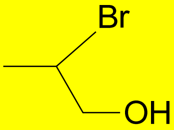
(3) Aqueous Br_2 is added to **H** to form **N**.

(4) **N** and **M** are reacted in the presence of anhydrous $FeBr_3$. Compound **P** with molecular formula $C_{13}H_{20}O$ is produced.

(5) Hot acidified potassium dichromate(VI) is then added to **P** to produce ibuprofen.

Using the structure of ibuprofen and the information provided, draw the structures of **L**, **N** and **P**.

[3]

		L:  [1] **p**:  [1] (only allow 1°) **N:**  [1]
		[Total: 9]

END OF PAPER

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY 9729/03

JC2 Preliminary Examination 19 September 2018
Paper 3 Free Response 2 hours

Candidates answer on separate paper.
Additional materials : Writing Papers
Data Booklet
2 Cover Pages (one for Section **A** and one for Section **B**)

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

This document consists of **12** printed pages and **0** blank page.

Section A

Answer **all** the questions in this section.

1 Hydrogen sulfide, H_2S, is a colourless gas with the characteristic foul odour of rotten eggs. It is very poisonous, corrosive and flammable. It occurs naturally in volcanic gases and natural gas and is often produced from the microbial breakdown of organic matter.

(a) H_2S burns readily in oxygen to form water and an acidic gas which briskly decolourises acidified potassium manganate(VII).

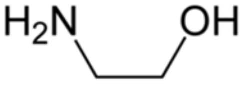
During the combustion process, sulfur atomises and a brightly coloured flame similar to that of its element is observed.

Construct a balanced chemical equation to represent the combustion reaction and predict the colour of the flame.

[2]

(b) The toxicity of H_2S is comparable with that of what carbon monoxide does to the human body, preventing cellular respiration. It is therefore critical to remove H_2S from raw natural gas. This process, commercially known as "*sweetening*", utilises amine treating technologies.

Common "*sweetening*" agents are as shown below.

Name	Chemical Structure	*pK_b*
Monoethanolamine (MEA)		4.55
Diethanolamine (DEA)		5.12
Methyldiethanolamine (MDEA)		5.48

(i) Describe how H_2S impedes cellular respiratory in the human body. [2]

(ii) Amine compounds are *weak Bronsted-Lowry bases*. What do you understand by the term "*weak Bronsted-Lowry bases*"? [1]

(iii) Explain the trend of the pK_b values of MEA, DEA and MDEA. [2]

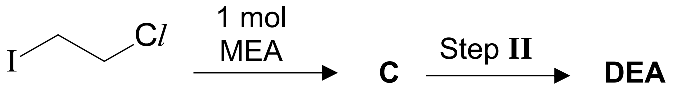
(iv) MEA consists of both amine and alcohol functional groups. It can be exploited in successive reactions involving halogeno organic compounds. A series of experiments are carried out to find out the different reactivity of dihalogeno compounds.

Complete the following of the organic syntheses, drawing the structures of the intermediates, products and stating the reagents and conditions where appropriate.

Reaction (A):

$$ClCH_2COCl \xrightarrow{\text{MEA}} \textbf{A} \xrightarrow{\text{Na (s)}} \textbf{Cyclic compound B}\ (C_4H_7NO_2)$$

Reaction (B):



[4]

(c) Zinc oxide is also used to scavenge hydrogen sulfide in natural gas, where the by-product, zinc sulfide, may be easily filtered off.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The solubility of ZnS in pure water is 1.23 x 10^{-10} g dm^{-3} at 25 ^oC.

(i) Write an expression for the solubility product, K_{sp} of ZnS and calculate its value. State its units clearly.

[2]

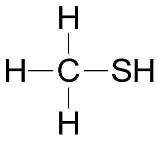
(ii) How would the solubility of ZnS in aqueous $Zn(NO_3)_2$ compared to that in pure water? Use *Le Chatelier's Principle* to justify your answer.

[2]

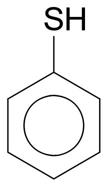
(iii) Equal volumes of 0.005 mol dm^{-3} Zn^{2+} solution and 0.002 mol dm^{-3} Na_2S solution were mixed. Predict if any precipitate could be filtered off this mixture.

[1]

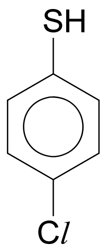
(d) Thiols are a class of organosulfur compounds known to have strong unpleasant odours. For instance, methanethiol, CH_3SH, is one of the main odourants of human faeces, body odour and bad breath. Other examples of common thiol structures are shown below.



methanethiol



thiophenol



chlorothiophenol

As thiols are the sulfur analogue of alcohols, their relative acidities are often compared. One notable difference is the ability of thiols to react with aqueous alkalis.

$$RSH + NaOH \rightarrow RS^-Na^+ + H_2O$$

The table below shows the pK_a values of alcohols and thiols.

Name of compound	**pK_a**
Butanol, $CH_3CH_2CH_2CH_2OH$	15
Phenol, C_6H_5OH	10
Buthanetiol, $CH_3CH_2CH_2CH_2SH$	10
Thiophenol, C_6H_5SH	6
Chlorothiophenol, C_6H_5ClS	***y***

(i) With reference to the information above, suggest an explanation for the different pK_a value of butanol as compared to buthanetiol.

[1]

(ii) Predict the value ***y*** and explain your answer.

[2]

(iii) Calculate the pH of the solution when 15 cm^3 of 0.10 mol dm^{-3} NaOH is added to 25 cm^3 of 0.10 mol dm^{-3} $CH_3CH_2CH_2CH_2SH$.

[2]

[Total: 21]

2 (a) (i) Draw a fully labelled diagram to show how the standard electrode of $Ni^{2+}(aq)$ /Ni(s) is being measured in a laboratory. Clearly label the direction of electrons flow and polarity of the electrodes in your diagram. [3]

(ii) Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$. Suggest how the value of the electrode potential of the $Ni^{2+}(aq)$ /Ni(s) half-cell will varies upon the addition of KCN and deduce the overall charge, *x*, on this complex. [3]

(b) Determine the E^θ_{cell} and the ΔG^θ when the $Ni^{2+}(aq)/Ni(s)$ half-cell is connected with the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell. [2]

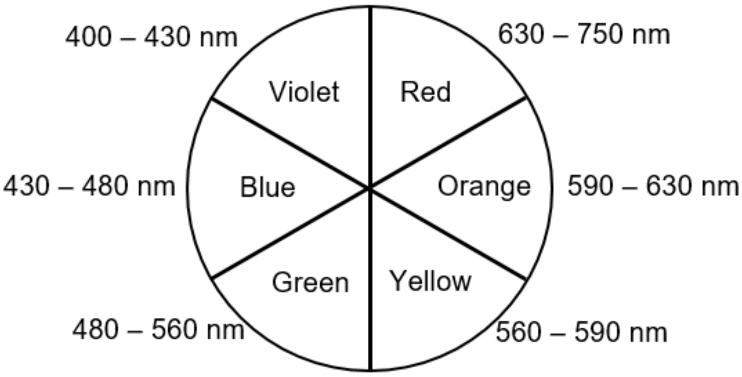
(c) An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$$NiSO_4 \xrightarrow{\text{KCN}} \underset{\text{green precipitate}}{\textbf{D}} \xrightarrow{\text{more KCN}} \underset{\text{yellow solution}}{\textbf{E}} \xrightarrow{\text{KCN in excess}} \underset{\text{red solution}}{\textbf{F}}$$

- The oxidation state of nickel does **not** change during the reactions.
- None of **D**, **E** or **F** contains sulfur.
- **D** contains no potassium.
- The K: Ni ratio in **E** is 2:1.
- The K: Ni ratio in **F** is 3:1

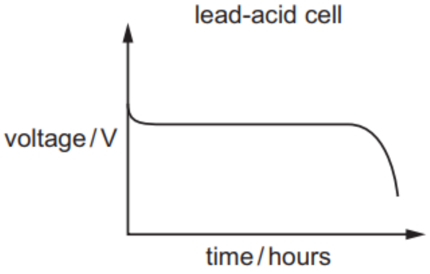
(i) Use the information to suggest the formulae of **D** and **F**. [2]

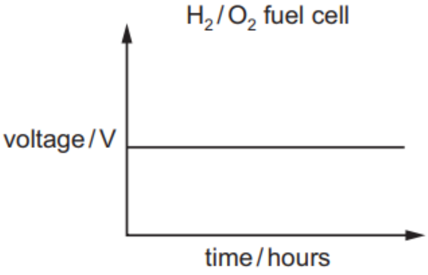
(ii) Using the colour wheel provided, suggest if **E** or **F** has a larger energy gap when the d-orbital split into two different energy levels.



[1]

(d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.





Suggest a reason why.

(i) The voltage of the lead-acid cell changes after several hours. [1]

(ii) The voltage of the fuel cell remains constant. [1]

(e) Describe, using the orientation of the d-orbitals, the splitting of degenerate d-orbitals into two energy levels in octahedral complexes such as $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. [4]

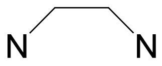
(f) 1,2-diaminoethane, *en*, is a bidentate ligand.

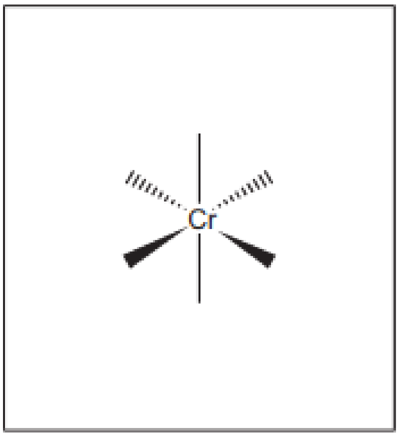
(i) What is meant by the terms *bidentate* and *ligand*? [2]

(ii) There are isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

When all the four nitrogen atoms of the *en* ligands are on the same plane, it is consider a trans configuration. When two of the nitrogen on the *en* ligands are on different plane, it is consider a cis configuration.

Using the three-dimensional diagram below, draw and label the cis-trans isomers on the writing paper you are provided.

(You may use  to represent *en.*)



[2]

[Total: 21]

3 **(a)** Solutions of iron(II) compounds are commonly prepared in the laboratory.

(i) By selecting two appropriate half equations from the *Data Booklet*, explain why iron(II) solutions are normally stored in the presence of acids instead of bases.

[3]

(ii) With the aid of suitable equations and standard electrode potential values from the *Data Booklet*, explain why an acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide.

Decomposition of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

State and explain the type of catalysis involved. [3]

(iii) Using an appropriate sketch of the Boltzmann distribution; explain why the addition of acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. [3]

(b) Strontium hydroxide is a strong base and has several industrial applications such as plastic stabiliser and paint drier.

The standard enthalpy change of neutralisation was determined experimentally by mixing known volumes of aqueous hydrochloric acid and aqueous strontium hydroxide in a calorimeter. The following results were obtained:

- Initial temperature = 25.0 ^{o}C
- Final temperature = 35.4 ^{o}C
- Volume of 2 mol dm^{-3} hydrochloric acid = 50.0 cm^3
- Volume of 0.77 mol dm^{-3} of strontium hydroxide = 50.0 cm^3
- Heat capacity of calorimeter = 9.43 J K^{-1}

(i) Define *standard enthalpy change of neutralisation*. [1]

(ii) Use the data above to calculate the standard enthalpy change of neutralisation in kJ mol^{-1}. [3]

(iii) The enthalpy change of neutralisation between aqueous strontium hydroxide and aqueous ethanoic acid was found to be different from the value calculated in **b(ii)**.

State and explain how the magnitude of this value differ from **b(ii)**.

[2]

(c) Aqueous strontium hydroxide is formed when solid strontium metal reacts with water

$$Sr(s) + 2H_2O(l) \rightarrow Sr^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

By using the following enthalpy changes and your answer in **b(ii)**, draw an energy cycle to calculate the enthalpy change for the above reaction involving strontium and water.

	kJ mol^{-1}
Enthalpy change for $Sr(s) \rightarrow Sr^{2+}(g) + 2e^-$	+1772
Enthalpy change of hydration of strontium ions	−1337
Enthalpy change for $2H^+(aq) + 2e^- \rightarrow H_2(g)$	−850

[3]

Total [18]

Section B

Answer **one** question in this section.

4 **(a)** Four samples of Period 3 chlorides, **G**, **H**, **J** and **K** are examined.

- These chlorides reacted completely in water, leaving no precipitates. These solutions were tested with universal indicator paper. **G**, **J** and **K** were found to be acidic, while **H** was found to be neutral.
- The melting points of **H** and **J** are approximately 10 times higher than the melting points of **G** and **K**.
- Solid anhydrous **G** is required in the reaction of phenylmethanol with chlorine to form C_7H_7OCl.
- Solid anhydrous **K** reacts with phenylmethanol to form C_7H_7Cl at room temperature.

(i) Identify the chlorides **G**, **H**, **J** and **K**. [2]

(ii) Explain why **H** forms a neutral solution. [2]

(iii) Draw the structure of the resulting compound, C_7H_7OCl. [1]

(iv) Draw the structure of the resulting compound, C_7H_7Cl. [1]

(v) Suggest why chloride **K** has to be anhydrous for the reaction between chloride **K** and phenymethanol to occur. Write a chemical equation to support your answer. [2]

(vi) Using structure and bonding, explain why chloride **J** has a melting point approximately 10 times higher than chloride **G** and **K**. [1]

(b) The reaction of silicon tetrachloride with moist ethoxyethane, produces either oxochlorides, Si_2OCl_6 or $Si_3O_2Cl_8$.

When 0.10g of one of the oxochloride completely reacted with water, all of its chlorine was converted into chloride ions, and produced 0.303 g of silver chloride precipitate when an excess of aqueous silver nitrate was added.

Deduce the identity of the oxochloride. [2]

(c) Fluorine bomb calorimetry has been used to investigate inorganic substances such as silicon compounds that cannot be completely burned in conventional calorimetric reagents such as oxygen under high pressure.

The enthalpy change of reaction of the following silicon containing compounds were investigated during a fluorine bomb calorimeter.

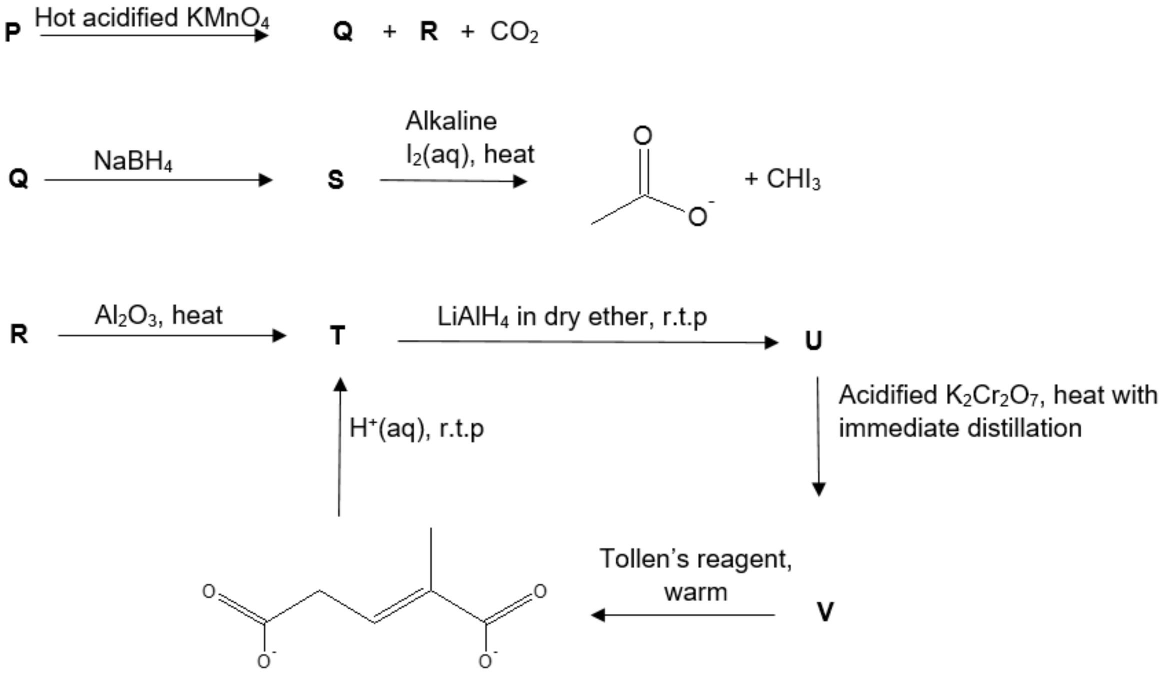
$$Si_3N_4 + 6F_2 \rightarrow 3SiF_4 + 2N_2 \qquad \Delta H = -828.9\ kJ\ mol^{-1}$$
$$SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF \qquad \Delta H = -2631\ kJ\ mol^{-1}$$

The following enthalpy change of formation is also given below.

Compound	ΔH_f /kJ mol^{-1}
HF(g)	-272.6
Si_3N_4(s)	-3686.1

Calculate the standard enthalpy change of formation of SiF_4.
Hence, calculate the standard enthalpy change of formation of SiH_4. [2]

(d) Linalool, **P**, is a compound which gives the sweet scent of lavender. Its structure can be deduced from the following series of reactions.



(i) Draw the structures of **S** and **Q**. [2]

(ii) Draw the structures of **R**, **T**, **U** and **V**. [4]

(iii) Hence, deduce the structure of linalool, **P**. [1]

[Total: 20]

5 This question is about the reactions of halogen containing organic compounds.

(a) The Finkelstein reaction, named after the German chemist, Hans Finkelstein, involves the replacement of the halogen atom in a halogenoalkane by an iodide ion from a solution of sodium iodide dissolved in propanone. This reaction goes almost to completion and a precipitate of sodium halide is formed as shown below.

$$RX + NaI \rightleftharpoons RI + NaX$$

A series of experiment can be carried out to determine the order of reaction with respect to a halogenoalkane, C_4H_9Br, and iodide ion. Different concentrations of C_4H_9Br and sodium iodide were used and the following initial rates were obtained.

Experiment Number	$[C_4H_9Br]$ / mol dm^{-3}	[NaI] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.04	0.60	5.68×10^{-5}
2	0.02	0.30	1.42×10^{-5}
3	0.60	0.60	8.52×10^{-4}

(i) Use these data to deduce the order of reaction with respect to each reactant, showing how you arrive at your answers. Hence, write a rate equation for the reaction. [3]

(ii) Based on your answer in **(a)(i)**, deduce a suitable structure for the halogenoalkane, C_4H_9Br which contains a chiral carbon. [2]

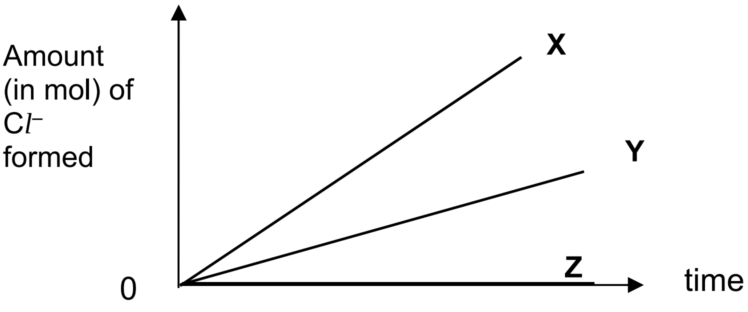
(iii) Using your answer in **(a)(i)** and **(a)(ii)**, describe a mechanism that is consistent with your rate equation. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [2]

(iv) Sodium chloride is precipitated during the Finkelstein reaction due to its limited solubility in propanone.

Explain why the Finkelstein reaction goes almost to completion despite the C-I bond being weaker than the C-C*l* bond. [1]

(b) Halogen-containing organic compounds can be hydrolysed under suitable conditions to produce the corresponding halide ions.

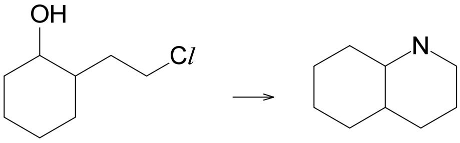
A student investigated the amount of Cl^- produced by hydrolysing ethanoyl chloride, chloroethane and chlorobenzene and the results are shown below.



Deduce **X**, **Y** and **Z**.

[3]

(c) In no more than 4 steps, outline how the following transformation can be achieved. State the reagents and conditions for each step, as well as the structures of any intermediates formed.



[4]

(d) When ester **A** ($C_6H_{11}O_2Cl$) is heated with alkaline $KMnO_4$, two products are formed. Acidification of the two products give **B** and **C**.

C gives a yellow precipitate when warmed with aqueous alkaline iodine. When sodium borohydride is added to **C**, compound **D** is formed. **D** reacts with hot concentrated sulfuric acid to form **E** ($C_4H_6O_2$) that exhibits cis-trans isomerism.

B, **C, D** and **E** all produce effervescence when reacted with aqueous Na_2CO_3.

Draw the structures of **A**, **B**, **C**, **D** and **E**.

[5]

[Total: 20]

END

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/03

JC2 Preliminary Examination **19 September 2018**
Paper 3 Free Response **2 hours**

Candidates answer on separate paper.

Additional materials : Answer Paper
Data Booklet
2 Cover Pages

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
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Answer **all** questions.

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Section A

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(a) H_2S burns readily in oxygen to form water and an acidic gas which briskly decolourises acidified potassium manganate(VII).

During the combustion process, sulfur atomises and a brightly coloured flame similar to that of its element is observed.

Construct a balanced chemical equation to represent the combustion reaction and predict the colour of the flame.

[2]

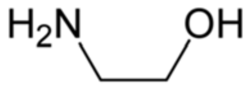
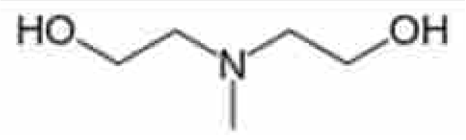
$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O$ **[1]** Blue flame **[1]**

FYI:

- SO_2 to SO_3 cannot work as activation energy to form SO_3 is high
- Sulfur element burns in oxygen producing blue flame – Periodicity Notes

(b) The toxicity of H_2S is comparable with that of what carbon monoxide does to the human body, preventing cellular respiration. It is therefore critical to remove H_2S from raw natural gas. This process, commercially known as "*sweetening*", utilises amine treating technologies.

Common "*sweetening*" agents are as shown below:

Name	**Chemical Structure**	***pK_b***
Monoethanolamine (MEA)		4.55
Diethanolamine (DEA)		5.12
Methyldiethanolamine (MDEA)		5.48

(i) Describe how H_2S impedes cellular respiratory in the human body.

[2]

H_2S is a strong ligand and **bonds irreversibly** **[1]** via a stronger dative bond with the **iron atom of haemoglobin**, **thus preventing haemoglobin from carrying oxygen** **[1]** to be transported around the body.

(ii) Amine compounds are *weak Bronsted-Lowry bases*. What do you understand by the term "*weak Bronsted-Lowry bases*"?

[1]

They **ionise partially** in aqueous solution by **accepting a proton.** **[1]**

(iii) Explain the trend of the pK_b values of MEA, DEA and MDEA.

[2]

Since pK_b increases from MEA to DEA to MDEA, it shows that basicity: MEA > DEA > MDEA.

MDEA is the **least basic** as it has **most / 3 alkyl groups / R-groups surrounding the N atom**, **[1]** compared to DEA which has 2 and MEA which has only 1 alkyl group.

Thus, there is **most steric hindrance about the N atom in MDEA**, making it **least available to accept a proton** **[1]** via dative bonding, followed by DEA and MEA.

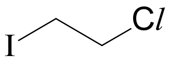
(iv) MEA consists of both amine and alcohol functional groups. It can be exploited in successive reactions involving halogeno organic compounds. A series of experiments are carried out to find out the different reactivity of dihalogeno compounds.

Complete the following of the organic syntheses, drawing the structures of the intermediates, products and stating the reagents and conditions where appropriate.

Reaction (A):

$$ClCH_2COCl \xrightarrow{\text{MEA}} \textbf{A} \xrightarrow{\text{Na (s)}} \textbf{Cyclic compound B}\ (C_4H_7NO_2)$$

Reaction (B):

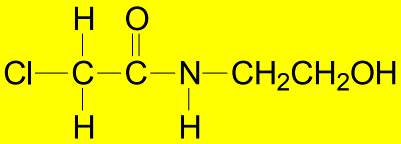


$$\xrightarrow{\text{1 mol MEA}} \textbf{C} \xrightarrow{\text{Step II}} \textbf{DEA}$$

[4]

Reaction (A):

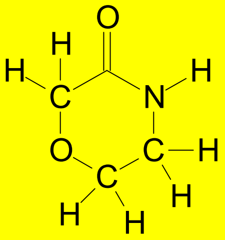
A:



$ClCH_2C(=O)NHCH_2CH_2OH$

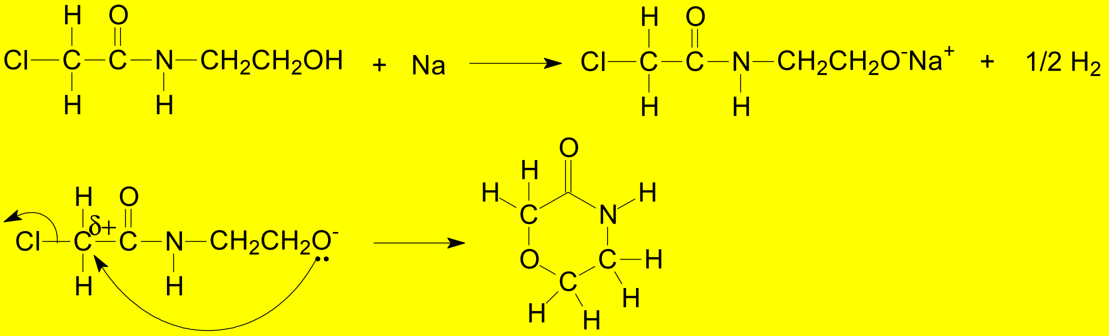
[1]

B:

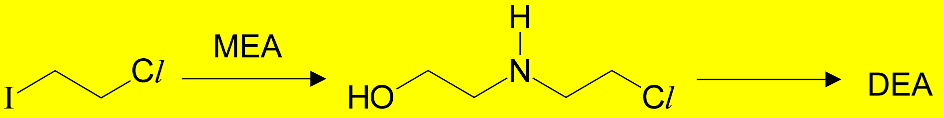


[1]

Explanation for step 2:



Reaction (B):



C **[1]**

Step II: NaOH (aq), heat [1]

FYI:

- C-I bond is weaker than C-Cl bond, hence will undergo NS more readily, when 1 mol MEA is added

(c) Zinc oxide is also used to scavenge hydrogen sulfide in natural gas, where the by-product, zinc sulfide, may be easily filtered off.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

The solubility of ZnS in pure water is 1.23×10^{-10} g dm^{-3} at 25 °C.

(i) Write an expression for the solubility product, K_{sp} of ZnS and calculate its value. State its units clearly.

[2]

$K_{sp} = [Zn^{2+}][S^{2-}]$ **[1]**

[ZnS] in mol dm^{-3} = $(1.23 \times 10^{-10}) / (65.4+32.1) = 1.26 \times 10^{-12}$ mol dm^{-3}

$K_{sp} = (1.26 \times 10^{-12})^2 =$ **1.6×10^{-24} mol^2 dm^{-6}** **[1] for both**

(ii) How would the solubility of ZnS in aqueous $Zn(NO_3)_2$ compared to that in pure water? Use *Le Chatelier's Principle* to justify your answer.

[2]

$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^-$

$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$ --- (1)

In presence of aqueous $Zn(NO_3)_2$, **[Zn^{2+}] increases**,

By Le Chatelier's Principle, the above **equilibrium position of (1) shifts left to decrease [Zn^{2+}].** **[1]**

Solubility of ZnS is **reduced** due to **common ion effect.** **[1]**

(iii) Equal volumes of 0.005 mol dm^{-3} Zn^{2+} solution and 0.002 mol dm^{-3} Na_2S solution were mixed. Predict if any precipitate could be filtered off this mixture.

[1]

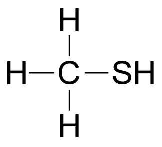
Ionic product = $[Zn^{2+}][S^{2-}] = \left(\frac{0.005}{2}\right)\left(\frac{0.002}{2}\right)$

$= 2.5 \times 10^{-6}$ mol^2 dm^{-6}

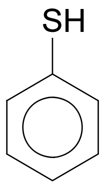
Since **IP > K_{sp}, ZnS ppt will be formed** and the ppt could be filtered off.

[1] with correct calculation of IP and explanation

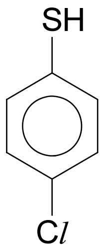
(d) Thiols are a class of organosulfur compounds known to have strong unpleasant odours. For instance, methanethiol, CH_3SH, is one of the main odourants of human faeces, body odour and bad breath. Other examples of common thiol structures are shown below.



methanethiol



thiophenol



chlorothiophenol

As thiols are the sulfur analogue of alcohols, their relative acidities are often compared. One notable difference is the ability of thiols to react with aqueous alkalis.

$$RSH + NaOH \rightarrow RS^-Na^+ + H_2O$$

The table below shows the pK_a values of alcohols and thiols.

Name of compound	**pK_a**
Butanol, $CH_3CH_2CH_2CH_2OH$	15
Phenol, C_6H_5OH	10
Buthanetiol, $CH_3CH_2CH_2CH_2SH$	10
Thiophenol, C_6H_5SH	6
Chlorothiophenol, C_6H_5ClS	***y***

(i) With reference to the information above, suggest an explanation for the different pK_a value of butanol as compared to buthanetiol.

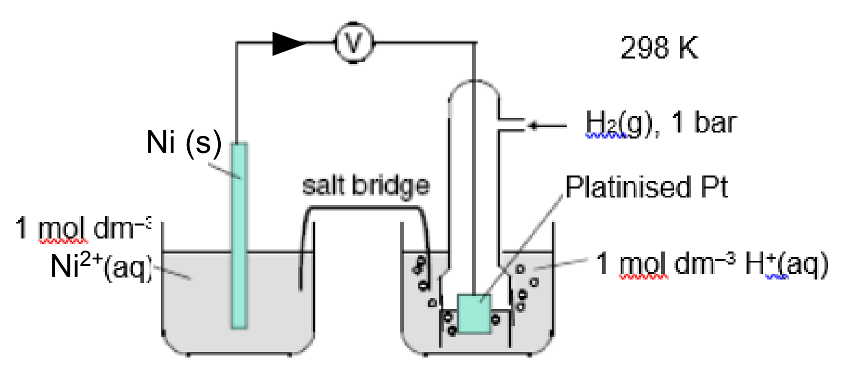
[1]

pK_a values of thiols is **generally lower** than that of alcohols, showing that thiols are **more acidic** than alcohols.

S-H bond in buthanetiol is **weaker than O-H bond** [1] in butanol due to larger atomic radius of S, resulting in less effective overlap of S-H covalent bond. Hence, the dissociation of H^+ for RSH will occur more readily, making thiols more acidic.

OR

			Thiols consists of a **larger S radius** than O which **allows the negative charge on its conjugate base RS$^-$ to be dispersed more**, stabilising it to a greater extent, making it more acidic than alcohols.
		(ii)	Predict the value ***y*** and explain your answer. [2]
			Value: 2 (accept value 2 to 5) **[1]** **Chlorothiophenol is more acidic** than thiophenol as the **electronegative Cl atom present disperses the negative charge on its conjugate base, stabilising it more / to a greater extent** than thiophenol Hence it has a lower pKa value. **[1]** *(need not take reference to thiophenol, as long as reasoning is logical)*
		(iii)	Calculate the pH of the solution when 15 cm^3 of 0.10 mol dm^{-3} NaOH is added to 25 cm^3 of 0.10 mol dm^{-3} $CH_3CH_2CH_2CH_2SH$. [2]
			$CH_3CH_2CH_2CH_2SH + NaOH \rightarrow CH_3CH_2CH_2CH_2S^-Na^+ + H_2O$ Amt of NaOH = $\frac{15}{1000}$ x 0.10 = 0.0015 mol Amt of RSH = $\frac{25}{1000}$ x 0.10 = 0.0025 mol Since RSH (weak acid) is in excess, a buffer solution is formed. Amt of excess RSH = 0.0025 – 0.0015 = 0.0010 mol **[1] for mol calculations** pH = pK_a + lg $\frac{[salt]}{[acid]}$ = 10 + lg $\frac{\frac{0.0015}{40}}{\frac{0.0010}{40}}$ = **10.2** **[1]**
			[Total: 21]

2	**(a)**	**(i)**	Draw a fully labelled diagram to show how the standard electrode of $Ni^{2+}(aq)$ /Ni(s) is being measured in a laboratory. Clearly label the direction of electrons flow and polarity of the electrodes in your diagram. [3]
			Direction of electron flow [1]  Oxidation (anode) Reduction (cathode) Negative polarity Positive polarity [1] for both [1] for correct placement of Fe^{2+}, Fe electrode, Pt electrode, H^+ and H_2 (g); for correct indication of 1 mol dm^{-3} for **Fe^{2+} and H^+, 298 K and 1 bar** Immediate zero cases: (1) No salt bridge (2) No water line (3) No voltmeter (4) Battery is drawn in the diagram
		(ii)	Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$. Suggest how the value of the electrode potential of the $Ni^{2+}(aq)$ /Ni(s) half-cell will vary upon the addition of KCN and deduce the overall charge, *x*, on this complex. [3]
			$Ni^{2+}(aq) + 2e \rightleftharpoons Ni(s)$ When KCN is added to $Ni^{2+}(aq)$/Ni (s) half cell, **Ni^{2+} form a complex with CN^- ions and $[Ni^{2+}]$ decreases**. By Le Chatelier's Principle, the **equilibrium position shifts to the left to increase the $[Fe^{2+}]$**. [1] Oxidation is more likely to occur and electrode potential of **Ni^{2+}/Ni becomes more negative /less positive** [1] To solve for x: +2+2(-1)+2(-1) = x **x = – 2** [1]
	(b)		Determine the E^θ_{cell} and the ΔG^θ when the $Ni^{2+}(aq)$/Ni(s) half-cell is connected with the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell. [2]
			E^θ_{cell} = +0.77 – (–0.25) = 1.02 V [1] $\Delta G^\theta = -nFE^\theta_{cell}$ = - (2)(96500)(1.02) = - 196860 J mol^{-1} [1]

(c) An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$$NiSO_4 \xrightarrow{\text{KCN}} \underset{\text{green precipitate}}{\textbf{D}} \xrightarrow{\text{more KCN}} \underset{\text{yellow solution}}{\textbf{E}} \xrightarrow{\text{KCN in excess}} \underset{\text{red solution}}{\textbf{F}}$$

- The oxidation state of nickel does **not** change during the reactions.
- None of **D**, **E** or **F** contains sulfur.
- **D** contains no potassium.
- The K: Ni ratio in **E** is 2:1.
- The K: Ni ratio in **F** is 3:1

(i) Use the information to suggest the formulae of **D** and **F**. [2]

D is $Ni(CN)_2$ [1] **E** is $K_2Ni(CN)_4$ **F** is $K_3Ni(CN)_5$ [1]

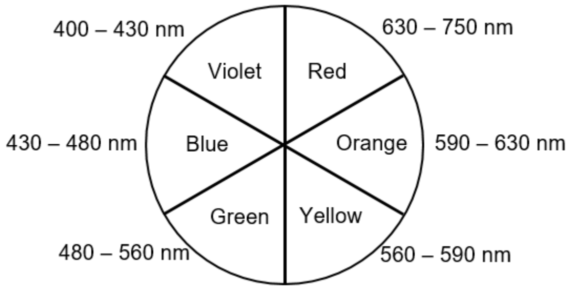
Do not accept $Ni(CN)_4{}^{2-}$ for D and $Ni(CN)_5{}^{3-}$ for E as question require the input of formulae.

Thinking process:
For green ppt of **D** to form it must be Ni^{2+} interacting with CN^- resulting in $Ni(CN)_2$. In addition, **D** must not contain potassium which further justify the formula.

As more KCN is added, complex formation will occur as we introduce more CN^- ligand. Given K to Ni ration is 2:1, it means that the complex anion containing Ni need to have a charge of 2– since its required 2 K^+ counter ion. Thus, **E** must have $[Ni(CN)_4]^{2-}$ as the complex anion and as such the **formula** of **E** is $K_2Ni(CN)_4$

When even more KCN is added, complex formation will continue to occur as we more CN^- ligands are being introduced. Given K to Ni ration is now 3:1, it means that the complex anion containing Ni need to have a charge of 3– since its required 3 K^+ counter ion. Thus, **F** must have $[Ni(CN)_4]^{3-}$ as the complex anion and as such the **formula** of **F** is $K_3Ni(CN)_4$

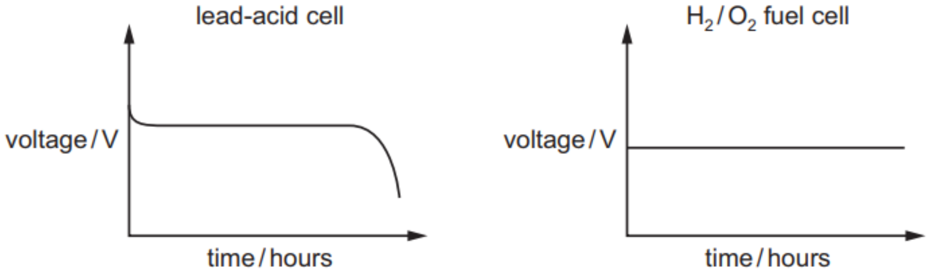
(ii) Using the colour wheel provided, suggest if solution **E** or **F** has a larger energy gap when the d-orbital split into two different energy levels.

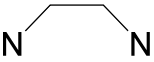
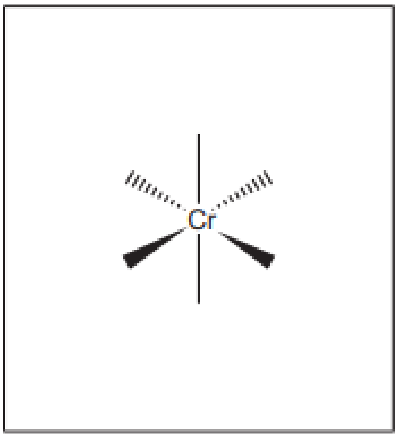
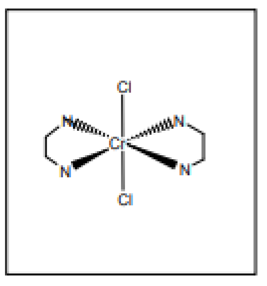
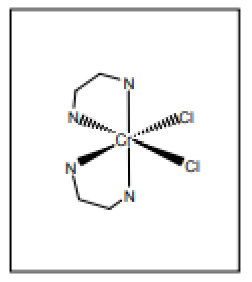
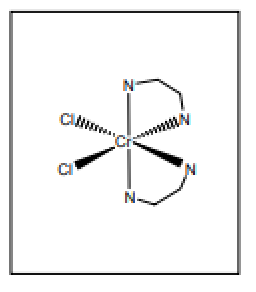


[1]

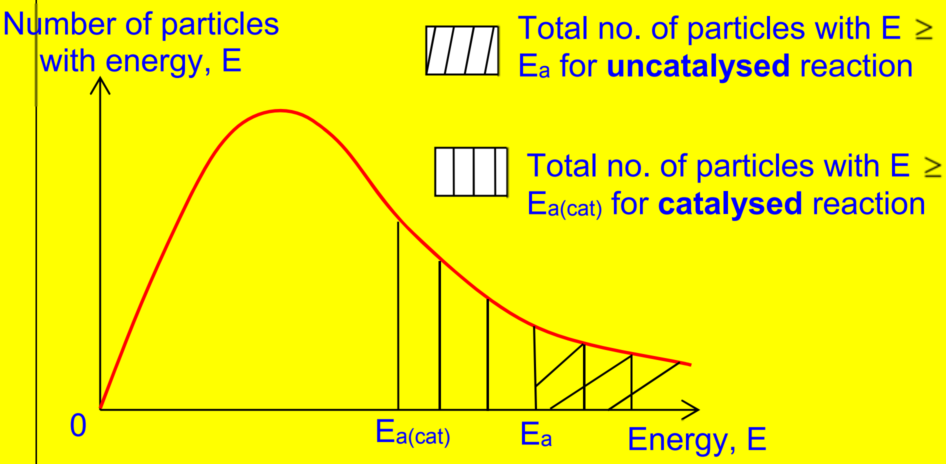
E is red solution thus it is **transmitting light of higher wavelength which means it is absorbing lower wavelength of light with higher energy**.

This means the **energy gap in E is larger**. [1] with valid reasoning

	(d)	The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.  Suggest a reason why.	
		(i)	The voltage of the lead-acid cell changes after several hours [1]
			Reagents (PbO_2 /H_2SO_4) are being used up. [1] Or Concentration of the reagents decreases.
		(ii)	The voltage of the fuel cell remains constant [1]
			As fuel is being continuously supplied, the fuel has not run out. [1]
	(e)	Describe, using the orientation of the d-orbitals, the splitting of degenerate d-orbitals into two energy levels in octahedral complexes such as $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$. [4]	
		In an **octahedral** complex, the ligands are modelled as six point negative charges that surround the positively charged transition metal ion. Each ligand forms a dative bond with the transition metal ion via a lone pair of electrons along the **x, y and z axes**. [1] When the ligands approach the transition metal ion along the x, y, and z axes, there is **inter-electronic repulsion between the lone pair of electrons from the donor atom of the ligand and the electrons in the d orbitals of the transition metal ion**. This causes the energies of these d electrons to increase to different extents. [1] When ligands approach the x, y and z axes, the **electrons in the d_{x2-y2} and d_{z2} orbitals will experience greater repulsion** than those in the d_{xy}, d_{yz} and d_{xz} orbitals. [1] Hence, the five d orbitals will be split into **2 energy levels - the d_{x2-y2} and d_{z2} orbitals at a higher energy level than the d_{xy}, d_{yz} and d_{xz}** orbitals as shown in the diagram below. [1]	

	(f)	1,2-diaminoethane, *en*, is a bidentate ligand.	
		(i)	What is meant by the terms *bidentate* and *ligand*? [2]
			Bidentate: a species that forms **two dative bonds** or donate two lone pairs of electrons. [1] Ligand: a species that uses a **lone pair** of electrons to form a **dative** bond to a **metal atom/metal ion.** [1]
		(ii)	There are isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$. When all the four nitrogen atoms of the *en* ligands are on the same plane, it is consider a trans configuration. When two of the nitrogen on the *en* ligands are on different plane, it is consider a cis configuration. Using the three-dimensional diagrams below, draw and label the cis-trans isomers on the writing paper you are provided. (You may use  to represent *en.*)  [2]
			 [1]  OR  [1]
			[Total: 21]

3	**(a)**	Solutions of iron(II) compounds are commonly prepared in the laboratory.	
		(i)	By selecting two appropriate half equations from the *Data Booklet*, explain why iron(II) solutions are normally stored in the presence of acids instead of bases. [3]
			In acidic medium: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77$ V In basic medium: $Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $E^\theta = -0.56$ V In acidic medium, **the E^θ value is more positive**. **[1]** Hence **position of equilibrium lies more to the right** and **[1]** Fe (II) is **more stable in acidic medium**. Or Fe^{2+} in **acidic medium is a weaker reducing agent** compared to $Fe(OH)_2$ in basic medium. **[1]**
		(ii)	With the aid of suitable equations and standard electrode potential values from the *Data Booklet*, explain why an acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. Decomposition of hydrogen peroxide: $2H_2O_2 \rightarrow 2H_2O + O_2$ State and explain the type of catalysis involved. [3]
			$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\theta = +1.77$ V $O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\theta = +0.68$ V $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\theta = +0.77$ V Step 1: **$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$** **$E^\theta_{cell} = 1.77 - 0.77 = +1.00$ V >0** **Since $E^\theta_{cell} > 0$, reaction is feasible.** Step 2: **$2Fe^{3+} + H_2O_2 \rightarrow 2Fe^{2+} + O_2 + 2H^+$** **$E^\theta_{cell} = 0.77 - 0.68 = +0.09$ V >0** **Since $E^\theta_{cell} > 0$, reaction is feasible.** **[2]** Fe^{2+} is a **homogenous catalyst** since it is in the **same physical state** as the reactants and it take part in the reaction but is regenerated. **[1]**

		(iii)	Using an appropriate sketch of the Boltzmann distribution; explain why the addition of acidic solution of iron(II) can catalyse the decomposition of hydrogen peroxide. [3]
			 When a catalyst is present, - **activation energy is lowered** - **more reactant particles with energy ≥ $E_{a(cat)}$** - **more effective collisions** - **rate of reaction is proportional to the frequency of effective collisions** - rate of reaction increases **[3]**
	(b)	Strontium hydroxide is a strong base and has several industrial applications such as plastic stabiliser and paint drier. The standard enthalpy change of neutralisation was determined experimentally by mixing known volumes of aqueous hydrochloric acid and aqueous strontium hydroxide in a calorimeter. The following results were obtained: - Initial temperature = 25.0 °C - Final temperature = 35.4 °C - Volume of 2 mol dm^{-3} hydrochloric acid = 50.0 cm^3 - Volume of 0.77 mol dm^{-3} of strontium hydroxide = 50.0 cm^3 - Heat capacity of calorimeter = 9.43 J K^{-1}	
		(i)	Define *standard enthalpy change of neutralisation*. [1]
			Standard enthalpy change of neutralisation is the **energy evolved** when an **acid and a base** react to form **one mole of water** under **standard conditions**. **[1]**
		(ii)	Use the data above to calculate the standard enthalpy change of neutralisation in kJ mol^{-1}. [3]

$Q = m_{water} \times c_{water} \times \Delta T + C_{calorimeter} \times \Delta T$
$= (50+50) \times 4.18 \times (35.4 - 25.0) + 9.43 \times (35.4 - 25.0)$
$= 4445.3$ J [1]

$2HCl + Sr(OH)_2 \rightarrow SrCl_2 + 2H_2O$
$2HCl \equiv Sr(OH)_2 \equiv 2H_2O$

Amount of HCl = $\frac{50}{100} \times 2 = 0.1 mol$

Amount of $Sr(OH)_2$ = $\frac{50}{100} \times 0.77 = 0.0385 mol$

$Sr(OH)_2$ is the limiting reagent
Amount of H_2O formed = 0.0385 x 2 =0.077 mol [1]

$\Delta H_n = -\frac{Q}{n_{H_2O}} = -\frac{4445.3}{0.077} = -57731 J mol^{-1} = -57.7 kJ mol^{-1}$ [1]

(iii) The enthalpy change of neutralisation between aqueous strontium hydroxide and aqueous ethanoic acid was found to be different from the value calculated in **b(ii)**.

State and explain how the magnitude of this value differ from **b(ii)**.

[2]

The magnitude is **lower** than the value in **b(ii)**. [1]

CH_3COOH is a **weak acid which dissociate slightly** in aqueous solution. Some of the **energy evolved from the neutralisation process is used to further dissociate** the weak acid. [1]

(c) Aqueous strontium hydroxide is formed when solid strontium metal reacts with water

$$Sr(s) + 2H_2O(l) \rightarrow Sr^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

By using the following enthalpy changes and your answer in **b(ii)**, draw an energy cycle to calculate the enthalpy change for the above reaction involving strontium and water.

	kJ mol^{-1}
Enthalpy change for $Sr(s) \rightarrow Sr^{2+}(g) + 2e^-$	+1772
Enthalpy change of hydration of strontium ions	−1337
Enthalpy change for $2H^+(aq) + 2e^- \rightarrow H_2(g)$	−850

[3]

$$\begin{tikzcd}
& Sr(s) + 2H_2O(l) \arrow[r] \arrow[dl, "+1772"'] & Sr^{2+}(aq) + 2OH^-(aq) + H_2(g) & \\
Sr^{2+}(g) + 2H_2O(l) + 2e^- \arrow[r, "-1337"] & Sr^{2+}(aq) + 2H_2O(l) + 2e^- \arrow[rr, "+57.7 \times 2"] & & 2H^+(aq) + 2OH^-(aq) + Sr^{2+}(aq) + 2e^- \arrow[ul, "-850"']
\end{tikzcd}$$

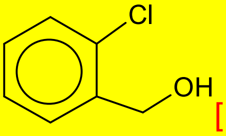
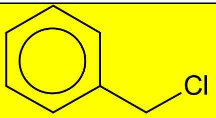
[2]

$\Delta H_{rxn} = +1772 - 1337 + 57.7 \times 2 - 850 = -299.6$ kJ mol^{-1} [1]

Total= [18]

Section B

Answer **one** question in this section.

4	**(a)**	Four samples of Period 3 chlorides, **G**, **H**, **J** and **K** are examined. • These chlorides reacted completely in water, leaving no precipitates. These solutions were tested with universal indicator paper. **G**, **J** and **K** were found to be acidic, while **H** was found to be neutral. • The melting points of **H** and **J** are approximately 10 times higher than the melting points of **G** and **K**. • Solid anhydrous **G** is required in the reaction of phenylmethanol with chlorine to form C_7H_7OCl. • Solid anhydrous **K** reacts with phenylmethanol to form C_7H_7Cl at room temperature.	
		(i)	Identify the chlorides **G**, **H**, **J** and **K**. [2]
			G – $AlCl_3$ H - $NaCl$ J – $MgCl_2$ K – PCl_5
		(ii)	Explain why **H** forms a neutral solution. [2]
			It dissolves in water to form Na^+ and Cl^-. As Na^+ has a low charge density [1], it is unable to polarise/hydrolyse water molecules and hence remains a neutral solution. [1]
		(iii)	Draw the structure of the resulting compound, C_7H_7OCl. [1]
			 [1] positon of Cl at 2,3,4 are acceptable
		(iv)	Draw the structure of the resulting compound, C_7H_7Cl. [1]
			 [1]
		(v)	Suggest why chloride **K** has to be anhydrous for the reaction between chloride **K** and phenymethanol to occur. Write a chemical equation to support your answer. [2]
			$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl\ (aq)$ [1] PCl_5 undergoes hydrolysis with water to form H_3PO_4. [1]

(vi) Using structure and bonding, explain why chloride **J** has a melting point approximately 10 times higher than chloride **G** and **K**.

[1]

$MgCl_2$ is a giant ionic lattice structure which requires a **larger amount of energy** to overcome the **strong ionic bond** [electrostatic forces of attraction between the oppositely charged ions (Mg^{2+} and Cl^-)].

$AlCl_3$ and PCl_5 are simple molecular structures which require **lesser energy** to overcome the **weak intermolecular forces of attraction between the molecules**. [1]

(b) The reaction of silicon tetrachloride with moist ethoxyethane, produces either oxochlorides, Si_2OCl_6 or $Si_3O_2Cl_8$.

When 0.10g of one of the oxochloride completely reacted with water, all of its chlorine was converted into chloride ions, and produced 0.303 g of silver chloride precipitate when an excess of aqueous silver nitrate was added.
Deduce the identity of the oxochloride.

[2]

Amount of $AgCl$ = amount of Cl^- present = $\frac{0.303}{107.9+35.5}$ = 0.002113mol

Amount of Cl^- in Si_2OCl_6 = $6 \times \frac{0.1}{2(28.1)+16.0+6(35.5)}$ =0.002104 mol

Amount of Cl- in $Si_3O_2Cl_8$ = $8 \times \frac{0.1}{3(28.1)+2(16.0)+8(35.5)}$ = 0.002 mol

Since **amt of Cl^- in Si_2OCl_6 ≈amt of Cl- in the $AgCl$**, [1]
the oxochloride is **Si_2OCl_6** [1]

(c) Fluorine bomb calorimetry has been used to investigate inorganic substances such as silicon compounds that cannot be completely burned in conventional calorimetric reagents such as oxygen under high pressure.
The enthalpy change of reaction of the following silicon containing compounds were investigated during a fluorine bomb calorimeter.

$Si_3N_4 + 6F_2 \rightarrow 3SiF_4 + 2N_2$ $\Delta H = -828.9\ kJ\ mol^{-1}$
$SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF$ $\Delta H = -2631\ kJ\ mol^{-1}$

The following enthalpy change of formation is also given below:

Compound	ΔH_f /kJ mol^{-1}
HF(g)	-272.6
Si_3N_4(s)	-3686.1

Calculate the standard enthalpy change of formation of SiF_4.
Hence, calculate the standard enthalpy change of formation of SiH_4.

[2]

$3\Delta H_f(SiF_4) = -3686.1 - 828.9 = -4515\ kJmol^{-1}$

$\Delta H_f(SiF_4) = -1505\ kJ\ mol^{-1}$ [1]

$$\begin{tikzcd} SiH_4 + 4F_2(g) \arrow[rr, "-2631"] & & SiF_4 + 4HF \\ & Si(s) + 2H_2(g) + 2F_2(g) \arrow[ul, "\Delta H_f(SiH_4)"] \arrow[ur, "-1505"] \arrow[ur, "4(-272.6)"'] & \end{tikzcd}$$

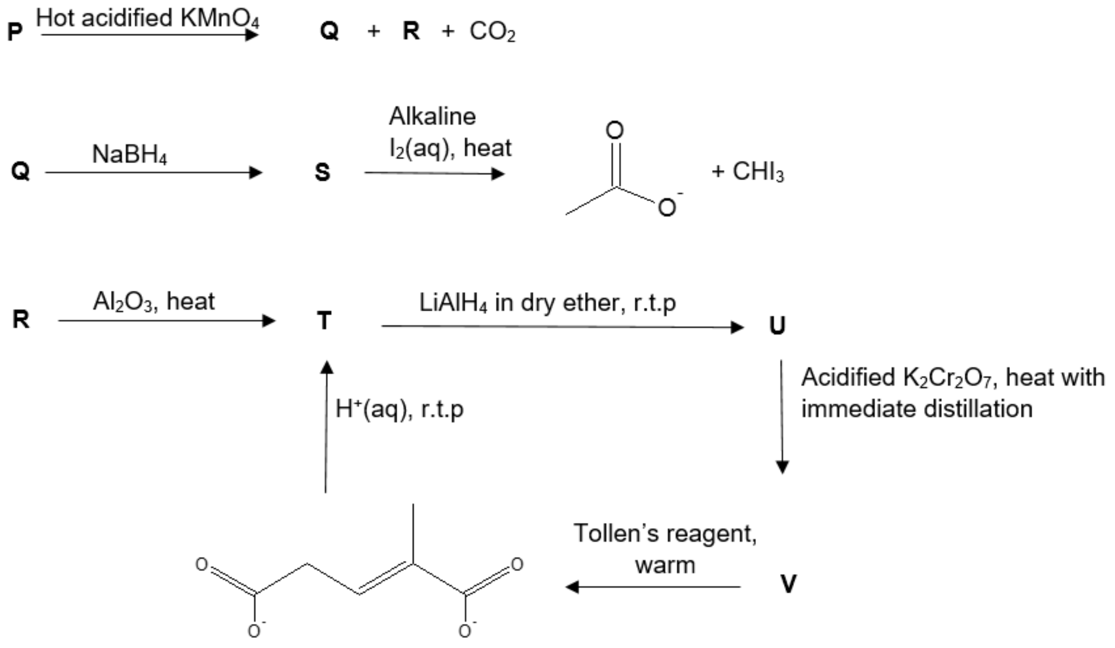
(energy cycle not required)

$-2631 = -\Delta H_f(SiH_4) - 1505 + 4(-272.6)$

$\Delta H_f(SiH_4) = 2631 - 1505 + 4(-272.6)$

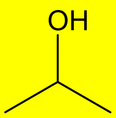
= **$+35.6\ kJ\ mol^{-1}$** [1]

(d) Linalool, **P**, is a compound which gives the sweet scent of lavender. Its structure can be deduced from the following series of reactions.

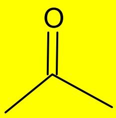


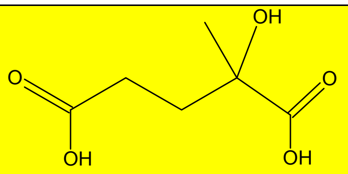
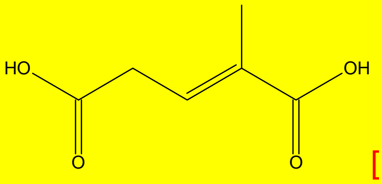
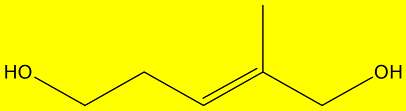
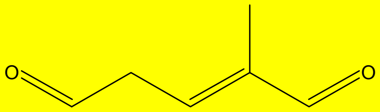
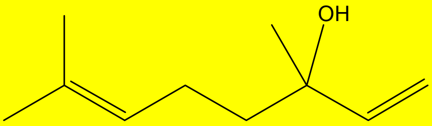
(i) Draw the structures of **S** and **Q**. [2]

S:



Q:



		(ii)	Draw the structures of **R**, **T**, **U** and **V**. [4]
			R:  [1] **T:**  [1] **U:**  [1] **V:**  [1]
		(iii)	Hence, deduce the structure of linalool, **P**.
			P:  [1]
			[Total: 20]

5 This question is about the reactions of halogen containing organic compounds.

(a) The Finkelstein reaction, named after the German chemist, Hans Finkelstein, involves the replacement of the halogen atom in a halogenoalkane by an iodide ion from a solution of sodium iodide dissolved in propanone. This reaction goes almost to completion and a precipitate of sodium halide is formed as shown below.

$$\mathrm{RX + NaI \rightleftharpoons RI + NaX}$$

A series of experiment can be carried out to determine the order of reaction with respect to a halogenoalkane, C_4H_9Br, and iodide ion. Different concentrations of C_4H_9Br and sodium iodide were used and the following initial rates were obtained.

Experiment Number	$[C_4H_9Br]$ / mol dm^{-3}	[NaI] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.04	0.60	5.68×10^{-5}
2	0.02	0.30	1.42×10^{-5}
3	0.60	0.60	8.52×10^{-4}

(i) Use these data to deduce the order of reaction with respect to each reactant, showing how you arrive at your answers. Hence, write a rate equation for the reaction.

[3]

Let rate = $k\,[C_4H_9Br]^x[I^-]^y$

Comparing experiments 1 and 3,

$$\frac{rate\,1}{rate\,3} = \frac{k(0.04)^x(0.6)^y}{k(0.6)^x(0.6)^y}$$

$$\frac{5.68 \times 10^{-5}}{8.52 \times 10^{-4}} = \left(\frac{0.04}{0.6}\right)^x$$

$$x = 1$$

$\therefore$ Order of reaction w.r.t. C_4H_9Br = **1** **[1]**

Comparing experiments 1 and 2,

$$\frac{rate\,1}{rate\,2} = \frac{k(0.04)^1(0.6)^y}{k(0.02)^1(0.3)^y}$$

$$\frac{5.68 \times 10^{-5}}{1.42\ x\ 10^{-5}} = \left(\frac{0.04}{0.02}\right)\left(\frac{0.6}{0.3}\right)^y$$

$$y = 1$$

$\therefore$ Order of reaction w.r.t. iodide = **1** **[1]**

rate = $k\,[C_4H_9Br][I^-]$ **[1]**

(ii) Based on your answer in **(a)(i)**, deduce a suitable structure for the halogenoalkane, C_4H_9Br which contains a chiral carbon.

[2]

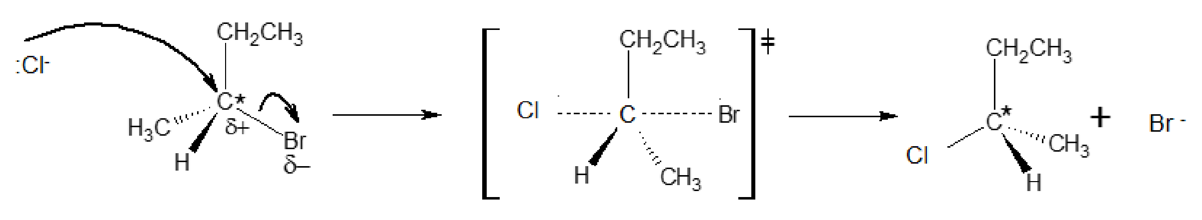
$CH_3CH_2CH(Br)CH_3$. [1]

From the rate equation, the **slow step consists of 1 C_4H_9Br molecule and 1 I^- reacting with each other.** This is consistent with a **S_N2** mechanism. However, since C_4H_9Br contains a chiral carbon, the compound must be a **secondary** halogenoalkane. [1]

(iii) Using your answer in **(a)(i)** and **(a)(ii)**, describe a mechanism that is consistent with your rate equation. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[2]

Nucleophilic substitution, S_N2



(iv) Sodium chloride is precipitated during the Finkelstein reaction due to its limited solubility in propanone.

Explain why the Finkelstein reaction goes almost to completion despite the C-I bond being weaker than the C-C*l* bond.

[1]

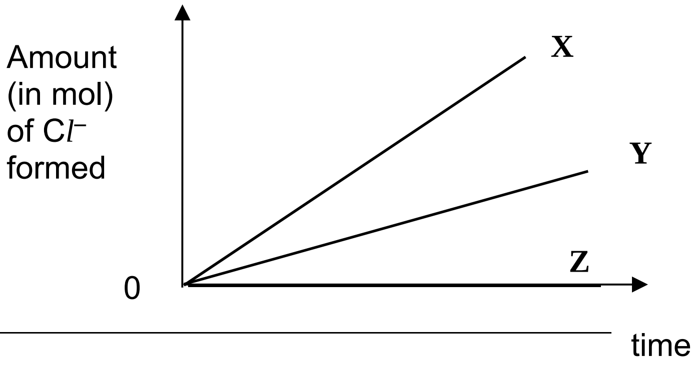
$RCl_{(propanone)} + NaI_{(propanone)} \rightleftharpoons RI_{(propanone)} + NaCl\,(s)$

As NaC*l* is precipitated out of propanone solution, **$[Cl^-]$ decreases** continuously.

By Le Chatelier's principle, the e**quilibrium position shifts to the right to increase $[Cl^-]$.** Hence the reaction goes almost to completion. [1]

(b) Halogen-containing organic compounds can be hydrolysed under suitable conditions to produce the corresponding halide ions, X^-.

A student investigated the amount of Cl^- produced by hydrolysing ethanoyl chloride, chloroethane and chlorobenzene and the results are shown below.



Deduce **X**, **Y** and **Z**.

[3]

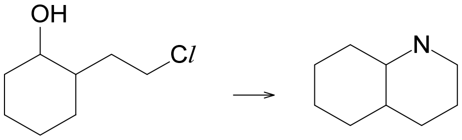
X is **ethanoyl chloride**. **Y** is **chloroethane** and **Z** is **chlorobenzene**. **[1]**

Ethanoyl chloride hydrolyses at the fastest rate. This is because the **carbonyl C atom has 2 very electronegative atoms (O and C*l*) bonded to it**
This makes the **carbonyl C atom highly electron deficient**, **hence nucleophilic substitution occurs very readily**. **[1]**

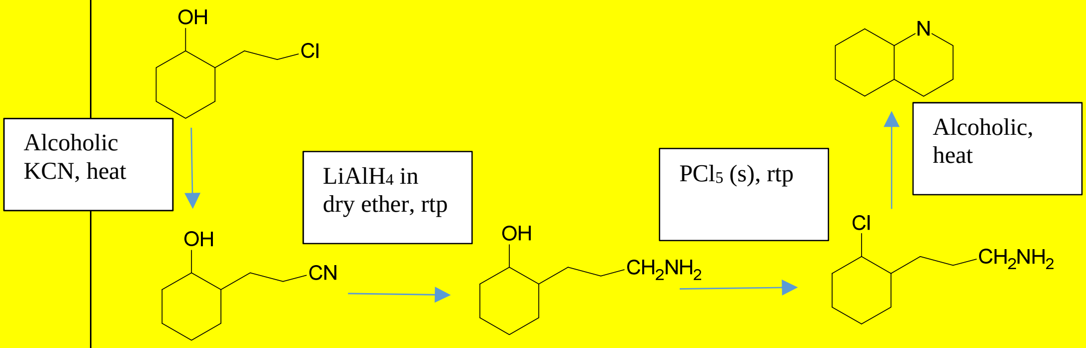
Chlorobenzene hydrolyses the slowest because the **lone pair of electrons** of the halogen atom can **delocalise into the π electron cloud of the benzene ring**.

This results in **partial double bond** character in C-Cl bond and the **strengthening** of the C-Cl bond. **[1]**

(c) In no more than 4 steps, outline how the following transformation can be achieved. State the reagents and conditions for each step, as well as the structures of any intermediates formed.



[4]



[1] each intermediate + R+C

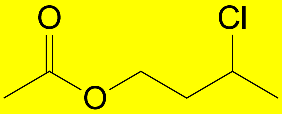
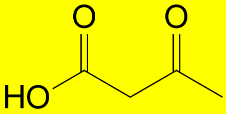
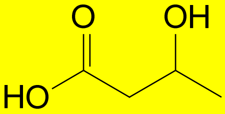
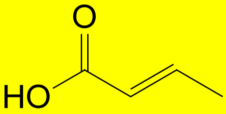
(d) When ester **A** ($C_6H_{11}O_2Cl$) is heated with alkaline $KMnO_4$, two products are formed. Acidification of the two products give **B** and **C**.

C gives a yellow precipitate when warmed with aqueous alkaline iodine. When sodium borohydride is added to **C**, compound **D** is formed. **D** reacts with hot concentrated sulfuric acid to form **E** ($C_4H_6O_2$) that exhibits cis-trans isomerism.

B, **C, D** and **E** all produce effervescence when reacted with aqueous Na_2CO_3.

Draw the structures of **A**, **B**, **C**, **D** and **E**.

[5]

			A:  **[1]** **B:** CH_3COOH **[1]** **C:**  **[1]** **D:**  **[1]** **E:**  **[1]**
			[Total: 20]

END

2018 JC2 H2 Chemistry Prelim Practical Examination Confidential Instructions

To prepare for 7 labs of 24 students each. 3 shifts.

Apparatus list:
For each student,

Apparatus	**Quantity**
50 cm^3 burettes	2
Glass rod	1
Retort stand and burette clamp	2
10 cm^3 pipette	1
25 cm^3 pipette	1
Pipette filler	1
250 cm^3 graduated flask, labelled **diluted FA 1**	1
Dry funnel	1
Funnel	1
250 cm^3 conical flask	1
250 cm^3 **DRY** conical flask, labelled **FA 6**	1
200 cm^3 clean, dry Styrofoam cup	2
250 cm^3 beaker, labelled **reaction mixture**	1
50 cm^3 measuring cylinder	1
25 cm^3 measuring cylinders	1
10 cm^3 measuring cylinder	2
Stopwatch, reading to at least 0.1 s	1
Thermometer (–10 °C to +110 °C, at 1 °C)	1
Test-tube rack	1
Test-tubes	8 (plus extra at teacher's bench)
Test tube holder	1
Bunsen burner and lighter	1
Blue and red litmus papers	
Wooden splints	
Wash bottle containing deionised water	1
Pen for writing on glass	1
Paper towels	some
dropping pipettes	6 (plus extra at teacher's bench)
Burette clip	2
Test-tube brush	1
Large brush for cleaning conical flask	1
Filter paper	
Delivery tube (for QA)	1

Plastic gloves	1 pair
Goggles	1
Beaker for waste	1

Chemicals:

Label	**Per candidate**	**Identity**	**Preparation**
FA 1	100 cm^3	0.200 mol dm^{-3} potassium iodate(V), KIO_3	42.80 g dm^{-3} of anhydrous KIO_3)
FA 2	30 cm^3	1.00 mol dm^{-3} calcium nitrate tetrahydrate, $Ca(NO_3)_2.4H_2O$	236.2 g dm^{-3} of hydrated $Ca(NO_3)_2.4H_2O$ If anhydrous calcium nitrate, $Ca(NO_3)_2$, the solution should contain 164.1 g dm^{-3} of the anhydrous salt
FA 3	250 cm^3	0.0400 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$	6.324 g dm^{-3} of anhydrous $Na_2S_2O_3$ If hydrated sodium thiosulfate is used, $Na_2S_2O_3.5H_2O$, the solution should contain 9.924 g dm^{-3} of the hydrated salt
FA 4	100 cm^3	0.2 mol dm^{-3} potassium iodide, KI	33 g dm^{-3} of anhydrous KI
FA 5	25 cm^3	2 mol dm^{-3} hydrochloric acid, HC*l*	
Starch solution	10 cm^3	2% starch solution	20 g dm^{-3} of soluble starch
FA 7		Mg powder	0.20 ± 0.02g
FA 8	40 cm^3	1.0 mol dm^{-3} sulfuric acid	
FA 9		Mg powder	0.20 ± 0.02g
FA 10		Mg powder	0.20 ± 0.02g
FA 11	70 cm^3	0.1 mol dm^{-3} copper (II) sulfate	Dissolve 249.6 g of $CuSO_4.5H_2O$ in each dm^3 of solution.
FA12		$MnSO_4$ and $Zn(NO_3)_2$	Dissolve: 35.0 g of manganese(II) sulphate, $MnSO_4.H_2O$; (or 45.0 g of manganese(II) sulphate, $MnSO_4.4H_2O$) 60.0 g of zinc nitrate, $Zn(NO_3)_2.6H_2O$ in distilled water and make up to 1 dm_3.

Bench reagents:

Sodium hydroxide
Calcium hydroxide
Aqueous ammonia
Nitric acid
Hydrochloric acid
Barium nitrate
Silver nitrate
Aluminium foil
Potassium permanganate
Sulfuric acid

Bench reagents:

For each student,

Label	**Identity**	**Preparation**
Dilute sulfuric acid	1.0 mol dm^{-3} H_2SO_4	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of deionised water with continuous stirring. Make the solution up to 1 dm^3 with deionised water. Care: concentrated sulfuric acid is very corrosive
Dilute nitric acid	2.0 mol dm^{-3} HNO_3	
Aqueous sodium hydroxide	2.0 mol dm^{-3} NaOH	Dissolve 80.0 g of NaOH in each dm^3 of solution. **Care:** *the process of solution is exothermic and any concentrated solution is very corrosive.*

Aqueous calcium hydroxide	Saturated aqueous calcium hydroxide, $Ca(OH)_2$	Prepare fresh limewater by leaving distilled water to stand over solid calcium hydroxide for several days, shaking occasionally. Decant or filter the solution.
Aqueous barium chloride		
Aqueous silver nitrate	0.05 mol dm^{-3} silver nitrate	Dissolve 8.5 g of $AgNO_3$ in each dm^3 of solution.
Litmus paper (blue and red)		
$KMnO_4$		
Aqueous iodine		
Filter paper		

SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY

9729/04

JC2 Preliminary Examination
Paper 4 Practical

24 August 2018
2 hr 30 min

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 & 19.

Shift
Laboratory

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/13
2	/29
3	/13
TOTAL	**/ 55**

This document consists of **19** printed pages and **1** blank pages.

Answer **all** the questions in the spaces provided.

1 Determination of a value for the solubility product, K_{sp}, of calcium iodate(V), $Ca(IO_3)_2$

Calcium iodate is used in the manufacture of disinfectants, antiseptics, and deodorants. Its solubility in water is low. When calcium iodate(V) is mixed with water, the following equilibrium is established.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^{-}(aq)$$

You are to perform an experiment to determine the solubility product, K_{sp}, of calcium iodate(V).

You will first prepare a saturated solution of calcium iodate(V) by mixing specific volumes of potassium iodate(V), KIO_3 and calcium nitrate, $Ca(NO_3)_2$.

The mixture is then filtered after leaving to stand for some time. The filtrate can then be analysed to determine the amount of iodate(V) ions left as follows:

- Excess potassium iodide, KI, is added to an acidified solution of the filtrate, liberating iodine.

$$IO_3^{-}(aq) + 5I^{-}(aq) + 6H^{+}\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l) \quad \textbf{reaction 1}$$

- The liberated iodine is then titrated with a standard solution of sodium thiosulfate.

$$2S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow 2I^{-}\,(aq) + S_4O_6^{2-}\,(aq) \quad \textbf{reaction 2}$$

FA 1	0.200 mol dm^{-3} potassium iodate(V), KIO_3
FA 2	1.00 mol dm^{-3} calcium nitrate, $Ca(NO_3)_2$
FA 3	aqueous sodium thiosulfate, $Na_2S_2O_3$
FA 4	aqueous solution of potassium iodide, KI
FA 5	dilute hydrochloric acid, HC*l*
Starch indicator	

(a) Preparing the reaction mixture

1. Transfer 50 cm^3 of **FA 1** using a measuring cylinder to the beaker labelled **reaction mixture**.
2. Using another measuring cylinder, transfer 20 cm^3 of **FA 2** into the same beaker.
3. A precipitate will form. Stir the mixture thoroughly and leave it to stand for several minutes to allow equilibrium to be reached.

While waiting, follow the instructions given in part (b).

(b) The concentration of **FA 1** provided is too high. You will first prepare a diluted solution of **FA 1** of known concentration and use it to standard the sodium thiosulfate solution provided.

1. Using a burette, transfer 10.00 cm^3 of **FA 1** into a 250 cm^3 graduated flask, labelled **diluted FA 1**.
2. Make up to the mark with deionised water and mix thoroughly.

Standardisation of FA 3

1. Fill a burette with **FA 3**.
2. Using a pipette, transfer 25.0 cm^3 of **diluted FA 1** into a conical flask.
3. Using a measuring cylinder, add about 10 cm^3 of **FA 4** to the flask.
4. Using another measuring cylinder, add about 2 cm^3 of **FA 5** to the flask.
5. Add **FA 3** from the burette into the flask until a pale yellow colour is obtained.
6. Add about 5 drops of starch solution into the flask. Continue adding **FA 3** until the blue-black colour just disappears.
7. Perform sufficient titrations to obtain accurate results for the end-point. Rinse the conical flask between each titration.

Record your titration results in the space below. Make certain that your recorded results show the precision of your working.

[2]

(iii) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

[1]

(iv) Calculate the concentration of $S_2O_3^{2-}$ ions in the **FA 3** solution.

[1]

Analysing the filtrate

(c) **(i)** 1. Filter the reaction mixture through a dry filter paper into a dry conical flask, labelled **FA 6**. This is the filtrate, **FA 6**. Do not wash the white precipitate with water.

2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.
3. Using a measuring cylinder, add about 10 cm^3 of FA 4 to the flask.
4. Using another measuring cylinder, add about 2 cm^3 of **FA 5** to the flask.
5. Add **FA 3** from the burette into the flask until a pale yellow solution is obtained.
6. Add about 5 drops of starch indicator and continue adding **FA 3** until the blue-black colour just disappears.
7. Perform sufficient titrations to obtain accurate results for the end-point. Rinse the conical flask between each titration.

Record your titration results in the space below. Make certain that your recorded results show the precision of your working.

(ii) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

Calculations

(d) **(i)** Calculate the amount of $S_2O_3^{2-}$ ions present in the volume of **FA 3** obtained in **(c)(ii)**.

[1]

(ii) Calculate the amount of IO_3^- ions present in 10.0 cm^3 of the filtrate, **FA 6**.

[1]

(iii) Hence, calculate the total amount of IO_3^- ions present in the filtrate, **FA 6**.

[1]

(e) **(i)** Calculate the initial amount of IO_3^- ions and Ca^{2+} ions present in the reaction mixture prepared in **(a)**.

[1]

(ii) Calculate the amount of IO_3^- ions precipitated as $Ca(IO_3)_2$.

[1]

(iii) Hence, calculate the amount of Ca^{2+} ions left in **FA 6**.

[1]

(f) **(i)** Use your answer in parts **(d)(iii)** and **(e)(iii)** to calculate a value for the solubility product, K_{sp}, of calcium iodate(V). Include units in your answer.

[1]

(g) Another student performed this experiment and obtained a value for the solubility product, K_{sp}, of 3.45×10^{-5}. A literature value for this solubility product is 6.71×10^{-6} at 20 °C.

You should assume that apparatus of the same precision was used in each case.

State a possible reason for the higher value of K_{sp} obtained by the student and suggest an improvement which might allow a value closer to the literature value to be obtained.

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[2]

[Total: 13]

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2 You are to determine the enthalpy change of reaction, Δ*H*, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

As copper is an unreactive metal it does not react with dilute acids. You will need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will conduct experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

Determining the enthalpy change for Reaction 1

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

(a) Method

FA 8 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

- Weigh the bottle containing **FA 7**. Record the mass.
- Support the Styrofoam cup in the 250 cm^3 beaker.
- Use the measuring cylinder to transfer 25 cm^3 of **FA 8** into the Styroofoam cup.
- Measure the temperature of **FA 8** in the cup and start the stop clock. Record this temperature as being the temperature at time = 0.
- Measure, and record, the temperature of this **FA 8** every half minute for 2 minutes.
- At time = 2½ minutes add the **FA 7** to the acid and stir carefully to reduce acid spray.
- Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
- Continue stirring occasionally throughout this time.
- Weigh the bottle that had contained **FA 7**. Record the mass.
- Calculate and record the mass of **FA 7** added to the sulfuric acid.
- Rinse the cup with water and shake to dry.

Recording

[6]

(b) (i) On the grid below plot a graph of temperature (*y*-axis) against time (*x*-axis).

[2]

(ii) Complete the graph by drawing two, straight lines of best fit

- One to show the temperature up to time = 2 ½ minutes
- One to show the temperature after time = 2 ½ minutes

[1]

(iii) From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2 ½ minutes.

Temperature change = ………………^{o}C

[1]

(c) Calculations

(i) In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?

…………………………………………………………………………………………....

…………………………………………………………………………………………...

[1]

(ii) Calculate the energy change that occurred during the reaction in **(a)**.
[Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0 ^oC.]

Energy change = …………………J

[1]

(iii) Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium.
[*A*r : Mg, 24.3]

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

Enthalpy change of Reaction 1 = ………………..kJ mol^{-1}

[2]

(d) Planning: Determining the enthalpy change for Reaction 2

The enthalpy change of reaction for **Reaction 2** can be determine using a **non-graphical approach**.

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

(i) Plan an investigation to determine mean temperature rise, mean mass of magnesium used and the enthalpy change of reaction for **Reaction 2**.

You are provided with

- **FA 11**, 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$
- **FA 9** and **FA 10** magnesium powder samples in weighing bottles
- the equipment normally found in a school or college laboratory.

You are to take precaution to ensure that the copper(II) sulfate was in excess in these reactions and **not more than 30 cm^3** is used for each experiment.

In your plan you should include brief details of

- the volume of $CuSO_4$ you plan to use (you may assume the mass of Mg(s) used to be the same as in reaction 1),
- the apparatus that you would use,
- the procedure that you would follow and the measurements that you would take,
- a suitable table for your results.

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……………………………………………………………………………………………………

[6]

(ii) **Perform** the experiment you have planned in **(d)(i)**, clearly calculating the

- mean temperature change and
- mean mass of magnesium used.

Hence, determine the enthalpy change, in kJ mol^{-1} for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0^{o}C]
[A_r : Mg, 24.3]

[4]

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(e) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtain your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

Enthalpy change for **Reaction 3** = …………………kJ mol^{-1}

[2]

(f) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest **two** reasons why the method used for **Reaction 2** was less accurate. Explain your answers.

1 …………………………………………………………………………………..

…………………………………………………………………………………..

…………………………………………………………………………………..

2……………………………………………………………………………………

…………………………………………………………………………………..

…………………………………………………………………………………..

[2]

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[1]

[Total: 29]

3 **FA 12** contains two cations and two anions from those listed on pages 18 and 19.

In all tests, the reagent should be added gradually until no further change is observed, with shaking after each addition.
Record your observations in the spaces provided.
Your answers should include
- details of colour changes and precipitates formed,
- the names of gases evolved and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs, writing any deductions you made alongside the observations on which they are based.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

	Test	*Observations* [3]	*Possible Cation* [3]
(a)	Place 3 cm^3 **FA 12** in a test tube, add aqueous sodium hydroxide, drop by drop, until no further change is seen.		
(b)	Filter the mixture from **(a)** and **collect the filtrate for later tests** Leave the residue in the filter paper and observe it again after several minutes.		
(c)	Extract about 1 cm^3 of the filtrate using a teat pipette into a clean test tube. Add dilute nitric acid, drop by drop, until no further change is seen.		

Test for anions

Test **(e)** has been conducted and the observation is recorded.

You are to complete test **(f)** and devise **two** more tests to confirm the identity of the anions present in **FA 12**.

In the space provided below, clearly state the tests, observations and deductions.

	Test [2]	*Observation* [3]
(e)	Add 1 cm^3 of **FA 12** into a clean test-tube. Add 2 cm^3 of aqueous hydrochloric acid.	No effervescence observed
(f)	Add 1 cm^3 of **FA 12** into a clean test-tube Add 3 drops of aqueous silver nitrate.	
(g)		
(h)		

Anions present in **FA12**: ………………and …………………. [1]

[Total: 13]

Qualitative Analysis Notes
[ppt. = precipitate]
(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	

CHEMISTRY 9729/04

JC2 Preliminary Examination **24 August 2018**
Paper 4 Practical **2 hr 30 min**

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory in the boxes provided.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages __ & __.

Shift
Laboratory

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/13
2	/29
3	/13
TOTAL	**/ 55**

All calculations final answers to 3 or 4 sf (unless answer is exact) and must have units – overall minus 1 except question (f)(i).
Markers to indicate on front page and tutors to minus from final marks.

This document consists of 19 printed pages and 1 blank pages.

Answer **all** the questions in the spaces provided.

1 Determination of a value for the solubility product, K_{sp}, of calcium iodate(V), $Ca(IO_3)_2$

Calcium iodate is used in the manufacture of disinfectants, antiseptics, and deodorants. Its solubility in water is low. When calcium iodate(V) is mixed with water, the following equilibrium is established.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^{-}(aq)$$

You are to perform an experiment to determine the solubility product, K_{sp}, of calcium iodate(V).

You will first prepare a saturated solution of calcium iodate(V) by mixing specific volumes of potassium iodate(V), KIO_3 and calcium nitrate, $Ca(NO_3)_2$.

The mixture is then filtered after leaving to stand for some time. The filtrate can then be analysed to determine the amount of iodate(V) ions left as follows:

- Excess potassium iodide, KI, is added to an acidified solution of the filtrate, liberating iodine.

$$IO_3^{-}(aq) + 5I^{-}(aq) + 6H^{+}\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l) \quad \textbf{reaction 1}$$

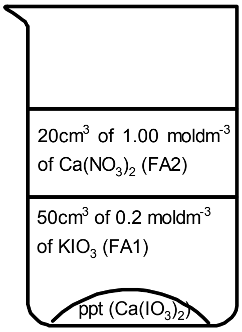
- The liberated iodine is then titrated with a standard solution of sodium thiosulfate.

$$2S_2O_3^{2-}\,(aq) + I_2\,(aq) \rightarrow 2I^{-}\,(aq) + S_4O_6^{2-}\,(aq) \quad \textbf{reaction 2}$$

FA 1	0.200 mol dm^{-3} potassium iodate(V), KIO_3
FA 2	1.00 mol dm^{-3} calcium nitrate, $Ca(NO_3)_2$
FA 3	aqueous sodium thiosulfate, $Na_2S_2O_3$
FA 4	aqueous solution of potassium iodide, KI
FA 5	dilute hydrochloric acid, HC*l*
Starch indicator	

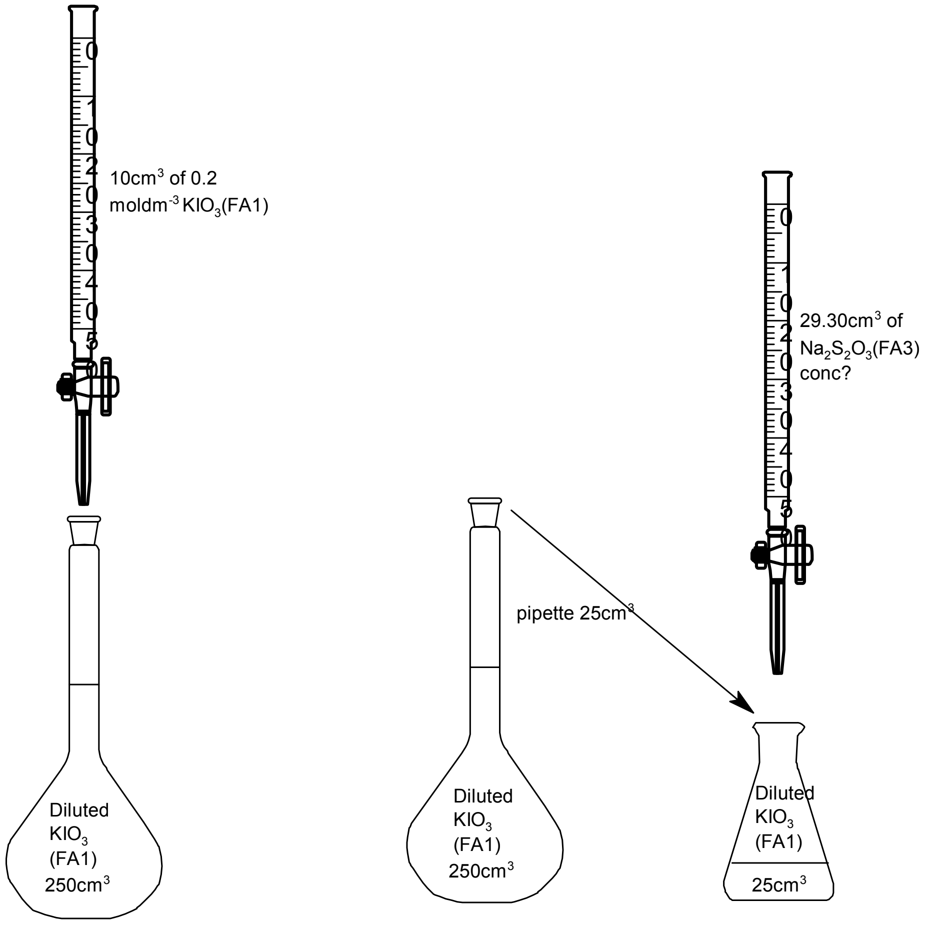
(a) **Preparing the reaction mixture**

1. Transfer 50 cm^3 of **FA 1** using a measuring cylinder to the beaker labelled **reaction mixture**.
2. Using another measuring cylinder, transfer 20 cm^3 of **FA 2** into the same beaker.
3. A precipitate will form. Stir the mixture thoroughly and leave it to stand for several minutes to allow equilibrium to be reached.



While waiting, follow the instructions given in part (b).

(b)	**(i)**	**Dilution of FA 1** The concentration of **FA 1** provided is too high. You will first prepare a diluted solution of **FA 1** of known concentration and use it to standardise the sodium thiosulfate solution provided.
		1. Using a burette, transfer 10.00 cm^3 of **FA 1** into a 250 cm^3 graduated flask, labelled **diluted FA 1**.
		2. Make up to the mark with deionised water and mix thoroughly.

	(ii)	**Standardisation of FA 3**
		1. Fill a burette with **FA 3**.
		2. Pipette 25.0 cm^3 of **diluted FA 1** into a conical flask.
		3. Using a measuring cylinder, add about 10 cm^3 of **FA 4** to the flask.
		4. Using another measuring cylinder, add about 2 cm^3 of **FA 5** to the flask.
		5. Add **FA 3** from the burette into the flask until a pale yellow colour is obtained.
		6. Add about 5 drops of starch indicator into the flask. Continue adding **FA 3** until the blue-black colour just disappears.
		7. Perform sufficient titrations to obtain accurate results for the end-point. Rinse the conical flask between each titration. 

Record your titration results in the space below. Make certain that your recorded results show the precision of your working. [5]

Final burette readings / cm^3	29.25	29.35
Initial burette reading /cm^3	0.00	0.00
Volume of **FA 3** used / cm^3	29.25	29.35
	√	√

(iii) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume. [1]

Volume of **FA 3** used = (29.25 + 29.35) / 2 = 29.30 cm^3

(iv) Calculate the concentration of $S_2O_3^{2-}$ ions in the **FA 3** solution. [1]

Amount of KIO_3 in 250 cm^3 of **diluted FA 1**
= Amount of KIO_3 in 10 cm^3 of **concentrated FA 1**

$$= 0.2 \times \frac{10}{1000} = 0.002 \text{ mol}$$

Amount of KIO_3 in 25 cm^3 of **diluted FA 1** = 0.002/10 = 0.0002 mol

$IO_3^- \equiv 3I_2 \equiv 6S_2O_3^{2-}$

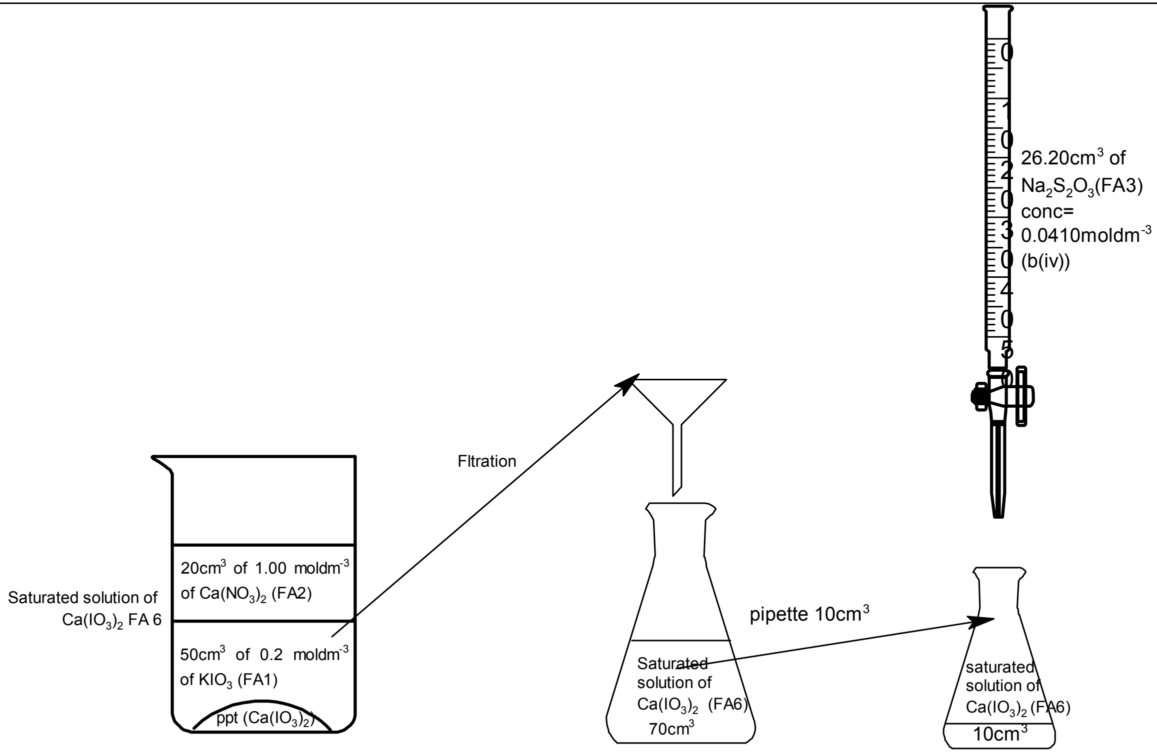
Amount of $S_2O_3^{2-}$ in 29.30 cm^3 of **FA 3** = 0.0002 x 6 = 0.0012 mol

$$[S_2O_3^{2-}] \text{ of FA3} = 0.0012 / \left(\frac{29.30}{1000}\right) = \underline{\mathbf{0.0410 \text{ mol dm}^{-3}}}$$

Analysing the filtrate

(c) **(i)**

1. Filter the reaction mixture through a **dry** filter paper into a **dry** conical flask, labelled **FA 6**. This is the filtrate, **FA 6**. Do not wash the white precipitate with water.
2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.
3. Using a measuring cylinder, add about 10 cm^3 of **FA 4** to the flask.
4. Using another measuring cylinder, add about 2 cm^3 of **FA 5** to the flask.
5. Add **FA 3** from the burette into the flask until a pale yellow solution is obtained.
6. Add about 5 drops of starch indicator and continue adding **FA 3** until the blue-black colour just disappears.
7. Perform sufficient titrations to obtain accurate results for the end-point. Rinse the conical flask between each titration.



Record your titration results in the space below. Make certain that your recorded results show the precision of your working.

Final burette readings / cm^3	26.20	26.20
Initial burette reading/cm^3	0.00	0.00
Volume of **FA 3** used / cm^3	26.20	26.20
	√	√

(ii) From your titration results, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 3** used = (26.20 + 26.20) / 2 = 26.20 cm^3

Calculations

(d) **(i)** Calculate the amount of $S_2O_3^{2-}$ ions present in the volume of **FA 3** obtained in **(c)(ii)**.

Amount of $S_2O_3^{2-}$ = 0.0410 x ($\frac{26.20}{1000}$)= **<u>0.00107 mol</u>**

(ii) Calculate the amount of IO_3^- ions present in 10.0 cm^3 of the filtrate, **FA 6**. [1]

$IO_3^- \equiv 3I_2 \equiv 6S_2O_3^{2-}$

Amount of IO_3^- in 10.0 cm^3 of **FA 6**= 0.0010742 / 6 = **<u>1.79 x 10^{-4} mol</u>**

	(iii)	Hence, calculate the total amount of IO_3^- ions present in the filtrate, **FA 6**. [1] Total volume of mixture = 50 + 20 = 70 cm^3 Amount of IO_3^- in the filtrate (70 cm^3 of **FA 6**) = $1.79 \times 10^{-4} \times (70/10)$ = **1.25×10^{-3} mol**
(e)	**(i)**	Calculate the initial amount of IO_3^- ions and Ca^{2+} ions present in the reaction mixture prepared in **(a)**. [1] Initial amount of IO_3^- = 50/1000 x 0.2 = **0.0100 mol** Initial amount of Ca^{2+} = 20/1000 x 1.0 = **0.0200 mol**
	(ii)	Calculate the amount of IO_3^- ions precipitated as $Ca(IO_3)_2$. [1] Amount of IO_3^- precipitated as $Ca(IO_3)_2$ = Initial amount – amount in filtrate = 0.0100 – (1.25×10^{-3}) = 0.00875 mol
	(iii)	Hence, calculate the amount of Ca^{2+} ions left in **FA 6**. [1] $Ca^{2+} \equiv 2IO_3^-$ Amount of Ca^{2+} precipitated = 0.00875 / 2 = 0.004375 mol Amount of Ca^{2+} ions left in FA 6 = Initial amount – amount in precipitate = 0.02 – 0.004375 = **0.0156 mol**
(f)	**(i)**	Use your answer in parts **(d)(iii)** and **(e)(iii)** to calculate a value for the solubility product, K_{sp}, of calcium iodate(V). Include units in your answer. [2] Eqm $[Ca^{2+}] = \frac{0.015625}{0.07}$ = 0.223 mol dm^{-3} Eqm $[IO_3^-] = \frac{1.25 \times 10^{-3}}{0.07}$ = 0.01786 mol dm^{-3} $K_{sp} = [Ca^{2+}][IO_3^-]^2 = (0.223)(0.01786)^2$ = **7.11×10^{-5} mol^3 dm^{-9}**
(g)	Another student performed this experiment and obtained a value for the solubility product, K_{sp}, of 3.45×10^{-5}. A literature value for this solubility product is 6.71×10^{-6} at 20 °C. You should assume that apparatus of the same precision was used in each case. State a possible reason for the higher value of K_{sp} obtained by the student and suggest an improvement which might allow a value closer to the literature value to be obtained. [1]	
	Explanation: The student did not carry out the experiment at 20°C. Hence, the equilibrium position shifted to the right. OR	

When the student carried out the experiment, not all the ppt has formed / eqm has not been reached. Hence, the [Ca^{2+}] and [IO_3^-] is too high.

Improvement:

The student should **carry out the experiment at 20°C** by letting the mixture equilibrate in a thermostatically **controlled** water bath **maintained** at 20°C for a considerable amount of time before doing the filtration.

OR

The student should leave the reaction mixture for a **considerable time** before doing the filtration to **allow** the ppt to form / **equilibrium to be establish**.

[Total: 15]

2 You are to determine the enthalpy change of reaction, Δ*H*, for the reaction shown below.

$$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$$

As copper is an unreactive metal it does not react with dilute acids. You will need to find the enthalpy change of reaction for two reactions that do occur. The equations for these two reactions are below.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

You will conduct experiments to find the enthalpy changes for each of **Reaction 1** and **Reaction 2** and use these values to calculate the enthalpy change for the reaction of copper with sulfuric acid.

Determining the enthalpy change for Reaction 1

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

(a) **Method**

FA 8 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 7 is magnesium powder, Mg.

Read through the method before you start any practical work and prepare a suitable table for your results.

1. Weigh the bottle containing **FA 7**. Record the mass.
2. Support the Styrofoam cup in the 250 cm^3 beaker.
3. Use the measuring cylinder to transfer 25 cm^3 of **FA 8** into the Styrofoam cup.
4. Measure the temperature of **FA 8** in the cup and start the stop clock. Record this temperature as being the temperature at time = 0.
5. Measure, and record, the temperature of this **FA 8** every half minute for 2

minutes.

6. At time = 2½ minutes add the **FA 7** to the acid and stir carefully to reduce acid spray.
7. Measure the temperature of the mixture in the cup at time = 3 minutes and then every half minute up to time = 7 minutes.
8. Continue stirring occasionally throughout this time.
9. Weigh the bottle that had contained **FA 7**. Record the mass.
10. Calculate and record the mass of **FA 7** added to the sulfuric acid.
11. Rinse the cup with water and shake to dry.

[6]

(b) (i)	On the grid below plot a graph of temperature (*y*-axis) against time (*x*-axis).
	[2]
(ii)	Complete the graph by drawing two, straight lines of best fit • One to show the temperature up to time = 2 ½ minutes • One to show the temperature after time = 2 ½ minutes [1]

	(iii)	From your graph, use the two straight lines of best fit to calculate the change in temperature at time = 2 ½ minutes.

		Temperature change = ………………°C [1]

(c)	**Calculations**	
	(i)	In the reaction in **(a)**, the sulfuric acid was in excess. Without carrying out any additional tests, what observation could you have made during your experiment to confirm this?
		All the magnesium / solid dissolved / disappeared or all solid / Mg has gone / been used up or no solid / Mg left. **Not accepted: no more effervescence.**
	(ii)	Calculate the energy change that occurred during the reaction in **(a)**. [Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0 °C.]
		Correct use of $Q = mc\Delta T$ [1]
	(iii)	Use your answer to **(ii)** to calculate the enthalpy change, in kJ mol^{-1}, for the reaction between sulfuric acid and magnesium. [*Ar* : Mg, 24.3] $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**
		number of moles of magnesium = $\frac{mass\ measured}{24.3}$ mol $\Delta H = -\frac{Ans\ in\ (ii)/\ 1000}{no.of\ mol\ of\ Mg}$ Enthalpy change of Reaction 1 = ……………….kJ mol^{-1} [1]

(d)	**Planning: Determining the enthalpy change for Reaction 2**	
		The enthalpy change of reaction for **Reaction 2** can be determine using a **non-graphical approach**. $Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**
	(i)	Plan an investigation to determine mean temperature rise, mean mass of magnesium used and the enthalpy change of reaction for **Reaction 2**. You are provided with • **FA 11**, 1.00 mol dm^{-3} copper(II) sulfate, $CuSO_4$ • **FA 9** and **FA 10** magnesium powder samples in weighing bottles • the equipment normally found in a school or college laboratory. You are to take precaution to ensure that the copper(II) sulfate was in excess in these reactions and **not more than 30 cm^3** is used for each experiment.

In your plan you should include brief details of

- the volume of $CuSO_4$ you plan to use (you may assume the mass of Mg(s) used to be the same as in reaction 1),
- the apparatus that you would use,
- the procedure that you would follow and the measurements that you would take,
- a suitable table for your results.

[6]

Suggested Answer:

(1) Weigh the weighing bottle containing **FA 9**. Record the mass.

(2) Support the plastic cup in the 250 cm^3 beaker.

(3) Use the measuring cylinder to transfer 25 cm^3 of **FA 11** into the plastic cup.

(4) Measure the temperature of **FA 11** in the plastic cup and record the temperature.

(5) Add the **FA 9** to the **FA 11** in the cup and stir the mixture constantly.

(6) Measure and record the maximum temperature, reached during the reaction.

(7) Calculate and record the maximum temperature change that occurred during the reaction between **FA 9** and **FA 11**.

(8) Weigh the stoppered tube that had contained **FA 9**. Record the mass.

(9) Calculate and record the mass of **FA 9** added to the copper(II) sulfate.

(10) Empty the contents of the plastic cup into the 100 cm^3 beaker labelled **waste**.

(11) Rinse the plastic cup and shake to dry or dry with the cleaning paper provided.

(12) Repeat step (1) to (9) experiment using **FA 10** in place of **FA 9**.

	Expt with FA 3 and FA 4	Expt with FA 3 and FA 5
Volume of $CuSO_4$ / cm^3		
Initial mass of tube with Mg / g		
Final mass of tube with Mg / g		
Mass of Mg used / g		
Initial temperature / ^oC		

Final temperature/ °C		
Change in temperature / °C		

Indicative material	Mark
Relevant working for proposed volume of $CuSO_4$ to ensure that it is in excess	1
Proper use of apparatus	1
Sound process in taking mass	1
Rinse cup and dry before conducting second expt or use a new cup	1
Repeating the experiment using FA5	1
Table with at 8 readings · 4 × balance readings · 2 × initial temp · 2 × highest / max temp with unambiguous headings	1

If student copied the procedure in front, but instead of drawing graph, just take max T from table, penalise under sound process as they may miss the actual T max.

(ii) **Perform** the experiment you have planned in **(d)(i)**, clearly calculating the

- mean temperature change and
- mean mass of magnesium.

Hence, determine the enthalpy change, in kJ mol^{-1} for the reaction between magnesium and copper(II) sulfate.

[Assume that 4.2 J is needed to raise the temperature of 1.0 cm^3 of solution by 1.0°C]
[A_r : Mg, 24.3]

[3]

Indicative material	Mark
Proper recording of expt data (as in 1(a))	1
Conducted the experiment and determine the mean temperature change	1
Mean mass of magnesium determined	1
Working to calculate the enthalpy change using mean mas of magnesium and mean temperature change	1

Enthalpy change for Reaction 3

Reaction 3 is shown below.

$Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

(e) Use your values for the enthalpy changes for **Reactions 1** and **2** to calculate the enthalpy change for **Reaction 3**.

$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$ **Reaction 1**

$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$ **Reaction 2**

Show clearly how you obtain your answer.

(If you were unable to calculate the enthalpy changes for **Reactions 1** and **2**, you should assume that the value for **Reaction 1** is – 444 kJ mol^{-1} and that the value for **Reaction 2** is – 504 kJ mol^{-1}. Note: these are not the correct values.)

Method 1 (algebraic method):

$\cancel{Mg(s)} + H_2SO_4(aq) \rightarrow \cancel{MgSO_4}(aq) + H_2(g)$ **Reaction 1**

$\cancel{MgSO_4}(aq) + Cu(s) \rightarrow \cancel{Mg(s)} + CuSO_4(aq)$ **– Reaction 2**

Overall: $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2(g)$ **Reaction 3**

Thus, $\boxed{\Delta H_{rxn3} = \Delta H_{rxn1} - \Delta H_{rxn2}}$

Method 2 (energy cycle method) is also acceptable.

Enthalpy change for **Reaction 3** = …………………kJ mol^{-1} [2]

(f) **(i)** The method you used to determine the enthalpy change for **Reaction 1** was more accurate than the method you used to determine the enthalpy change for **Reaction 2**. Suggest **two** reasons why the method used for **Reaction 2** was less accurate. Explain your answers.

Any 2 accepted:

- Lower Δ H for Reaction 2 and so higher % error
- No correction made for loss of heat on cooling using temperature-correction graph, thus heat loss to surroundings for Reaction 2 not taken into account
- Not all Mg reacted / reaction does not go to completion in Reaction 2 (so not all energy released)
- Reaction 2 involving Mg takes place more slowly, so more heat was lost to surroundings

(ii) A student suggested that the accuracy of the method used for **Reaction 2** could be improved by using a larger volume of copper(II) sulfate. Is this a correct suggestion? Give a reason for your answer.

			No, since (larger volume of solution means) smaller Δ T, hence higher percentage error. OR Yes, since there would be a smaller T rise so less heat would be lost. Yes, since larger volume is used , hence smaller percentage error Not accepted: did not indicate whether the percentage error is for temperature or volume
			[Total: 29]

3 **FA 12** contains two cations and two anions from those listed on pages 18 and 19.

In all tests, the reagent should be added gradually until no further change is observed, with shaking after each addition.
Record your observations in the spaces provided.
Your answers should include

- details of colour changes and precipitates formed,
- the names of gases evolved and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs, writing any deductions you made alongside the observations on which they are based.

Marks are **not** given for chemical equations.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

	Test	*Observations* [3]	*Possible cation(s)* [3]
(a)	Place 3 cm^3 **FA 12** in a test tube, add aqueous sodium hydroxide, drop by drop, until no further change is seen.	✓*Cream/ Off-white ppt formed* ✓*Cream/ Off-white ppt turns brown on standing* *(traces of white ppt observed)*	✓*Mn^{2+}*
(b)	Filter the mixture from **(a)** and **collect the filtrate for later test** Leave the residue in the filter paper and observe it again after several minutes.	✓*Colourless filtrate* ✓*Off-white ppt turns brown on standing / brown residue*	✓*Mn^{2+}*
(c)	Extract about 1 cm^3 of the filtrate using a teat	✓*White ppt reformed*	

	pipette into a clean test tube. Add dilute nitric acid, drop by drop, until no further change is seen.	✓*White ppt soluble in excess* HNO_3	✓Zn^{2+} *or* Al^{3+} (Pb^{2+})

Test for anions

Test **(e)** has been conducted and the observation is recorded.

You are to complete test **(f)** and devise **two** more tests to confirm the identity of the anions present in **FA 12**.

In the space provided below, clearly state the tests, observations and deductions.

	Test	*Observation*
(e)	Add 1 cm^3 of **FA 12** into a clean test-tube. Add 2 cm^3 of aqueous hydrochloric acid.	No effervescence observed No brown gas
(f)	Add 1 cm^3 of **FA 12** into a clean test-tube Add 3 drops of aqueous silver nitrate.	*No ppt* Solution remains colourless Small amount of white/cream ppt which immediately dissolves
(g)	To 1 cm^3 FA 12, add 3 drops of aqueous barium nitrate. Then add 1 cm^3 of aqueous nitric acid/ hydrochloric acid. OR Extract about 1 cm^3 of the filtrate using a dropping pipette/dropper into a clean test tube. Add 3 drops of aqueous barium nitrate.	*White ppt* *White ppt insoluble*
(h)	To 1 cm^3/ depth FA 12, add (3 drops X) 2 cm^3/ equal volume/depth of aqueous NaOH follow by a small piece of *Al* foil with warming	*Effervescence observed* *Gas evolved turns moist/damp red litmus turns blue*

Anions present in **FA12**: ………………and ………………… [1]

SO_4^{2-} and NO_3^- both correct

[Total: 13]

END

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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TEMASEK
JUNIOR COLLEGE

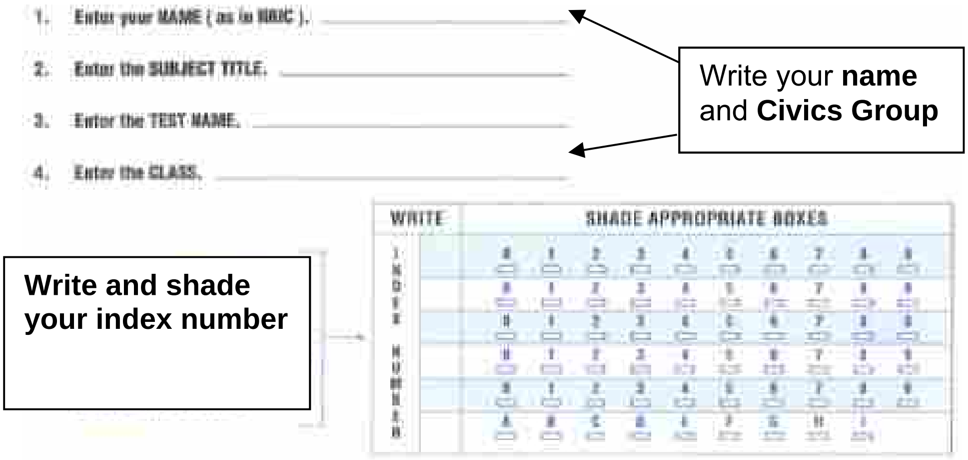
CHEMISTRY **9729/01**

Paper 1 Multiple Choice **15th September 2018**
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.



1. Enter your NAME (as in NRIC).
2. Enter the SUBJECT TITLE.
3. Enter the TEST NAME.
4. Enter the CLASS.

WRITE | SHADE APPROPRIATE BOXES

Write your **name** and **Civics Group**

Write and shade your index number

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages.

Section A

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the separate Answer Sheet (OMS).

1 Some isotopes are unstable and undergo nuclear (radioactive) reactions. In one type of reaction, an unstable nucleus assimilates an electron from an inner orbital of its electron cloud. The net effect is the conversion of a proton and an electron into a neutron.

Which of the following describes this type of reaction?

A $^{11}C \rightarrow {}^{12}C$

B $^{111}I \rightarrow {}^{111}Te$

C $^{76}Br \rightarrow {}^{75}Br$

D $^{76}Kr \rightarrow {}^{75}Br$

2 Sodium hydrogencarbonate can be prepared from sodium sulfate by a three-step process:

$Na_2SO_4(s) + 4C(s) \rightarrow Na_2S(s) + 4CO(g)$

$Na_2S(s) + CaCO_3(s) \rightarrow CaS(s) + Na_2CO_3(s)$

$Na_2CO_3(s) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$

What is the mass of sodium hydrogencarbonate that could be formed from 100 kg of the sodium sulfate, assuming a 90% yield in each step?

A 106 kg **B** 96 kg **C** 86 kg **D** 43 kg

3 Which of the following reactions is a redox reaction?

A $2NO_2 \rightarrow N_2O_4$

B $6HCl + As_2O_3 \rightarrow 2AsCl_3 + 3H_2O$

C $SbF_3 + F_2 \rightarrow SbF_5$

D $Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$

4 When 2.6 g of a metal X are added to copper(II) sulfate solution 4.8 g of copper are obtained. The relative atomic mass of X is 52. Which one of the following cations of X is produced?

A X^{4+} **B** X^{3+} **C** X^{2+} **D** X^{+}

5 20.0 cm^3 of 0.02 mol dm^{-3} bromate(V), BrO_3^-, was found to react completely with 80.0 cm^3 of 0.01 mol dm^{-3} hydroxylamine, NH_2OH. BrO_3^- ions are reduced as follows:

$$BrO_3^- + 6e^- + 6H^+ \rightarrow Br^- + 3H_2O$$

Which of the following could be the half-equation for the oxidation of hydroxylamine?

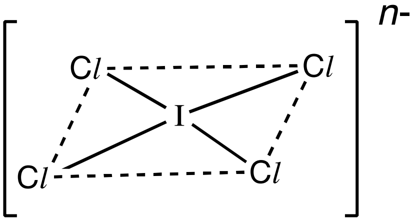
A $NH_2OH \rightarrow \frac{1}{2} N_2O + 2H^+ + \frac{1}{2} H_2O + 2e^-$

B $NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$

C $NH_2OH \rightarrow NO + 3H^+ + 3e^-$

D $NH_2OH + 2H_2O \rightarrow NO_3^- + 7H^+ + 6e^-$

6 An ion ICl_4^{n-} has a square planar structure as shown below.



What is the value of *n*?

A 1

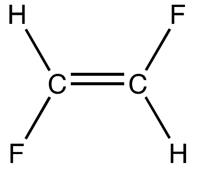
B 2

C 3

D 4

7 Which molecule has the largest dipole?

A



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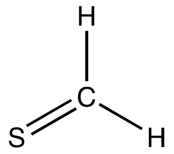

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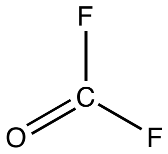

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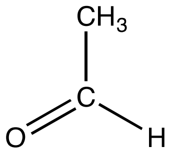
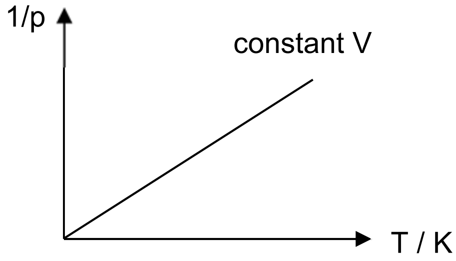


8 Which of the following graphs correctly describes the behaviour of a fixed mass of ideal gas?

A



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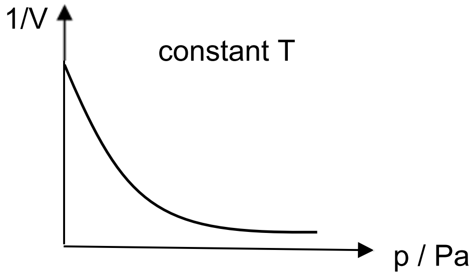
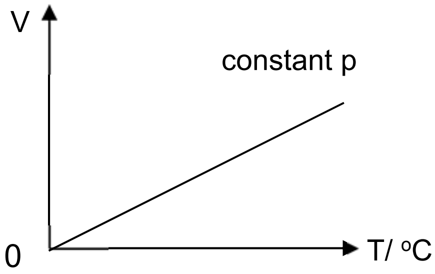


C



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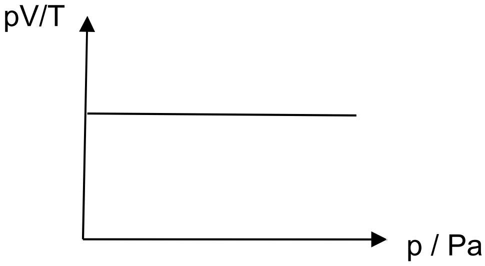


9 Phosphorus pentachloride reacts with limited amount of water to give a liquid and white fumes as shown in the equation below.

$$PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(g) \qquad \Delta H^\ominus = -640 \text{ kJ mol}^{-1}$$

The following enthalpy changes are given:

$\Delta H_f^\ominus$ $PCl_5(s)$ = – 444 kJ mol^{-1}

$\Delta H_f^\ominus$ $HCl(g)$ = – 92 kJ mol^{-1}

$\Delta H_c^\ominus$ $H_2(g)$ = – 286 kJ mol^{-1}

What is the standard enthalpy change of formation of $POCl_3(l)$?

A – 1278 kJ mol^{-1} **B** – 1186 kJ mol^{-1} **C** + 94 kJ mol^{-1} **D** + 274 kJ mol^{-1}

10 Which quantity is not required in the calculation of the lattice energy of calcium hydride, CaH_2,using the Born-Haber cycle?

A first electron affinity of hydrogen

B second electron affinity of hydrogen

C first ionisation energy of calcium

D second ionisation energy of calcium

11 Compound **M**, $CH_3CH{=}CHCHC\mathit{l}CH_3$, reacts readily with alcoholic KCN according to the following equation:

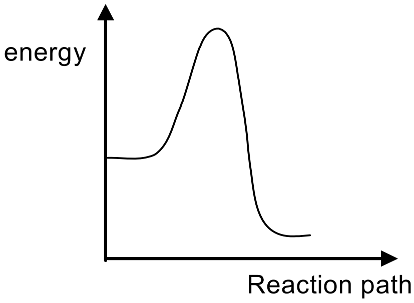
$$CH_3CH{=}CHCHC\mathit{l}CH_3 + CN^- \rightarrow CH_3CH{=}CHCH(CN)CH_3 + C\mathit{l}^-$$

The following kinetics data were collected:

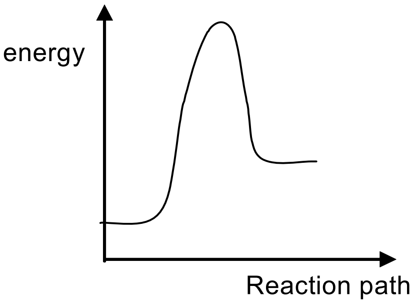
Experiment	**[M] / mol dm^{-3}**	**[CN$^-$] / mol dm^{-3}**	**Relative Rate**
1	0.1	0.1	1
2	0.2	0.1	2
3	0.3	0.3	3

Which diagram represents the reaction profile for this reaction?

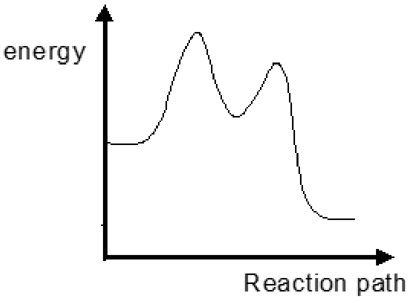
A



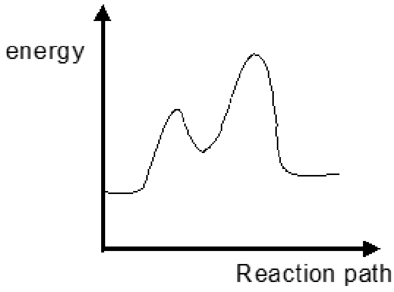
B



C



D



12 The radioactive decay of isotopes **P** and **Q** follow first-order kinetics.

Isotope **P** decreases from 1800 counts per minute to 450 counts per minute in six months. Isotope **Q** decreases from 5400 counts per minute to 1350 counts per minute in four months.

In a separate experiment, a sample containing a mixture of the two isotopes was left to decay, and the molar ratio of **P** : **Q** was found to be 1 : 1 after six months.

What is the molar ratio of **P** : **Q** at the beginning?

A 1 : 2 **B** 1 : 4

C 2 : 1 **D** 4 : 1

13 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table. The following statements were made about the properties of **X**, **Y** and **Z**, and their compounds.

1 The oxide of **Z** does not dissolve in excess dilute NaOH(aq).

2 When a sample containing equimolar quantities of each oxide is mixed with water, the solution obtained is highly acidic.

3 Only the chlorides of **Y** and **Z** give an acidic solution with water.

Based on the statements above, identify elements **X**, **Y** and **Z**.

	X	**Y**	**Z**
A	Na	S	Mg
B	Mg	P	Si
C	A*l*	S	Mg
D	Na	P	Si

14 Which of the following statements are true?

1 The lattice energy of magnesium oxide is more negative than the lattice energy of barium oxide.

2 The solubility product of magnesium hydroxide is smaller than that of calcium hydroxide.

3 The reducing power of strontium is weaker than that of barium.

4 Barium nitrate decompose more readily than magnesium nitrate.

A 1, 2 and 3 only **B** 1, 3 and 4 only **C** 1, 2 and 4 only **D** 2, 3 and 4 only

15 Astatine (At) is an element in Group 17. Which of the following statements is correct?

A Silver astatide reacts with aqueous ammonia to form a soluble complex.

B HAt(aq) is a weaker acid than HC*l*(aq).

C Astatine reacts with aqueous iron(II) sulfate to form iron(III) ions and astatide.

D The enthalpy change of formation of hydrogen astatide is less exothermic than that of hydrogen chloride.

16 A sample of 0.300 mol of HBr gas was decomposed in a sealed container at temperature T. The resulting equilibrium mixture was found to contain 0.015 mol of Br_2.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g) \qquad \Delta H \text{ is positive}$$

Which of the following statements are true for the reaction?

1 The mole fraction of HBr(g) is 0.27 at equilibrium

2 The equilibrium constant $K_c = 3.09 \times 10^{-3}$

3 The K_c will increase if reaction is carried out at higher temperature.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

17 Which statement(s) about indicators is always correct?

1 The pH working range is greater for indicators with higher pK_a values.

2 The pK_a value of an indicator is within its pH working range.

3 The mid-point of an indicator's colour change is at pH = 7.

4 The colour red indicates an acidic solution.

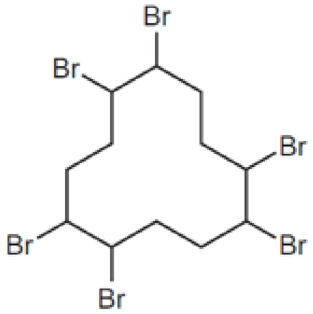
A 1 and 2 only

B 2 only

C 1 and 3 only

D 3 and 4 only

18 The compound shown is used as flame retardant.



Which statement about this molecule is **not** correct?

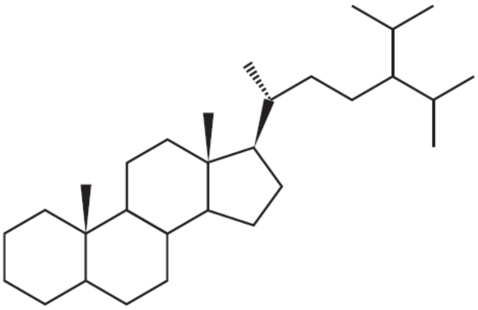
A The carbon atom ring is planar.

B It is immiscible in water.

C Its empirical formula is C_2H_3Br.

D The compound reacts with ethanolic sodium hydroxide to form $C_{12}H_{12}$.

19 The molecule 24-isopropylcholestane, which has been isolated from a class of sponge, can serve as a biomarker and has determined the first evolutionary appearances of some species.



Carbon atoms in a molecule are classified as primary, secondary, tertiary or quaternary, depending on whether they are directly bonded to one, two, three or four other carbon atoms.

How many tertiary carbons and how many chiral carbons are there in this molecule?

	Tertiary carbons	**Chiral carbons**
A	9	4
B	9	8
C	11	4
D	11	8

20 Which forms of isomerism will be shown by the molecule 2,4-dimethylhex-2-ene?

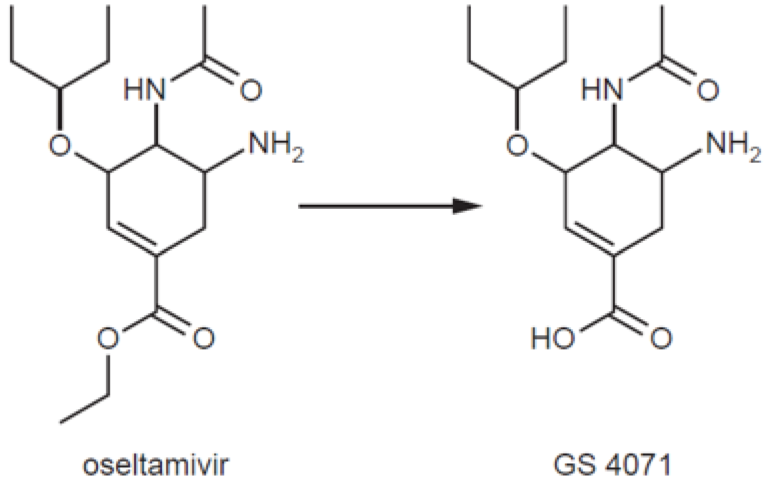
A Enantiomerism only

B Cis-trans isomerism only

C Both enantiomerism and cis-trans isomerism.

D Neither enantiomerism nor cis-trans isomerism.

21 Oseltamivir is an anti-viral drug that is converted to its active form, GS 4071, in the body after being administered. Assume that R-O-R is an inert functional group.



Which of the following statements are correct?

1 The reaction shown above is an elimination reaction.

2 There are three single C-C σ bonds formed by sp^2 - sp^2 overlap in oseltamir and GS 4071.

3 GS 4071 gives an orange precipitate with 2,4-dinitrophenylhydrazine.

4 When oseltamir is hydrolysed by aqueous HC*l*, 3 products are obtained

A 1 and 3 only

B 2 and 4 only

C 1, 2 and 3 only

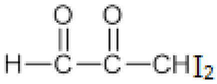
D 4 only

22 Compound **X** has the following properties.

- It causes decolourisation of purple acidified potassium manganate (VII).
- It gives yellow precipitate with alkaline aqueous iodine.

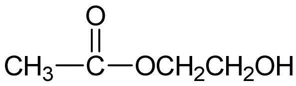
Which compound could be **X**?

A



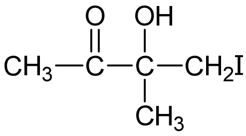
$HCOCOCHI_2$

B



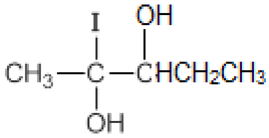
$CH_3COOCH_2CH_2OH$

C



$CH_3COC(OH)(CH_3)CH_2I$

D



$CH_3C(I)(OH)CH(OH)CH_2CH_3$

23 Consider the following four compounds, which are structural isomers of one another.

1 $CH_2ClCHClCOOH$

2 $CHCl_2CH_2COOH$

3 $CH_2OHCHClCOCl$

4 $ClCH_2OCOCH_2Cl$

Which sequence arranges the aqueous solution of the compounds of the same concentration in order of increasing pH?

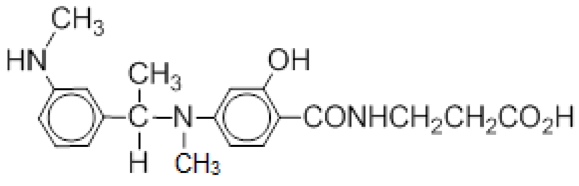
A 4 2 1 3

B 1 2 3 4

C 3 1 2 4

D 3 2 1 4

24 Which of the following statements regarding compound **T** is correct?



compound **T**

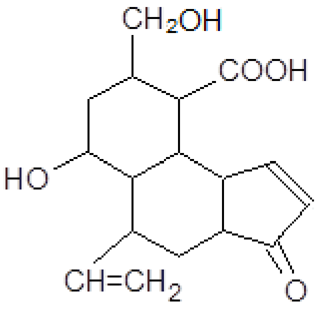
A 1 mol of compound **T** reacts with 4 mol of ethanoyl chloride.

B 1 mol of compound **T** reacts with 3 mol of cold dilute hydrochloric acid.

C 1 mol compound T reacts with 4 mol of hot dilute NaOH.

D Compound **T** reacts with excess aqueous bromine to give a product with five bromine atoms.

25 What is the correct number of hydrogen atoms incorporated per molecule of compound **Y** when it is reacted with each of the following reducing agents?



Compound **Y**

	Reducing agent	Number of hydrogen atoms incorporated per molecule of **Y**
1	H_2 / Ni	6
2	LiA/H_4 in dry ether	8
3	$NaBH_4$ in ethanol	2

A 1 only

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

26 In the presence of dilute alkali, some carbonyl compounds undergo Aldol condensation to form a conjugated enone compound. For example, ethanal forms but-2-enal according to the reaction scheme below.

$$2CH_3CHO \xrightarrow{OH^-} CH_3CH(OH)CH_2CHO \xrightarrow{OH^-} CH_3CH{=}CHCHO$$

but-2-enal

Which of the following gives the structure of the product formed when propanone undergoes the same reaction?

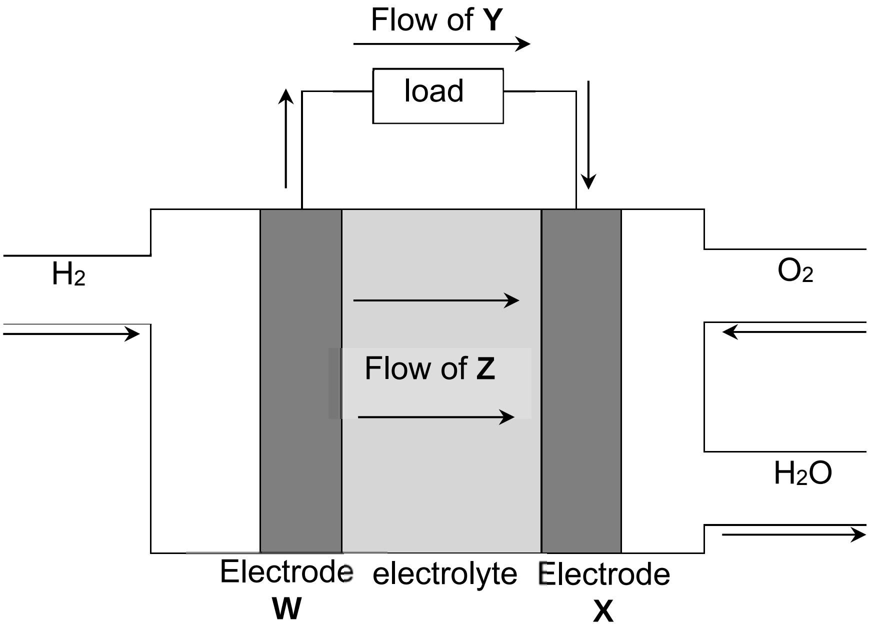
A $CH_3CH_2CH{=}C(CH_3)CHO$

B $(CH_3)_2C{=}C(CH_3)CHO$

C $CH_3CH_2CH{=}CHCOCH_3$

D $(CH_3)_2C{=}CHCOCH_3$

27 A diagram of a hydrogen/ oxygen fuel cell is shown below.



Which of the following shows the correct identities of **W**, **X**, **Y** and **Z**?

	W	**X**	**Y**	**Z**
A	anode	cathode	electron	H^+
B	anode	cathode	electron	OH^-
C	cathode	anode	electron	H^+
D	cathode	anode	OH^-	electron

28 The zinc/silver oxide cell is used for button cells in watch batteries and is based on the following half-cells:

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^\ominus = -0.76$ V

$Ag_2O(s) + H_2O(l) + 2e^- \rightleftharpoons 2Ag(s) + 2OH^-(aq)$ $E^\ominus = +0.34$ V

Which of the following statements are true for the zinc/ silver oxide cell?

1 Zinc is the positive electrode.

2 The $\Delta G^\ominus$ of the reaction is -212.3 kJ mol^{-1}.

3 E_{cell} becomes more positive when small amount of NaOH(s) is added to the Zn^{2+}/Zn half-cell.

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

29 The ground state electronic configuration of a transition element is shown.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

What oxidation states for this element are able to occur in its compounds?

1 +2

2 +3

3 +6

A 1, 2 and 3 **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

30 When copper(II) chloride is dissolved in water it gives a blue solution. When this solution is treated with an excess of concentrated hydrochloric acid it turns yellow.

What are the formulae of the copper species in the blue and yellow solutions?

	Blue	**Yellow**
A	$CuCl_2$	$[CuCl_4]^{2-}$
B	$CuCl_2(H_2O)_4$	$[CuCl_6]^{4-}$
C	$Cu(OH)_2$	$CuCl_2(H_2O)_4$
D	$[Cu(H_2O)_6]^{2+}$	$[CuCl_4]^{2-}$

2018 TJC JC2 H2 Chemistry Prelim MCQ Solutions

1	2	3	4	5	6	7	8	9	10
B	**C**	**C**	**B**	**C**	**A**	**D**	**D**	**B**	**B**
11	12	13	14	15	16	17	18	19	20
C	**A**	**D**	**A**	**D**	**C**	**B**	**A**	**B**	**A**
21	22	23	24	25	26	27	28	29	30
D	**A**	**C**	**D**	**C**	**D**	**A**	**C**	**B**	**D**

TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME										
CIVICS GROUP			/							
CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9729/02

Paper 2 Structured Questions **23 August 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 21
2	/ 13
3	/ 9
4	/ 8
5	/ 14
6	/ 10
Total	/ 75

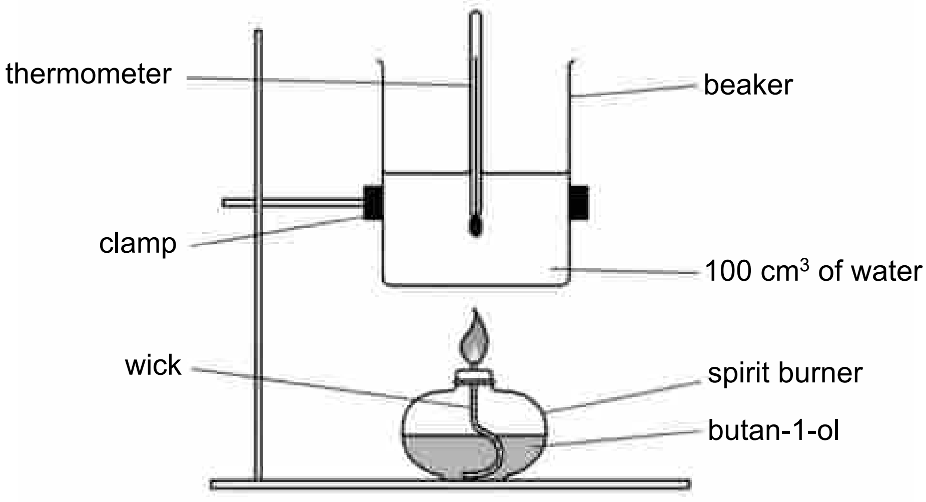
This document consists of **23** printed pages

SECTION A

Answer all questions in the spaces provided.

1 **(a)** For many compounds, the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy change of combustion can be used.

The enthalpy change of combustion of butan-1-ol can be found by a calorimetry experiment in which the heat given off during combustion is used to heat a known mass of water and the temperature change recorded.



temperature of water before heating = 25.0 °C

temperature of water after heating = 66.1 °C

mass of spirit burner and butan-1-ol before heating = 80.44 g

mass of spirit burner and butan-1-ol after heating = 79.70 g

(i) Explain the meaning of the term *standard enthalpy change of combustion*.

....

....

.... [1]

(ii) The heat transfer from the spirit burner to water is known to be only 70% efficient. From the data provided above, determine the enthalpy change of combustion of butan-1-ol.

[2]

(iii) The entropy change of combustion of butan-1-ol is -252 J K^{-1} mol^{-1}. Using your answer in **(a)(ii)**, calculate the Gibb's free energy for combustion of butan-1-ol at 298 K.

[1]

(b) The table below gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

name	formula	molar mass/ g mol^{-1}	density/ g cm^{-3}	$\Delta H_c^\ominus$ (298K)/ kJ mol^{-1}	$\Delta H_f^\ominus$ (298K)/ kJ mol^{-1}
methanol	CH_3OH	32	0.793^a	-726.0	-239.1
ethanol	CH_3CH_2OH	46	0.789^a	-1367.3	
liquid hydrogen	H_2	2	0.0711^b	$-285.8^\#$	
octane	$CH_3(CH_2)_6CH_3$	114	0.703^a	-5470.2	-250.0

[a] At 298K and 1 bar pressure

[b] At 20K and 1 bar pressure

[#] standard enthalpy change of combustion of hydrogen **gas**

(i) State the value of the standard enthalpy change of formation of hydrogen **gas**, H_2.

.... [1]

(ii) Calculate the density of gaseous hydrogen at 298 K and 1 bar pressure. Give your answers in g cm^{-3}.

[1]

(iii) Write the chemical equation that represents the standard enthalpy change of combustion of ethanol, including the state symbols.

....[1]

(iv) The standard enthalpy change of combustion of carbon is -393.5 kJ mol^{-1}. Using this value and the standard enthalpy change of combustion data in the table, calculate the standard enthalpy change of formation of ethanol.

Show your working clearly in the form of an energy cycle diagram.

[3]

(v) An important property of a fuel, especially when the fuel has to be lifted such as in aviation, is the energy released on combustion per gram of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298K for methanol.

[1]

(vi) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion per cm^3 of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for octane.

[1]

(vii) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with other fuels.

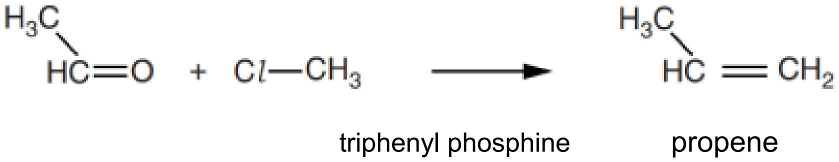
……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [1]

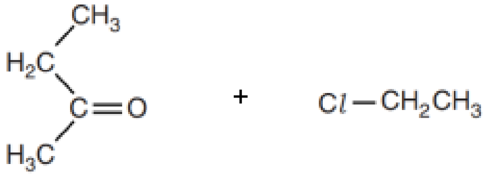
(c) Apart from alkanes and alcohols, alkenes are commonly used as fuel. Alkenes can be synthesised through the Wittig reaction, using halogenoalkane and carbonyl compound as the reactants in the presence of triphenyl phosphine.

The equation below shows the synthesis of propene using the Wittig reaction.



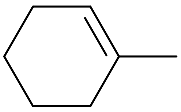
propene

(i) Draw the structures of the two cis-trans isomers formed from the reaction of the following compounds.



[2]

(ii) Draw the structural formula of the organic reactant used to generate 1-methylcyclohexene through the Wittig reaction.



1-methylcyclohexene

[1]

Alkenes react readily with interhalogen compound ICl to give halogenalkane. ICl reacts faster with alkenes than pure halogens and can be used to detemine the number of carbon-carbon double bonds present in organic compounds.

(iii) Suggest why ICl reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

....

....[1]

(iv) Name and describe the mechanism of reaction between propene and I*Cl* to give the major product. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(v) Draw the pair of enantiomers of the major product from the reaction between propene and I*Cl*.

[1]

[Total: 21]

2 **(a)** What do you understand by the *Brønsted–Lowry* theory of acids and bases?

……………………………………………………………………………………………

…………………………………………………………………………………… [1]

(b) **I** $C_2H_5N + H_2O \rightleftharpoons C_2H_5NH^+ + OH^-$ $K_c = 1.7 \times 10^{-9}$ mol dm^{-3}

II $C_6H_5O^- + CH_3CO_2H \rightleftharpoons C_6H_5OH + CH_3CO_2^-$ $K_c = 1.3 \times 10^{6}$ mol dm^{-3}

For each of the above equilibrium **I** and **II**,

(i) identify the two acids and the two bases present;

Equilibrium **I**. Two acids are ……………………………………………………………

Two bases are ……………………………………………………………

Equilibrium **II.** Two acids are ……………………………………………………………

Two bases are …………………………………………………….. [2]

(ii) using the given information, suggest, with reasons, which ion or molecule is the stronger acid, and which is the stronger base.

Equilibrium **I**: stronger acid: …………………………………

stronger base : …………………………………

Explanation for Equilibrium **I**:

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

Equilibrium **II**: stronger acid: ………………………………….

stronger base : …………………………………

Explanation for Equilibrium **II**:

……………………………………………………………………………………………

……………………………………………………………………………………………

………………………………………………………………………………………… [3]

(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

………………………………………………………………………………………… [1]

(ii) Explain why a buffer solution has been formed.

……………………………………………………………………………………………

…………………………………………………………………………………………… [1]

(iii) With the aid of an equation, explain how this buffer solution controls pH when an alkali is added.

……………………………………………………………………………………………

……………………………………………………………………………………………

………………………………………………………………………………………… [1]

(d) A biochemist plans to make up a buffer solution that has a pH of 5.00.

The biochemist adds solid calcium ethanoate to 400 cm^3 of 0.200 mol dm^{-3} ethanoic acid. He assumes that the volume of the solution remains constant at 400 cm^3 on dissolving the calcium ethanoate.

K_a for ethanoic acid = 1.75×10^{-5} mol dm^{-3}
M_r of calcium ethanoate = 158.1

(i) Calculate the mass of calcium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

[3]

(ii) When the biochemist prepares the buffer solution, the volume of solution increases slightly. Suggest whether the pH of the buffer solution would be the same, greater than, or less than pH = 5. Explain your reasoning.

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………… [1]

[Total: 13]

3 **(a)** **J**, **K**, **L** and **M** are consecutive elements in the same period of the Periodic Table. The oxide of **J** is basic, oxide of **K** is amphoteric, and the oxides of **L** and **M** are acidic. The halides of **M** can be used to convert alcohols to halogenoalkanes in the absence of water.

(i) Identify the elements **J**, **K**, **L** and **M**.

J: …………. **K**: …………. **L**: …………….. **M**: ………………

[1]

(ii) State and explain the variation of atomic radius from **J** to **M**.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [1]

(iii) Compare the melting points of **L** and **M** and explain your answer.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

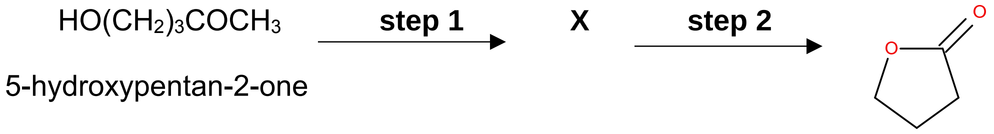
…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [2]

(b) Lactones are cyclic esters and are constituents in many natural products used in the flavours and fragrances industry. They also exhibit antioxidant, antimicrobial and anticancer activity.

Butano-4-lactone can be synthesised from 5-hydroxypentan-2-one via a 2-step route as shown.



5-hydroxypentan-2-one

butano-4-lactone

(i) State the reagents and conditions for **steps 1** and **2** and identify the intermediate **X** involved.

Step 1 : ……………………………………………………………………………………

……………………………………………………………………………………………

Step 2 : ……………………………………………………………………………………

……………………………………………………………………………………………

X is

[3]

(ii) Compound **Y** is a non-cyclic constitutional isomer of butano-4-lactone which exhibits enantiomerism. **Y** gives a reddish brown ppt in an alkaline solution of complexed Cu^{2+}(aq) and can also liberate carbon dioxide gas upon reaction with acidified $KMnO_4$.

Based on the above reactions, identify the functional groups in **Y** and suggest the structural formula of **Y**.

Functional groups in **Y :** ……………………………………………………………………

Structural formula of **Y :**

[2]

[Total: 9]

4 **(a)** Air comprises mainly nitrogen and oxygen, with trace quantities of other gases such as argon, carbon dioxide, and even ammonia.

(i) State two assumptions of the kinetic theory of gases.

………………………………………………………………………………………………

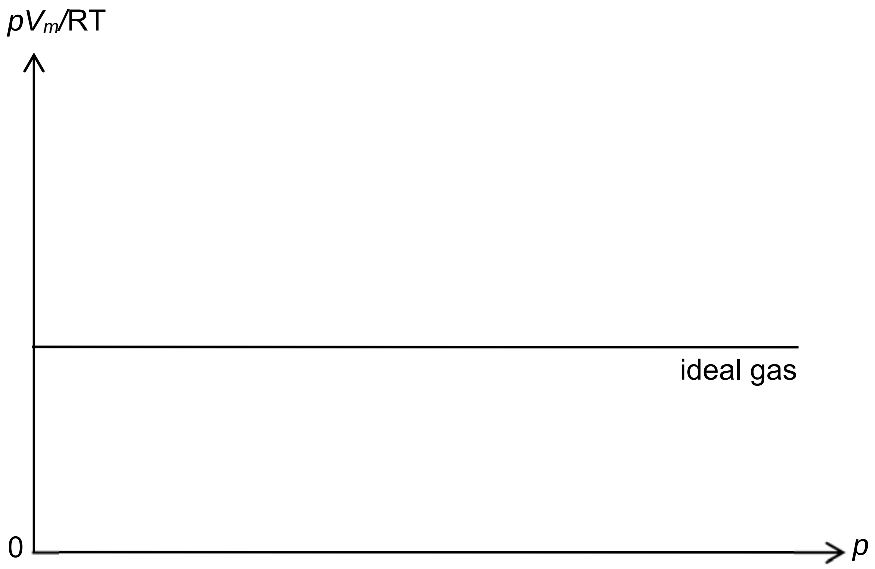
………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

(ii) A sketch of ***pV_m*/RT** against ***p*** for 1 mole of an ideal gas at 293 K is given below.



On the same axes, show how 1 mole each of carbon dioxide and ammonia will behave at 293 K. Label your graphs clearly.

[1]

(iii) Briefly explain your answer to **(a)(ii)**.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

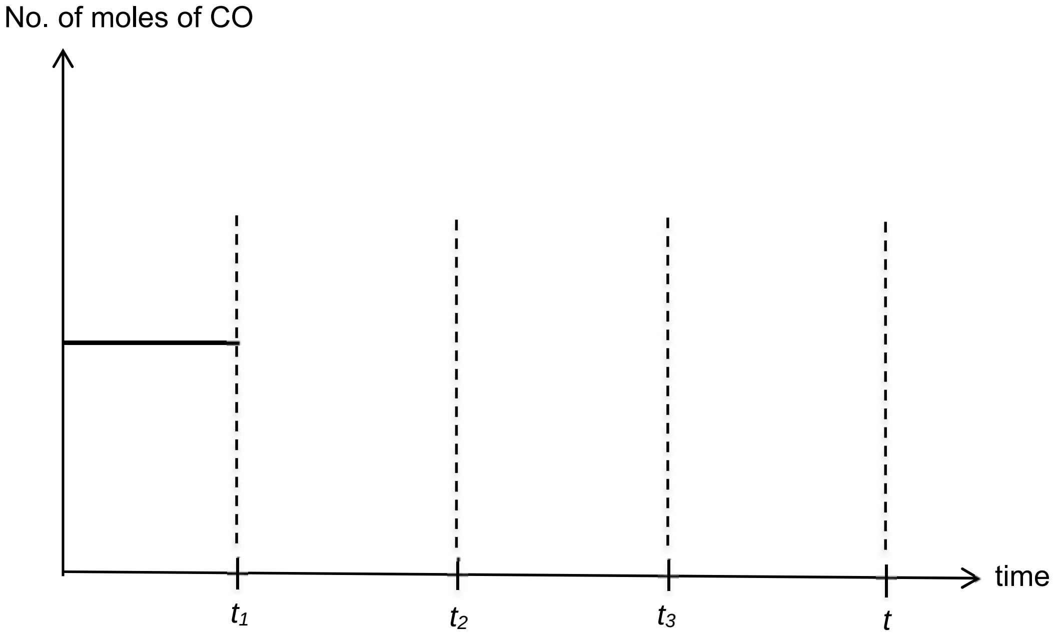
…………………………………………………………………………………………………… [2]

(b) Water gas is a synthesis gas that comprises carbon monoxide and hydrogen. The gas is made by passing steam over coke:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H > 0$$

The system was initially at equilibrium. At time ***t*₁**, the volume of the reaction vessel was suddenly reduced and the system allowed to reach equilibrium. Pressure was then increased by adding argon at constant volume at $\boldsymbol{t_2}$, followed by an increase in temperature at $\boldsymbol{t_3}$.

Sketch on the axes the graph that should be observed from time = t_1 to time = t when equilibrium is re-established once again.



[3]

[Total:8]

5 Chromium is a steely-grey lustrous metal. The name of this element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured.

(a) State and explain **one** difference in physical property between chromium and calcium.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [1]

(b) Chromium reacts with oxygen to form a series of oxides.

One of these oxides, chromium (IV) oxide, CrO_2, is often used to coat data tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give Cr^{3+}(aq) and $Cr_2O_7^{2-}$(aq). The resulting solution needed 20.0 cm^3 of 0.015 mol dm^{-3} Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

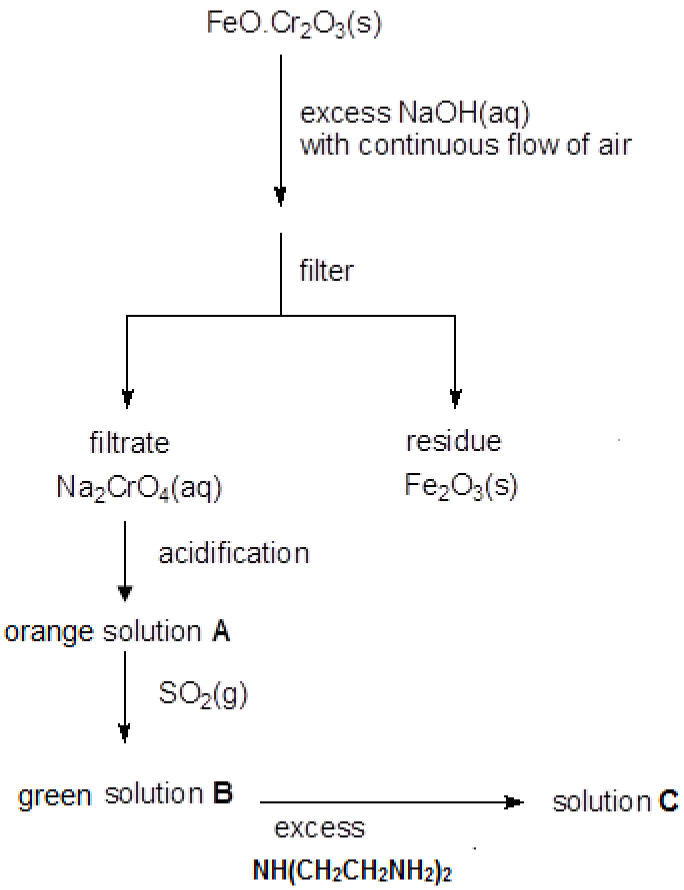
(i) Write an equation for the disproportionation of CrO_2 in acid solution showing how you arrived at the overall equation.

[2]

(ii) Use the data to calculate the mass of CrO_2 in the length of data tape.

[2]

(c) Chromite, $FeO.Cr_2O_3$, is the chief source of chromium. The reaction scheme below shows the conversion of chromite.

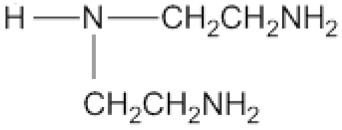


(i) Identify the chromium containing species present in solution **A** and in solution **B**.

Solution A: ....

Solution B : .... [2]

B reacts with excess tri-dentate ligand,diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, to form **C**.



diethylenetriamine

(ii) What type of reaction occurs when **B** is converted to **C**?

………………………………………………………………………………………… [1]

(iii) Letting the tri-dentate ligand be **L**, deduce the formula of the complex ion in **C**.

………………………………………………………………………………………… [1]

(iv) Explain why **B** is coloured.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………... [3]

(d) Ag_2CrO_4 is a brown-red crystalline solid and is a chemical precursor to modern photography.

The solubility product of Ag_2CrO_4 is 1.1×10^{-12}.

(i) Write an expression for the solubility product, K_{sp} of Ag_2CrO_4.

………………………………………………………………………………………….. [1]

(ii) Calculate the solubility of Ag_2CrO_4, in mol dm^{-3}.

[1]

[Total: 14]

6 This question is about the chemistry of Group 17 elements and their compounds.

(a) Although halogens and their compounds can be toxic, some are essential for the human body's functioning and are used in everyday products such as disinfectants and bleaching agents.

(i) State and explain how the oxidising power of the halogens vary down the group.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(ii) The halogens can react with each other to form interhalogen compounds such as IBr.

IBr reacts with water in which water is acting as the nucleophile. The equation for the reaction is as follows.

$$\text{IBr} + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}$$

State the type of reaction taking place and identify **X** and **Y**.

Type of reaction: ……………………………………………………………………

X: ………………………………… **Y**: ……………………………………………

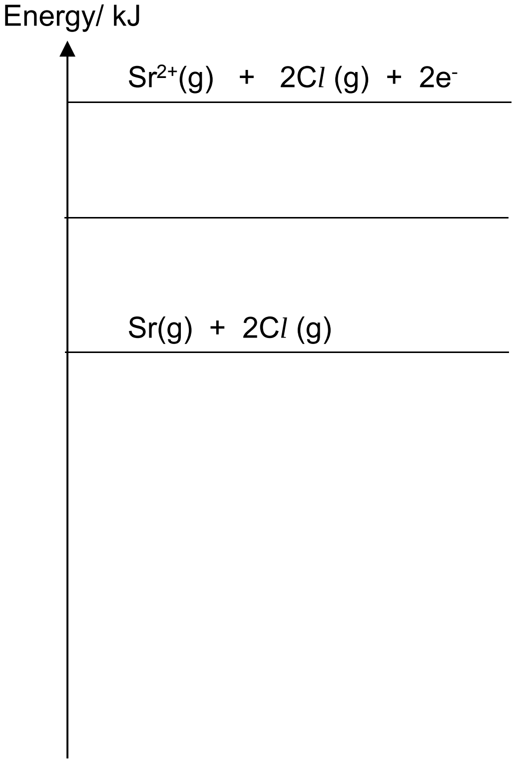
[2]

(b) **(i)** Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame which allows it to be used as a source of redness in fireworks.

On the incomplete outline below, construct the energy level diagram to calculate the lattice energy of $SrCl_2(s)$. Label all enthalpy changes involved and the chemical species at each stage.

Your diagram should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of formation of $SrCl_2(s)$	–828.9 kJ mol^{-1}
Standard enthalpy change of atomisation of Sr(s)	+164.4 kJ mol^{-1}
1st electron affinity of Cl(g)	–348.8 kJ mol^{-1}



[3]

(ii) Using your answer in **(b)(i)**, calculate the ΔH^{o}_{soln} of $SrCl_2(s)$, given the following data:

Standard enthalpy change of hydration of $Sr^{2+}(g)$	-1446 kJ mol^{-1}
Standard enthalpy change of hydration of $Cl^{-}(g)$	-378 kJ mol^{-1}

[1]

(iii) The standard enthalpy change of solution of $CaCl_2(s)$ is -87.7 kJmol^{-1}.

Explain the difference in the standard enthalpy change of solution of $SrCl_2(s)$ which you calculated in **(b)(ii)** and that of $CaCl_2(s)$.

[2]

[Total: 10]

TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME										
CIVICS GROUP			/							
CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9729/02

Paper 2 Structured Questions **23 August 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

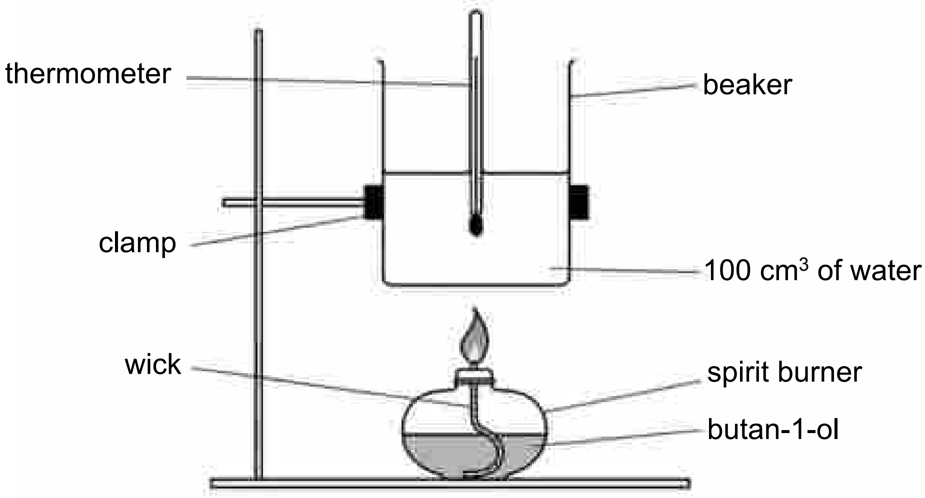
For Examiner's Use	
1	/ 21
2	/ 13
3	/ 9
4	/ 8
5	/ 14
6	/ 10
Total	/ 75

This document consists of **18** printed pages

SECTION A
Answer all questions in the spaces provided.

1 **(a)** For many compounds, the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy change of combustion can be used.

The enthalpy change of combustion of butan-1-ol can be found by a calorimetry experiment in which the heat given off during combustion is used to heat a known mass of water and the temperature change recorded.



temperature of water before heating = 25.0 °C

temperature of water after heating = 66.1 °C

mass of spirit burner and butan-1-ol before heating = 80.44 g

mass of spirit burner and butan-1-ol after heating = 79.70 g

(i) Explain the meaning of the term *standard enthalpy change of combustion*.

- **The *standard enthalpy change of combustion* of a substance, $\Delta H_c^\ominus$, is the heat energy evolved when <u>one mole of the substance</u> is <u>completely burnt in oxygen</u> at 298 K and 1 bar.**

[1]

(ii) The heat transfer from the spirit burner to water is known to be only 70% efficient. From the data provided above, determine the enthalpy change of combustion of butan-1-ol.

mass of butan-1-ol reacted = 80.44 – 79.70 = 0.74 g

No. of moles of butan-1-ol reacted = 0.74 / 74 = 0.0100 mol

amount of heat taken in by water = mcΔT

= 100 x 4.18 x (66.1 – 25.0)

- **= 17.2 kJ**

Heat provided by butan-1-ol = 100 x 17.2 / 70 = 24.6 kJ

enthalpy change of combustion of butan-1-ol = - 24.6/ 0.0100

- **= - 2460 kJ mol^{-1}**

[2]

(iii) The entropy change of combustion of butan-1-ol is -252 J K^{-1} mol^{-1}. Using your answer in **(a)(ii)**, calculate the Gibb's free energy for combustion of butan-1-ol at 298 K.

$\Delta G = \Delta H - T\Delta S$

$= -2460 - (298)(-252 \times 10^{-3})$

- **$= -2380$ kJ mol^{-1} (allow ecf from (a)(ii))**

[1]

(b) The table below gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

name	formula	molar mass/ g mol^{-1}	density/ g cm^{-3}	$\Delta H_c^\ominus$ (298K)/ kJ mol^{-1}	$\Delta H_f^\ominus$ (298K)/ kJ mol^{-1}
methanol	CH_3OH	32	0.793^a	-726.0	-239.1
ethanol	CH_3CH_2OH	46	0.789^a	-1367.3	
liquid hydrogen	H_2	2	0.0711^b	-285.8$^\#$	
octane	$CH_3(CH_2)_6CH_3$	114	0.703^a	-5470.2	-250.0

^{a} At 298K and 1 bar pressure

^{b} At 20K and 1 bar pressure

$^\#$ standard enthalpy change of combustion of hydrogen **gas**

(i) State the value of the standard enthalpy change of formation of hydrogen **gas**, H_2.

- **0 kJ mol^{-1} (by definition, elements in standard state are reference zero)**

[1]

(ii) Calculate the density of gaseous hydrogen at 298 K and 1 bar pressure. Give your answers in g cm^{-3}.

PV = nRT

PV = (m/Mr) RT

$$\rho = \frac{P \times Mr}{RT} = \frac{10^5 \times 2}{8.31 \times 298} = 80.8 \text{ g m}^{-3}$$

- **$= 8.08 \times 10^{-5}$ g cm^{-3}**

[1]

(iii) Write the chemical equation that represents the standard enthalpy change of combustion of ethanol, including the state symbols.

- **$CH_3CH_2OH\ (l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$**

[1]

(iv) The standard enthalpy change of combustion of carbon is -393.5 kJ mol^{-1}. Using this value and the standard enthalpy change of combustion data in the table, calculate the standard enthalpy change of formation of ethanol.

Show your working clearly in the form of an energy cycle diagram.

$$\begin{tikzcd}
2\,C(s) + 3\,H_2(g) + 7/2\,O_2(g) \arrow[rr, "\Delta H_f^{\ominus}"] \arrow[dr, swap, "2(-393.5) + 3(-285.8)"] & & CH_3CH_2OH(l) + 3\,O_2(g) \arrow[dl, "-1367.3"] \\
& 2\,CO_2(g) + 3\,H_2O(l) &
\end{tikzcd}$$

- **Energy cycle, balanced equations, state symbols**
  By Hess' law,
- **$\Delta H_f^{\ominus}$ -1367.3 = 2(-393.5) + 3(-285.8)**
- **$\Delta H_f^{\ominus}$ = -277.1 kJ mol^{-1}**

[3]

(v) An important property of a fuel, especially when the fuel has to be lifted such as in aviation, is the energy released on combustion per gram of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298K for methanol.

Enthalpy change of combustion per gram of fuel = -726/32 = -22.7 kJ g^{-1}
[1]

(vi) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion per cm^3 of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for octane.

Enthalpy change of combustion per cm^3 of fuel

= -5470.2/ (114/0.703) = -33.7 kJ cm$^{-3$} [1]

(vii) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with other fuels.

Enthalpy change of combustion value for hydrogen is for standard conditions, and so relates to gaseous hydrogen, not to liquid hydrogen.

Latent heat of vaporisation of hydrogen is not accounted for.

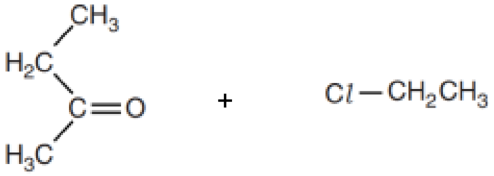
Allow comment about how the value of density of liquid hydrogen is unsuitable for the calculation of energy per unit volume for gaseous hydrogen. [1]

(c) Apart from alkanes and alcohols, alkenes are commonly used as fuel. Alkenes can be synthesised through the Wittig reaction, using halogenoalkane and carbonyl compound as the reactants in the presence of triphenyl phosphine.

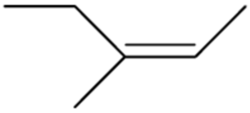
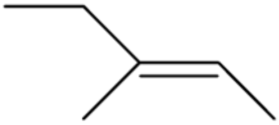
The equation below shows the synthesis of propene using the Wittig reaction.

triphenyl phosphine propene

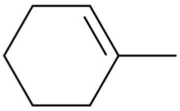
(i) Draw the structures of the two cis-trans isomers formed from the reaction of the following compounds.



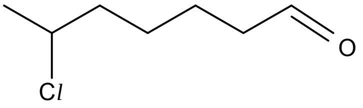
[2]

- 
- 

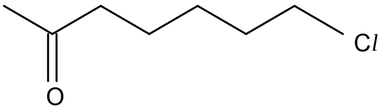
(ii) Draw the structural formula of the organic reactant used to generate 1-methylcyclohexene through the Wittig reaction.



1-methylcyclohexene

- 

OR



[1]

Alkenes react readily with interhalogen compound I*Cl* to give halogenalkane. I*Cl* reacts faster with alkenes than pure halogens and can be used to detemine the number of carbon-carbon double bonds present in organic compounds.

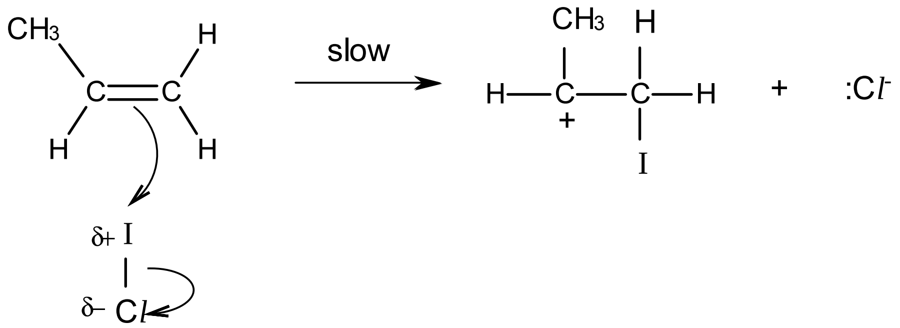
(iii) Suggest why I*Cl* reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

- **The I – C*l* bond has a permanent dipole. Since the iodine side (has a delta positive charge and) is more attracted to the electron-rich carbon-carbon double bond.**
  OR
  I – C*l* is a stronger electrophile because it has a permanent dipole and is more attracted to the C=C bond

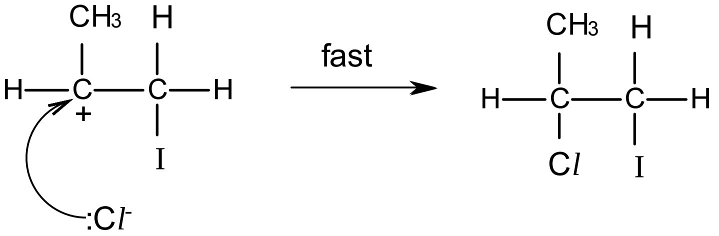
[1]

(iv) Name and describe the mechanism of reaction between propene and I*Cl* to give the major product. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

- **Electrophilic addition**
- **Step 1:**



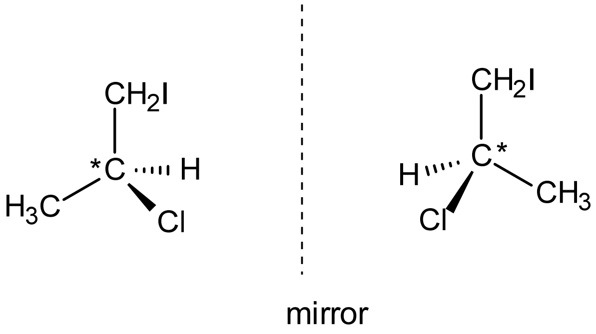
- **Step 2:**



deduct one mark if the minor product is formed through the reaction

[3]

(v) Draw the pair of enantiomers of the major product from the reaction between propene and IC*l*.



(award full credit if enantiomers of minor product shown)

[1]

[Total: 21]

2 **(a)** What do you understand by the *Brønsted–Lowry* theory of acids and bases?

Bronsted-Lowry acids are proton donors and bases are proton acceptors. [1]

(b) **I** $C_2H_5N + H_2O \rightleftharpoons C_2H_5NH^+ + OH^-$ $K_c = 1.7 \times 10^{-9}$ mol dm^{-3}

II $C_6H_5O^- + CH_3CO_2H \rightleftharpoons C_6H_5OH + CH_3CO_2^-$ $K_c = 1.3 \times 10^{6}$ mol dm^{-3}

For each of the above equilibrium **I** and **II**,

(i) identify the two acids and the two bases present;

Equilibrium **I**. Two acids are **H_2O and $C_2H_5NH^+$**

Two bases are **C_2H_5N and OH^-**

Equilibrium **II.** Two acids are **CH_3CO_2H and C_6H_5OH**

Two bases are **$C_6H_5O^-$ and $CH_3CO_2^-$** [2]

(ii) using the given information, suggest, with reasons, which ion or molecule is the stronger acid, and which is the stronger base.

Equilibrium **I**: stronger acid: **$C_2H_5NH^+$** stronger base : **OH^-**

Explanation for Equilibrium **I**: **Since $K_c < 1$, reaction proceeds to the greater extent in a direction in which a stronger acid ($C_2H_5NH^+$) and stronger base (OH^-) form a weaker acid and weaker base.**

Equilibrium II: stronger acid: **CH_3CO_2H** stronger base: **$C_6H_5O^-$**

Explanation for Equilibrium **II**: **Since $K_c > 1$, reaction proceeds to the greater extent in a direction in which a stronger acid (CH_3CO_2H) and stronger base ($C_6H_5O^-$) form a weaker acid and weaker base.**

Note: A stronger acid has a weaker conjugate base (the acid gives up its proton more readily because its conjugate base holds it less strongly) [3]

(c) A student adds an excess of aqueous ethanoic acid to solid calcium carbonate.

(i) Write a full equation for the reaction between ethanoic acid and solid calcium carbonate.

$2CH_3CO_2H + CaCO_3 \rightarrow (CH_3CO_2)_2Ca + CO_2 + H_2O$ [1]

(ii) Explain why a buffer solution has been formed.

Solution contains CH_3COOH and CH_3COO^- or solution contains a weak acid and its conjugate base. [1]

(iii) With the aid of an equation, explain how this buffer solution controls pH when an alkali is added.

On addition of an alkali, CH_3COOH will react with the added alkali resulting in no significant change in pH.

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ [1]

(d) A biochemist plans to make up a buffer solution that has a pH of 5.00.

The biochemist adds solid calcium ethanoate to 400 cm^3 of 0.200 mol dm^{-3} ethanoic acid. He assumes that the volume of the solution remains constant at 400 cm^3 on dissolving the calcium ethanoate.

K_a for ethanoic acid = 1.75 x 10^{-5} mol dm^{-3}
M_r of calcium ethanoate = 158.1

(i) Calculate the mass of calcium ethanoate that the biochemist needs to dissolve in the ethanoic acid to prepare this buffer solution.

$pK_a = -\log(1.75 \times 10^{-5}) = 4.57$

$pH = pKa + \log [CH_3COO^-]/[CH_3COOH]$

$\log [CH_3COO^-]/[CH_3COOH] = pH - pK_a = 5 - 4.57 = 0.243$

$[CH_3COO^-]/[CH_3COOH] = 10^{0.243} = 1.75$

• $[CH_3COO^-] = 1.75 \times 0.200 = 0.350$

Or from $K_a = [CH_3COO^-][H^+]/[CH_3COOH]$

• no of moles of CH_3COO^- in 400 cm^3 = 0.350 x (400/1000) = 0.140 mol

• mass of $(CH_3COO)_2Ca$ = (0.140 ÷ 2) x 158.1 = 11.07 or 11.1 g [3]

(ii) When the biochemist prepares the buffer solution, the volume of solution increases slightly. Suggest whether the pH of the buffer solution would be the same, greater than, or less than your calculated value in **(d)(i)**. Explain your reasoning.

pH is the same / constant because the ratio / proportion of [CH_3COO^-]/[CH_3COOH] is the same. [1]

[Total: 13]

3 (a) **J**, **K**, **L** and **M** are consecutive elements in the same period of the Periodic Table. The oxide of **J** is basic, oxide of **K** is amphoteric, and the oxides of **L** and **M** are acidic. The halides of **M** can be used to convert alcohols to halogenoalkanes in the absence of water.

(i) Identify the elements **J**, **K**, **L** and **M**.

J: **Mg** K: **Al** L: **Si** M: **P**

[1]

(ii) State and explain the variation of atomic radius from **J** to **M**.

- **Atomic radius decreases from L to M.**
  Nuclear charge increases as number of protons increases. Screening effect remains approximately constant as electrons are added to the same electronic shell. Hence the electrons are attracted more strongly by the nucleus.

[1]

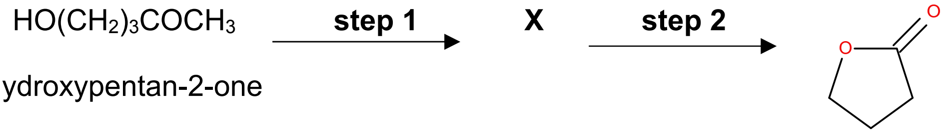
(iii) Compare the melting points of **L** and **M** and explain your answer.

- **L (Si) has a higher melting point than M (P) as Si as a giant molecular structure while P has a simple molecular structure.**
- **Melting L requires a lot of energy to break numerous strong covalent bonds compared to the weaker intermolecular instantaneous dipole - induced dipole forces of attraction between phosphorous molecules.**

[2]

(b) Lactones are cyclic esters and are constituents in many natural products used in the flavours and fragrances industry. They also exhibit antioxidant, antimicrobial and anticancer activity.

Butano-4-lactone can be synthesised from 5-hydroxypentan-2-one via a 2-step route as shown.



5-hydroxypentan-2-one

butano-4-lactone

(i) State the reagents and conditions for **steps 1** and **2** and identify the intermediate **X** involved.

- **step 1: alkaline aqueous iodine, heat, followed by acidification with dilute sulfuric acid**
- **step 2: concentrated sulfuric acid, heat**
- **X: $HO(CH_2)_3CO_2H$**

(Accept if student gives X: $HO(CH_2)_3CO_2^-$, then step 2 will be PCl_5, followed by heating)

[3]

(ii) Compound **Y** is a non-cyclic constitutional isomer of butano-4-lactone which exhibits enantiomerism. **Y** gives a reddish brown ppt in an alkaline solution of complexed Cu^{2+}(aq) and can also liberate carbon dioxide gas upon reaction with acidified $KMnO_4$.

Based on the above reactions, identify the functional groups in **Y** and suggest the structural formula of **Y**.

- **Aldehyde and terminal alkene**
- **CH_2=CHCH(OH)CHO**

[2]

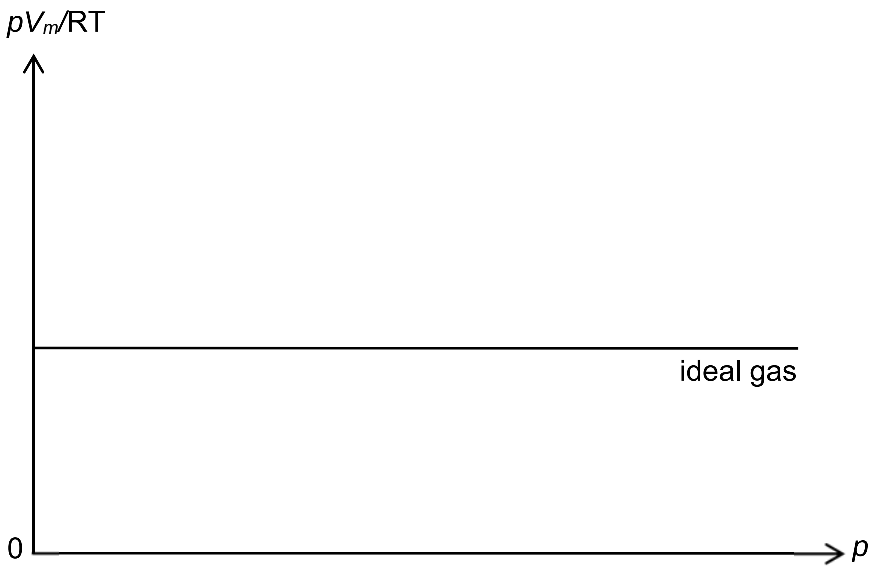
[Total: 9]

4 **(a)** Air comprises mainly nitrogen and oxygen, with trace quantities of other gases such as argon, carbon dioxide, and even ammonia.

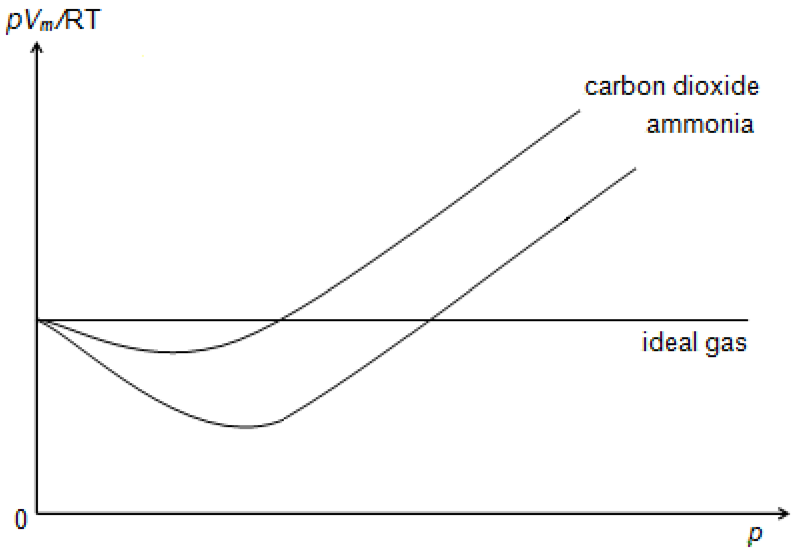
(i) State two assumptions of the kinetic theory of gases.

- **The gas consists of particles of <u>negligible volume</u> compared to the volume of the container it occupies.**
- **The gas particles exert <u>no attractive forces</u> on each other.** [2]

(ii) A sketch of ***pV$_m$*/RT** against ***p*** for 1 mole of an ideal gas at 293 K is given below.



On the same axes, show how 1 mole each of carbon dioxide and ammonia will behave at 293 K. Label your graphs clearly.



[Note: graphs don't cut/intercept each other]

[1]

(iii) Briefly explain your answer to **(a)(ii)**.

- **NH_3(g) experiences stronger hydrogen bonding between molecules compared to the weaker instantaneous dipole–induced dipole interactions between CO_2 molecules, hence it shows a greater negative deviation than CO_2 at low pressure.**

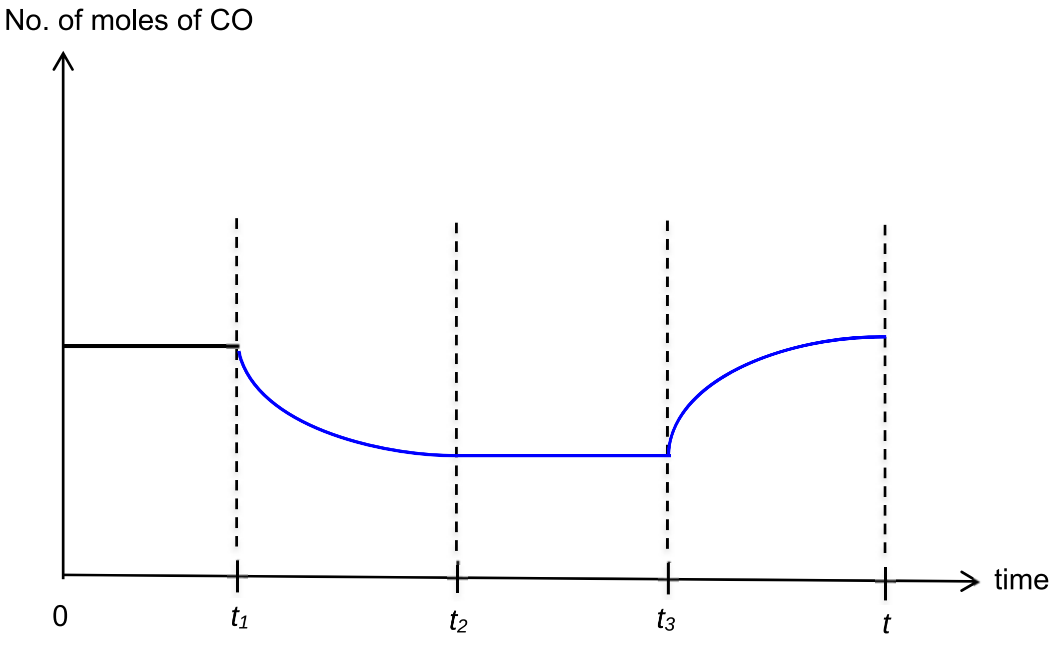
- **As CO_2 has a larger molecular size than NH_3, the volume taken up by CO_2 gas molecules is greater. Hence it shows a greater positive deviation than NH_3.** [2]

(b) Water gas is a synthesis gas that comprises carbon monoxide and hydrogen. The gas is made by passing steam over coke:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H > 0$$

The system was initially at equilibrium. At time ***t_1***, the volume of the reaction vessel was suddenly reduced and the system allowed to reach equilibrium. Pressure was then increased by adding argon at constant volume at ***t_2***, followed by an increase in temperature at ***t_3***.

Sketch on the axes the graph that should be observed from time = t_1 to time = t when equilibrium is re-established once again.



[3]

[Total:8]

5 Chromium is a steely-grey lustrous metal. The name of this element is derived from the Greek word "chrōma" meaning colour, because many of its compounds are intensely coloured.

(a) State and explain **one** difference in physical property between chromium and calcium. [1]

Cr has a <u>higher melting/boiling point</u> than Ca.

Cr has stronger metallic bonds as both the 3d and 4s electrons can be used in metallic bonding, hence more energy is required to overcome the stronger metallic bonds. Ca uses only 4s electron for metallic bonding.

Cr has a <u>greater density</u> than Ca.

Cr has a greater atomic mass but its atomic radius is smaller. Hence atomic volume is smaller. Since density = mass/volume, density of Cr is greater than Ca.

(b) Chromium reacts with oxygen to form a series of oxides.

One of these oxides, chromium (IV) oxide, CrO_2, is often used to coat data tapes, due to its high conductivity and ferromagnetic properties, which provide a good high audio-frequency response.

When the oxide from a length of tape was dissolved in dilute sulfuric acid, it disproportionates to give Cr^{3+}(aq) and $Cr_2O_7^{2-}$(aq). The resulting solution needed 20.0 cm^3 of 0.015 mol dm^{-3} Fe^{2+} solution to reduce the $Cr_2O_7^{2-}$ completely to Cr^{3+}.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(i) Write an equation for the disproportionation of CrO_2 in acid solution showing how you arrived at the overall equation.

$$CrO_2 + 4H^+ + e^- \rightarrow Cr^{3+} + 2H_2O \qquad \times 4$$

$$2CrO_2 + 3H_2O \rightarrow Cr_2O_7^{2-} + 6H^+ + 4e^- \qquad \times 1$$

$$\overline{6CrO_2 + 10H^+ \rightarrow 4Cr^{3+} + Cr_2O_7^{2-} + 5H_2O}$$

[2]

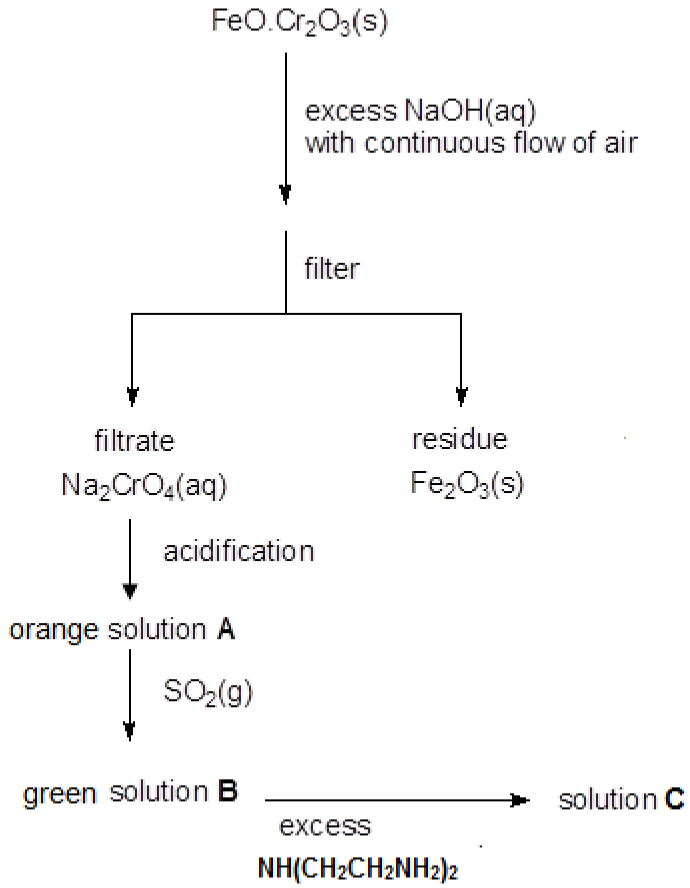
(ii) Use the data to calculate the mass of CrO_2 in the length of data tape.

$6CrO_2 \equiv Cr_2O_7^{2-} \equiv 6Fe^{2+}$

Amount of Fe^{2+} used = 0.015 x 0.0200 = 3.00 x 10^{-4} mol

- **Hence amount of CrO_2 = 3.00 x 10^{-4} mol**
- **Mass of CrO_2 = 3.00 x 10^{-4} x 84.0 = 0.0252 g** [2]

(c) Chromite, $FeO.Cr_2O_3$, is the chief source of chromium. The reaction scheme below shows the conversion of chromite.

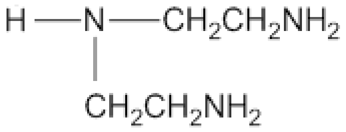


(i) Identify the chromium containing species present in solution **A** and in solution **B**.

Solution **A**: **$Cr_2O_7^{2-}$**

Solution **B**: **$[Cr(H_2O)_6]^{3+}$** [2]

B reacts with excess tri-dentate ligand,diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, to form **C**.



diethylenetriamine

(ii) What type of reaction occurs when **B** is converted to **C**?

- **Ligand substitution** [1]

(iii) Letting the tri-dentate ligand be **L**, deduce the formula of the complex ion in **C**.

- **$[CrL_2]^{3+}$** [1]

(iv) Explain why **B** is coloured.

- **The Cr^{3+} ion has partially filled d orbitals.**
- **The water ligands cause a splitting of the energy of d orbitals into 2 groups with an energy gap, ΔE, between them. The energy gap, ΔE, between the non-degenerate orbitals corresponds to the wavelength of light in the visible region of the electromagnetic spectrum.**
- **When a d-electron from lower energy group is promoted to the higher energy group, radiation in the visible region of the electromagnetic spectrum corresponding to ΔE is absorbed. Light energy (green) that is not absorbed will be seen as the colour of the complex.** [3]

(d) Ag_2CrO_4 is a brown-red crystalline solid and is a chemical precursor

to modern photography.

The solubility product of Ag_2CrO_4 is 1.1×10^{-12}.

(i) Write an expression for the solubility product, K_{sp} of Ag_2CrO_4.

- **$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$** [1]

(ii) Calculate the solubility of Ag_2CrO_4, in mol dm^{-3}.

Let the solubility of Ag_2CrO_4 be x mol dm^{-3}

$$Ag_2CrO_4(s) \rightleftharpoons \underset{2x}{2Ag^+(aq)} + \underset{x}{CrO_4^{2-}(aq)}$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$1.1 \times 10^{-12} = 4x^3$$

$$x = (1.1 \times 10^{-12}/4)^{1/3}$$

$$= 6.50 \times 10^{-5}$$

- **The solubility of Ag_2CrO_4 is 6.50×10^{-5} mol dm^{-3} .** [1]

[Total: 14]

6 This question is about the chemistry of Group 17 elements and their compounds.

(a) Although halogens and their compounds can be toxic, some are essential for the human body's functioning and are used in everyday products such as disinfectants and bleaching agents.

(i) State and explain how the oxidising power of the halogens vary down the group.

- **oxidising power of the halogens decreases.**
- **Down the group, $E^{\ominus}_{X/X^-}$ becomes less positive, there is lower tendency for X_2 to be reduced to X^- (Or electron affinity of the halogen decreases), thus oxidising power of halogens decreases from Cl_2 to I_2.**

[2]

(ii) The halogens can react with each other to form interhalogen compounds such as IBr.

IBr eacts with water in which water is acting as the nucleophile. The equation for the reaction is as follows.

$$\mathrm{IBr + H_2O \rightarrow H\mathbf{X} + HO\mathbf{Y}}$$

State the type of reaction taking place and identify **X** and **Y**.

- **hydrolysis**
- **X is bromine while Y is iodine.**

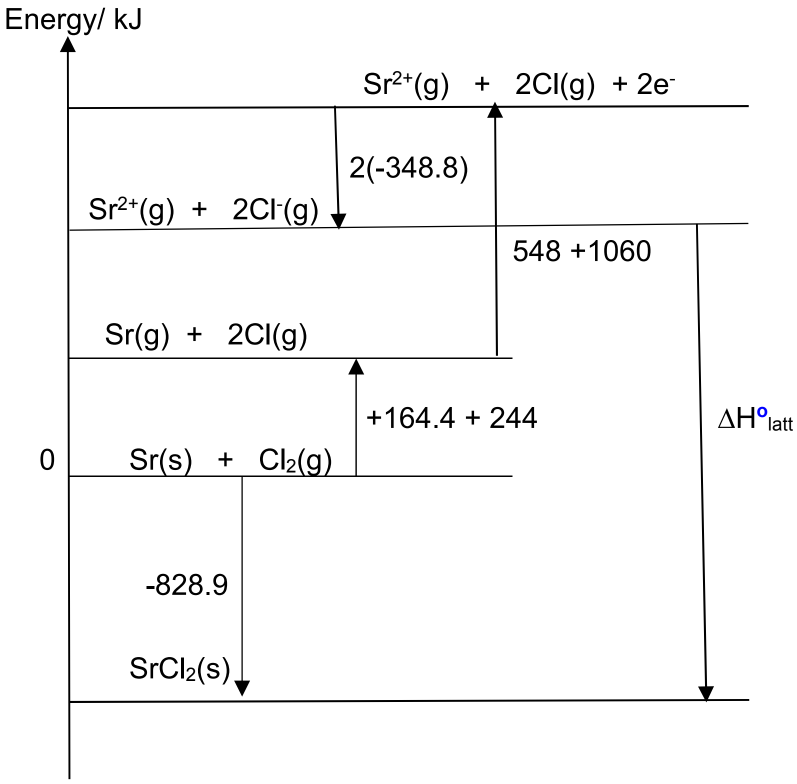
[2]

(b) **(i)** Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame which allows it to be used as a source of redness in fireworks.

On the incomplete outline below, construct the energy level diagram to calculate the lattice energy of $SrCl_2$(s). Label all enthalpy changes involved and the chemical species at each stage.

Your diagram should include relevant data from the *Data Booklet* together with the following data.

Standard enthalpy change of formation of $SrCl_2$(s)	–828.9 kJ mol^{-1}
Standard enthalpy change of atomisation of Sr(s)	+164.4 kJ mol^{-1}
1st electron affinity of Cl(g)	–348.8 kJ mol^{-1}



Using Hess' Law,

$-828.9 = 164.4 + 244 + 548 + 1060 + 2(-348.8) + \Delta H^o_{latt}$

- **ΔH^o_{latt} = -2148 kJ mol^{-1}**

[Energy level diagram:

1m for enthalpy change values and zero for elements

1m for correct relative energy levels and state symbols (not >2 missing]

[3]

(ii) Using your answer in **(b)(i)**, calculate the ΔH^o_{soln} of $SrCl_2(s)$, given the following data:

Standard enthalpy change of hydration of $Sr^{2+}(g)$	–1446 kJ mol^{-1}
Standard enthalpy change of hydration of $Cl^-(g)$	–378 kJ mol^{-1}

- **ΔH^o_{soln} = 2148 + (-1446) + 2(-378) = -54 kJ mol^{-1}**

[1]

(iii) The standard enthalpy change of solution of $CaCl_2(s)$ is -87.7 kJmol^{-1}.

Explain the difference in the standard enthalpy change of solution of $SrCl_2(s)$ which you calculated in **(b)(ii)** and that of $CaCl_2(s)$.

ΔH_{sol} = -(-Lattice Energies) + (-ΔH_{hyd}) = |L.E.| - | ΔH_{hyd} |

|L.E.| $\propto \frac{|q^+q^-|}{r^+ + r^-}$

| ΔH_{hyd} | $\propto \frac{|q|}{r}$

- **Cationic radius of Sr^{2+} ion is larger than Ca^{2+}, therefore the decrease in | ΔH_{hyd} | of Sr^{2+} is larger than the decrease in |L.E.|.**
- **ΔH_{sol} is expected to be more endothermic for $SrCl_2(s)$.**

[2]

[Total: 10]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**
Paper 3 Free Response **14th September 2018**
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** There are several stages in the industrial production of methanol from methane.

The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. Figures 1.1 and 1.2 show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

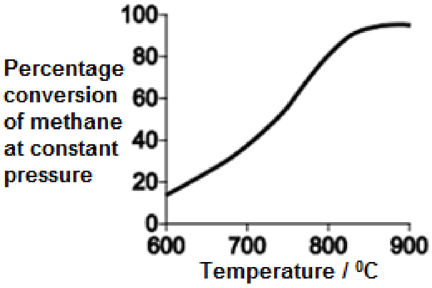


Figure 1.1

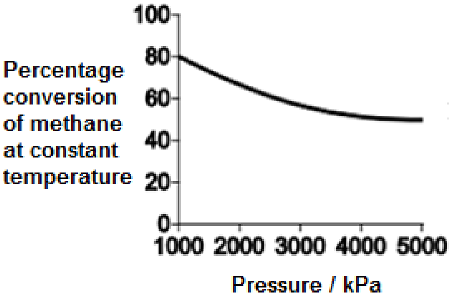


Figure 1.2

(i) Use the information from the graphs above to deduce the sign of the

- enthalpy change, ΔH and
- entropy change, ΔS

for the first stage industrial conversion reaction of methane and steam into the gaseous products. [2]

(ii) The optimum temperature for the industrial conversion of methane and steam into the gaseous products is between 780-880°C.

Explain why this is so. [2]

(b) The equation shows the final stage in the production of methanol.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

3.12 moles of carbon monoxide and 5.23 moles of hydrogen were placed in a sealed container. An equilibrium was established at 600 K and the total amount of gaseous molecules was found to be 7.63 moles. The total pressure was 630 kPa.

Calculate the equilibrium constant, K_p, for this reaction at 600 K and state its units. [3]

(c) Carbon monoxide also reacts with steam.

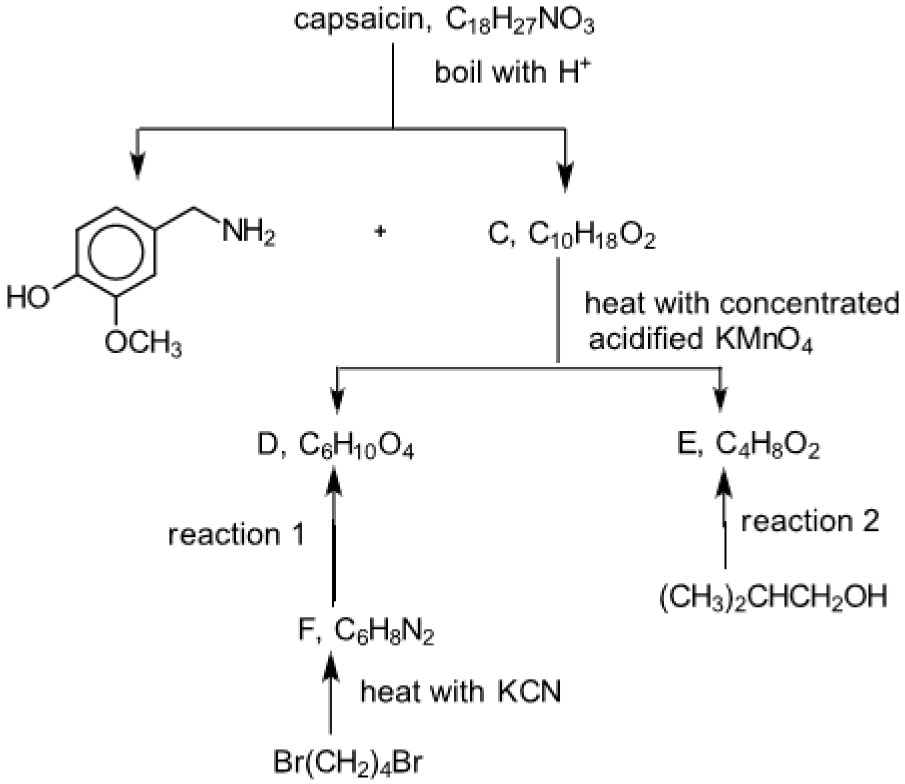
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

At 1100 ^{0}C, $K_c = 1.00$

In an experiment, 1 mole of carbon monoxide was mixed with 1 mole of steam, 2 moles of carbon dioxide and 2 moles of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium. [2]

(d) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.

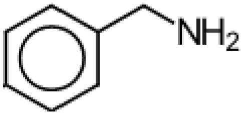


Capsaicin reacts with sodium metal and compounds C, D and E react with Na_2CO_3(aq).

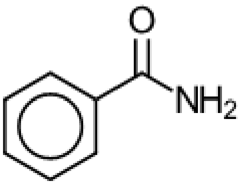
(i) Suggest the reagents and conditions for reactions 1 and 2. [2]

(ii) Draw the structural formulae for the compounds C, D, E, F and capsaicin in the above reaction scheme. [5]

(e)

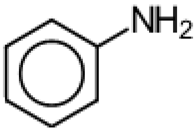


X



Y

and



Z

X, **Y** and **Z** are nitrogen containing compounds. State and explain the relative basicities of these 3 compounds. [3]

[Total:19]

2 This question is about nitrogen compounds and their roles in organic synthesis.

Azide is the anion with the formula N_3^-. Azide is used as a chemical preservative in hospitals and laboratories.

The azide ion in sodium azide (NaN_3) can be oxidised by iodine to form nitrogen gas. To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.

The amount of unreacted iodine is then titrated with standard sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm^3 of 0.050 mol dm^{-3} of aqueous iodine. The excess iodine was found to require 23.10 cm^3 of 0.040 mol dm^{-3} aqueous sodium thiosulfate for reaction.

(a) **(i)** Write the equation for the azide ion reacting with iodine. [1]

(ii) Calculate the percentage purity of sodium azide in the sample. [3]

(b) A student drew 4 structures **A** to **D** of the linear azide ion in Fig 2.1. His teacher commented one of the structures drawn was incorrect. Determine which is the **incorrect** structure, explaining your answer. [1]

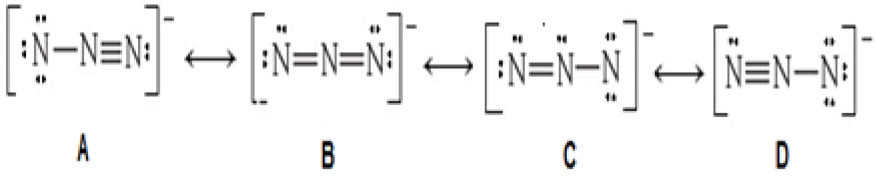


Fig. 2.1

(c) Azides, being very versatile, can play important roles in organic reactions. An azide ion is called a pseudohalide because it has some properties which are similar to those of chloride ions. As such organic azides, RN_3 have similar chemical properties as chloroalkanes.

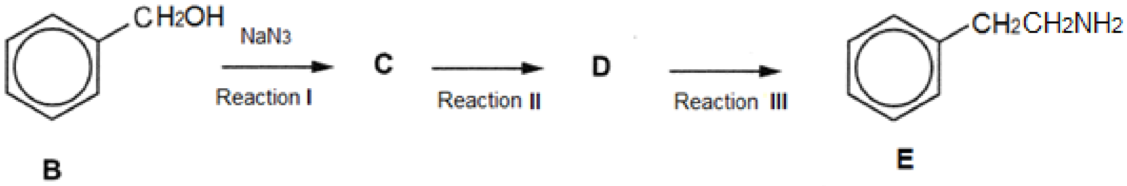
One organic reaction scheme, involving sodium azide to form amines is shown in Fig 2.2.

$$ROH \xrightarrow[\text{Reaction I}]{NaN_3} RN_3 \xrightarrow[\text{Reaction II}]{} RCN \xrightarrow[\text{Reaction III}]{} RCH_2NH_2$$

Fig. 2.2

(i) Identify the role of azide ion in Reaction **I**. [1]

The 3-stage synthesis of compound **E** from compound **B**, makes use of the reaction scheme shown in Fig. 2.2.



(ii) Suggest structures for intermediates **C** and **D**, and reagents and conditions for reactions **II** and **III**. [3]

(iii) State the *type of reaction* that occur during reaction **III**. [1]

A reaction scheme involving compound **B** is shown in Fig.2.3.

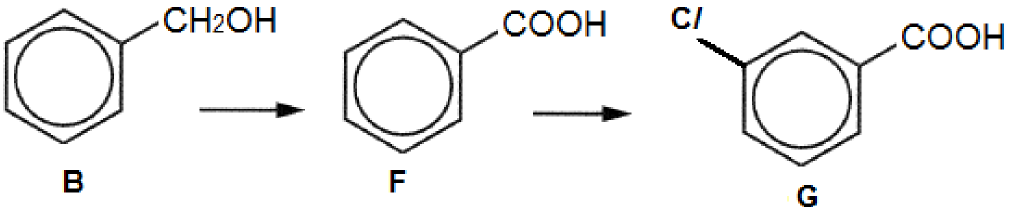


Fig. 2.3

(iv) Suggest the reagents and conditions for the conversion of **B** to **F** and for **F** to **G**. [2]

(v) Describe and explain how the acidity of **G** would compare to that of **F**. [2]

(d) Hydrogen azide, HN_3 has a boiling point of 37°C and ammonia, NH_3 has a boiling point of -33°C.

(i) Suggest a reason for the higher boiling point of hydrogen azide compared to ammonia. [1]

(ii) Explain why hydrogen azide is highly soluble in water. [1]

(e) Nitride is a compound of nitrogen where nitrogen has a oxidation state of -3. Nitrides are a large class of compounds with a wide range of properties and applications.

(i) State the electronic configuration of the nitride ion, N^{3-}. [1]

(ii) When a beam of nitride ions, N^{3-} was passed through an electric field, it deflected 63° towards the positive plate. Under identical conditions, a beam of azide ions, N_3^- was passed through the electric field. Determine the angle of deflection of the azide ion beam. [1]

[Total: 18]

3 Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than ethanoic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a bidentate ligand for metal cations.

Oxalic acid dissociates in water according to the following equations.

I HOOC-COOH + H_2O $\rightleftharpoons$ HOOC-COO$^-$ + H_3O^+ K_{a1}= 5.6 x 10^{-2} mol dm^{-3}

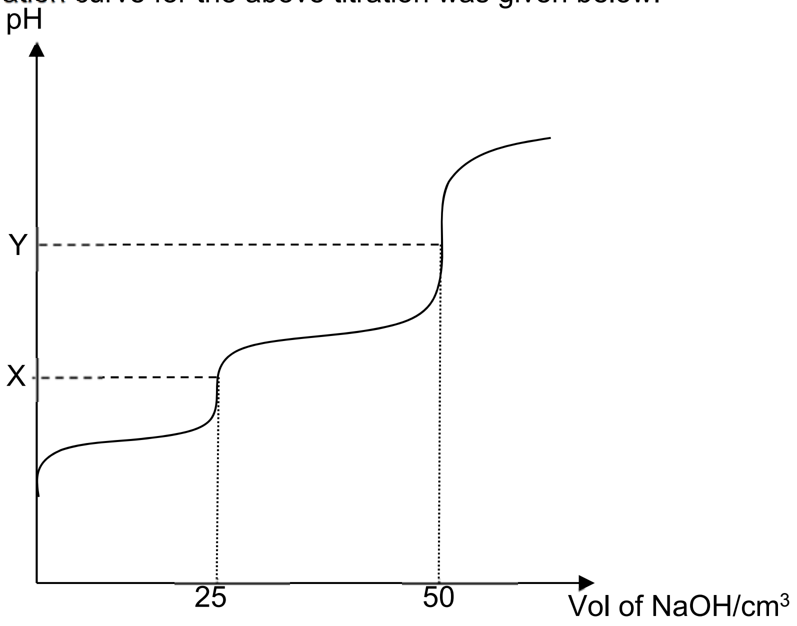
II HOOC-COO$^-$ + H_2O $\rightleftharpoons$ $^-$OOC-COO$^-$ + H_3O^+ K_{a2} = 5.4 x 10^{-5} mol dm^{-3}

(a) **(i)** Explain why the value of K_{a1} is larger than K_{a2}. [1]

(ii) Write expressions for acid dissociation constants for equation **I** and **II** above. [1]

(b) A 25 cm^3 sample of oxalic acid of concentration 0.100 mol dm^{-3} was titrated with sodium hydroxide of concentration 0.100 mol dm^{-3}.

The titration curve for the above titration was given below.



(i) State the major organic species present at points **X** and **Y.** In your answer, include the equation for the reaction that occurred to produce **each** of these two species. [2]

(ii) It has been proven that the $[H_3O^+]$ at the first equivalent point, **X**, is given by the expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Use the given expression to determine the pH value at point **X**. [1]

(iii) Calculate the pH value at the second equivalent point, **Y**, given that the $[OH^-]$ can be assumed to be entirely due to the hydrolysis of the organic species at Y. [2]

(c) Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.
Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?
Numerical value of solubility product of calcium oxalate, CaC_2O_4 = 2.7×10^{-9}. [2]

(d) Oxalate ions, $C_2O_4^{2-}$, is also able to combine chemically with certain metals commonly found in the human body. It is able to bond chemically, behaving as a *bidentate* ligand, to transition elements, such as iron to form a complex ion.

$$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O \qquad K_{stab} = 5.00 \times 10^4$$

(i) What do you understand by the term *bidentate* ligand. [1]

(ii) Suggest a reason why the stability constant, K_{stab} of the above is greater than 1. [1]

(iii) Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$.Hence suggest the shape for this complex. [2]

(e) Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of Br_2(aq) to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4-dinitrophenylhydrazine. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$.

Suggest structures for **A, B, C, D** and **E** and explain the reactions described. [10]

[Total: 23]

Turn over for Section B

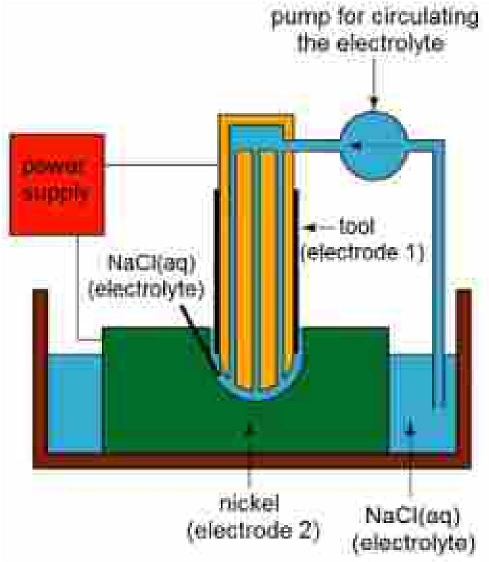
Section B

Answer **one** question from this section.

4 **(a)** Explain, with reference to relevant E^{θ} values, the industrial process of the electrolytic purification of a copper alloy consisting of nickel and silver impurities. [4]

(b) Electrochemical machining is a method used to cut small holes or cavities in metals such as nickel.

The diagram below illustrates the process. The tool (electrode 1) and nickel (electrode 2) are connected to a power supply. The electrodes are in contact with an electrolyte, NaCl(aq), which is being circulated using a pump. Some nickel is then removed by an electrochemical process when the power supply is switched on.



(i) State the polarity of each electrode. Write equation for the reaction occurring at each electrode. [2]

(ii) As the process takes place, a green solid is observed in the electrolyte. Suggest the identity of the solid. [1]

(c) Magnesium is a Group 2 element that occurs naturally only in combination with other elements. It is the third most abundant element present in seawater, after sodium and chlorine.

(i) Describe and explain, using E^{e} values, the relative reactivity of Group 2 elements as reducing agents. [2]

In China, magnesium is produced by electrolysis of molten magnesium chloride. Anhydrous magnesium chloride is fed continuously into electrolytic cells which are hot enough to melt it. Magnesium is produced at the cathode.

(ii) Determine the mass of magnesium produced when a current of 40.0 A was passed through one such electrolytic cell for 10 hours. [2]

The magnesium chloride raw material needed for the electrolysis is obtained from seawater or magnesium chloride-rich brine.

If seawater is used, it is first treated to produce magnesium hydroxide which is then converted to the oxide. The oxide is then heated with carbon in a stream of chlorine at a high temperature as shown in the equation below.

$$2MgO + C + 2Cl_2 \rightarrow 2MgCl_2 + CO_2$$

(iii) Identify the oxidising and reducing agents in the above reaction. [1]

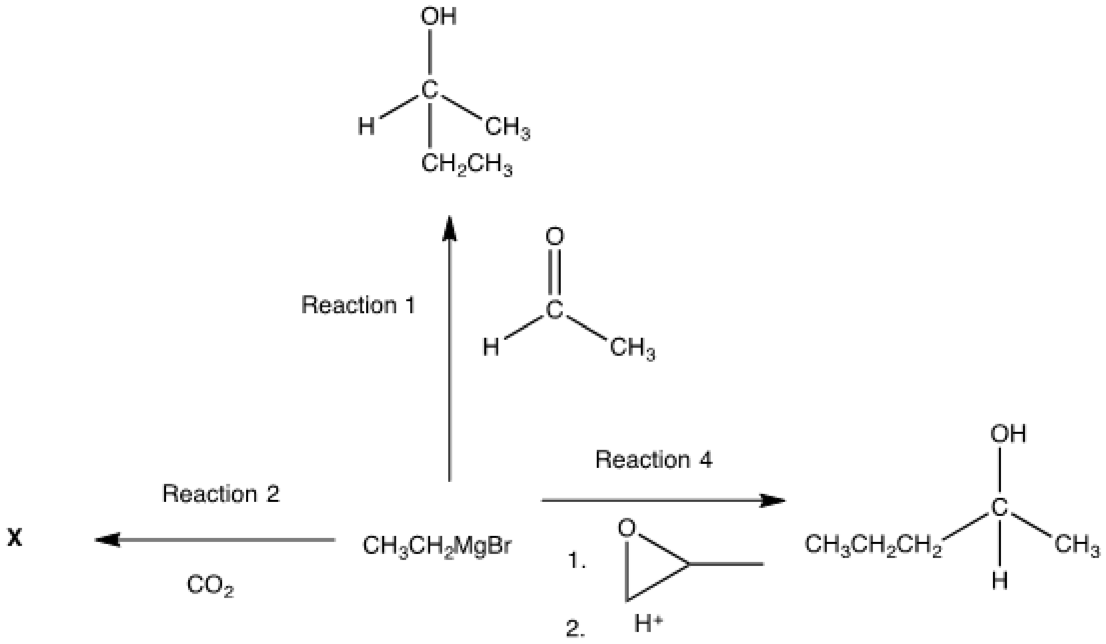
On the other hand, if magnesium chloride-rich brine is used, the solution is treated to remove impurities and concentrated by removing water. Dehydration has to be carried out in the presence of hydrogen chloride gas to avoid the reaction of magnesium chloride with water.

(iv) Describe and explain the reaction of magnesium chloride with water. Write equation where appropriate. [2]

Grignard reagents can be formed from the reaction of magnesium metal with an alkyl or aryl bromide as shown below.

R-Br + Mg → RMgBr where R represent an alkyl or aryl group

The following reaction scheme shows some reactions involving the Grignard reagent, CH_3CH_2MgBr. The Grignard reagent produces the carbanion, $^{-}$**:**CH_2CH_3, as the reacting species.



(v) Suggest the type(s) of reaction that occur in reaction 1 and hence explain why the product mixture obtained is optically inactive. [3]

(vi) Reaction 2 occurs in a similar manner to reaction 1. Suggest the structural formula of compound **X**. [1]

(vii) Reaction 3 occurs in two stages.

Stage 1 is a bimolecular nucleophilic substitution reaction.
Stage 2 is a protonation.

Draw the mechanism for stage 1. [2]

[Total: 20]

5 This question is about the chemistry of iron-containing compounds.

(a) Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth’s entire core. It exists in a wide range of oxidation states and undergo redox reactions readily.

(i) By means of a fully labelled diagram, describe how the standard electrode potential of the Fe^{3+}/Fe^{2+} system can be measured. Indicate the direction of electron flow. [3]

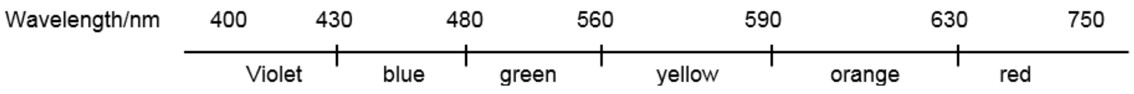
In Experiment 1, when aqueous iron(III) sulfate is boiled with an excess of potassium cyanide, an orange-red solution is obtained. The solution remains orange-red on addition of aqueous potassium iodide.

In Experiment 2, when aqueous iron(III) sulfate is added to aqueous potassium iodide, a brown solution is obtained.

(ii) State the type of reaction that occurred in each experiment. Write a balanced equation for any reaction that occurred. [3]

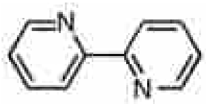
(iii) With reference to relevant $E^{\ominus}$ values, explain the observation in Experiment 1 upon addition of aqueous potassium iodide. [1]

The colour spectrum of the visible region of the electromagnetic spectrum is as shown:



Iron(II) ions form an intense red complex with 2,2'-bipyridine (bipy) according to the following equation:

$$3\text{bipy} + Fe^{2+} \rightleftharpoons [Fe(\text{bipy})_3]^{2+}$$



2,2'-bipyridine

The presence of ligands in complexes causes a splitting of the energy of d orbitals into two groups with an energy gap, ΔE, between them.

(iv) Given that aqueous iron(II) ion is green in colour, state and explain which ligand, water or 2,2'-bipyridine, results in a larger ΔE. [2]

(v) Draw a labelled diagram of one of the d orbitals at the **higher** energy level in $[Fe(\text{bipy})_3]^{2+}$. [1]

(b) In the laboratory, iron(II) ions function as a catalyst for the reaction of iodide with hydrogen peroxide.

In an experiment to investigate the kinetics of the reaction, hydrogen peroxide is added to a solution of potassium iodide in the absence of the iron(II) catalyst at 25 °C, and the iodide ions are oxidised according to the equation:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

The following data was obtained.

Expt	**Initial $[I^-]$ / mol dm^{-3}**	**Initial $[H_2O_2]$ / mol dm^{-3}**	**Initial $[H^+]$ / mol dm^{-3}**	**Initial rate of reaction / mol dm^{-3} s^{-1}**
1	0.01	0.01	0.0005	1.15×10^{-6}
2	0.01	0.02	0.0005	2.30×10^{-6}
3	0.02	0.01	0.0005	2.30×10^{-6}
4	0.01	0.01	0.001	1.15×10^{-6}

(i) Use the data above to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction. [3]

(ii) Calculate a value for the rate constant. Include units in your answer. [1]

(iii) Explain, with the aid of a suitable diagram, why the rate of decomposition of hydrogen peroxide is expected to proceed faster at 35 °C. [2]

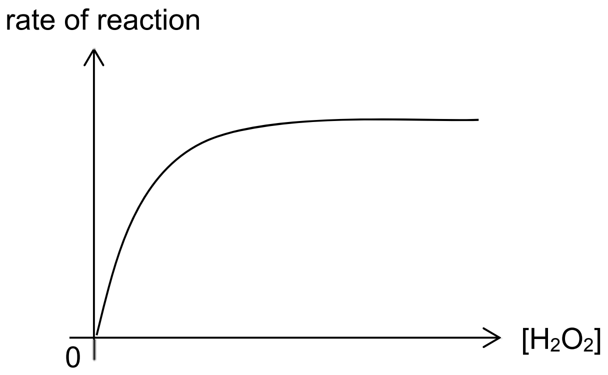
(c) Some protein-built enzymes form complexes with the metal ions at their active site. An example is catalase, which is an enzyme in the liver that breaks down harmful hydrogen peroxide into oxygen and water. It contains four iron-containing heme groups that allow the enzyme to react with the hydrogen peroxide.

The decomposition of hydrogen peroxide solution to form water and oxygen gas is as shown:

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$

(i) What do you understand by the term *enzyme*? [1]

(ii) A series of experiments were carried out to study the effect of hydrogen peroxide concentration on the rate of reaction, by using different concentrations of hydrogen peroxide at 25 °C. The following graph was obtained.



Account for the shape of the graph. [3]

[Total: 20]

TEMASEK
JUNIOR COLLEGE

CHEMISTRY **9729/03**

Paper 3 Free Response **14th September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** There are several stages in the industrial production of methanol from methane.

The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. Figures 1.1 and 1.2 show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

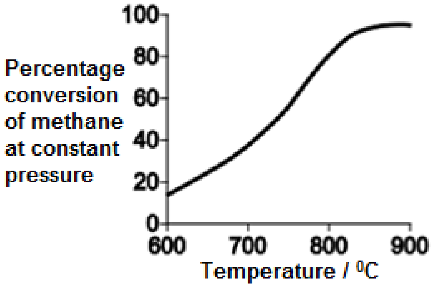


Figure 1.1

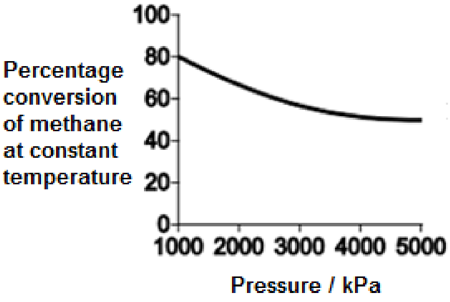


Figure 1.2

(i) Use the information from the graphs above to deduce the sign of the

- enthalpy change, ΔH and
- entropy change, ΔS

for the first stage industrial conversion reaction of methane and steam into the gaseous products. [2]

• the enthalpy change, ΔH

As temperature increases from 600 ^{0}C to 880 ^{0}C, % conversion of methane increases. This indicates that the forward reaction is favoured as it absorbs energy. Hence, forward reaction is endothermic, ΔH is positive.

• entropy change, ΔS

As pressure increases from 1000 kPa to 5000 kPa, % conversion of methane decreases. Forward reaction is not favoured and this indicates that the number of moles of gaseous products particles is more than the gaseous reactants particles. Hence, ΔS for the forward reaction is positive.

(ii) The optimum temperature for the industrial conversion of methane and steam into the gaseous products is between 780-880°C.

Explain why this is so. [2]

- **Lower than 780 ^{0}C, rate of reaction is slow / % conversion is low, hence not cost effective.**
- **Higher than 880 ^{0}C, results in high energy costs / expensive & also after a certain temperature, yield does not increase significantly. Therefore, there is no gain in using a higher temperature.**

(b) The equation shows the final stage in the production of methanol.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

3.12 moles of carbon monoxide and 5.23 moles of hydrogen were placed in a sealed container. An equilibrium was established at 600 K and the total amount of gaseous molecules was found to be 7.63 moles. The total pressure was 630 kPa.

Calculate the equilibrium constant, K_p, for this reaction at 600 K and state its units. [3]

Let the amount of CH_3OH produced be *x* mol

	$CO(g)$	+	$2H_2(g)$	$\rightleftharpoons$	$CH_3OH(g)$
Initial/mol	3.12		5.23		-
Change/mol	-x		-2x		+x
Equilibrium/mol	3.12-x		5.23-2x		x

Total moles of gas = (3.12-x) + (5.23-2x) + x = 7.63

x = 0.36

no. of moles of CO = 2.76; no. of moles of H_2 = 4.51; no of moles of CH_3OH = 0.36

$P_{(CO)}$ = (2.76/7.63) x 630 = 228 kPa
$P_{(H2)}$ = (4.51/7.63) x 630 = 372 kPa
$P_{(CH3OH)}$ = (0.36/7.63) x 630 = 29.7 kPa

$$K_p = \frac{p(CH_3OH)}{p(CO) \times p(H_2)^2}$$

$$K_p = \frac{29.7}{228 \times (372)^2}$$ **= 9.41 x 10^{-7} kPa^{-2}**

- **No. of moles of CO, H_2 & CH_3OH**
- **Partial pressures of CO; H_2 & CH_3OH**
- **Correct substitution & value for K_p, correct units**

(c) Carbon monoxide also reacts with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At 1100 ^{0}C, K_c = 1.00

In an experiment, 1 mole of carbon monoxide was mixed with 1 mole of steam, 2 moles of carbon dioxide and 2 moles of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium. [2]

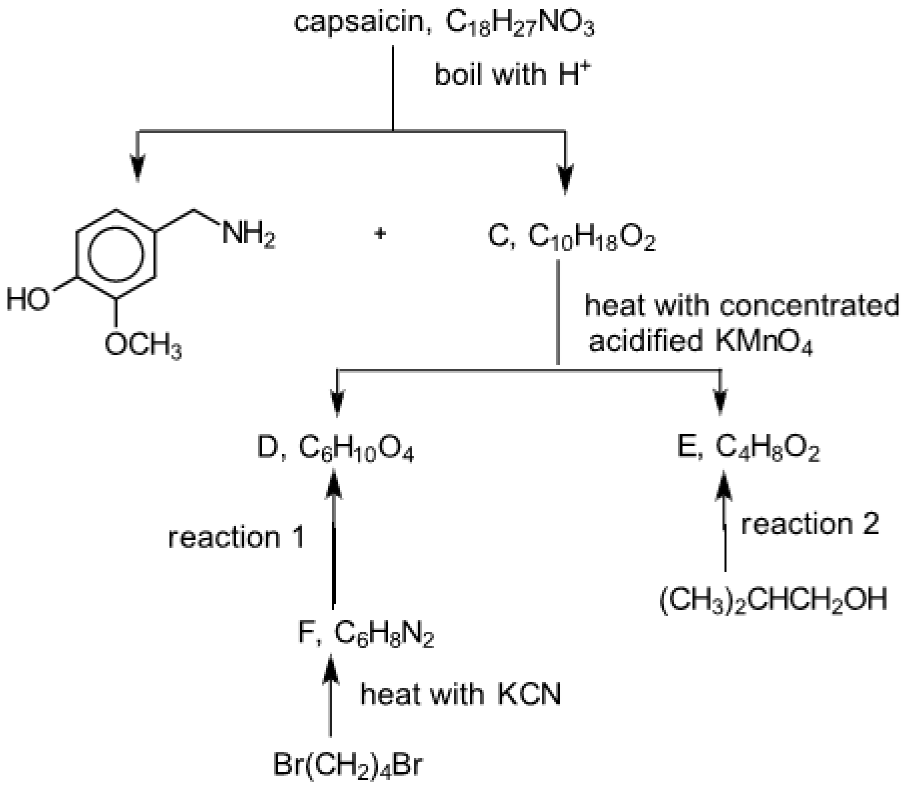
- the quotient / Q:
  $\frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{2 \times 2}{1 \times 1} = 4$, which is larger than K_c

Or K_c = 1, the <u>concentrations of products</u> must be <u>equal to concentrations of the reactants</u> at equilibrium

Or Kc = 1, <u>$[CO_2][H_2] = [CO][H_2O]$</u> at equilibrium

- **$[CO_2]$ & $[H_2]$ need to decrease and $[CO]$ & $[H_2O]$ need to increase**
  So position of equilibrium shifts to the left.

(d) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.



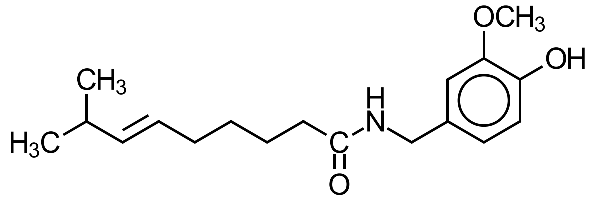
Capsaicin reacts with sodium metal and compounds C, D and E react with Na_2CO_3(aq).

(i) Suggest the reagents and conditions for reactions 1 and 2. [2]

- **Reaction 1: Aqueous HCl or H_2SO_4, heat**
- **Reaction 2: $KMnO_4$ or $K_2Cr_2O_7$ & dilute H_2SO_4(aq), heat under reflux**

(ii) Draw the structural formulae for the compounds C, D, E, F and capsaicin in the above reaction scheme. [5]

- **Capsaicin:**



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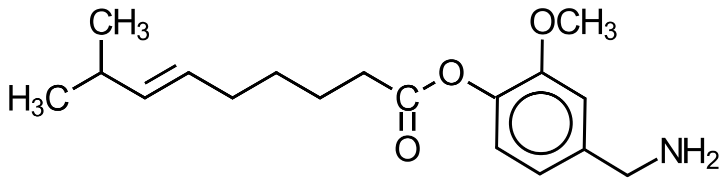
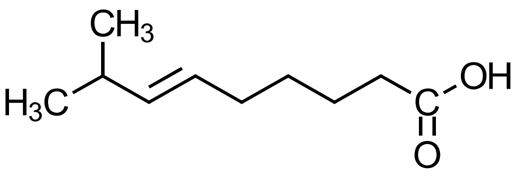
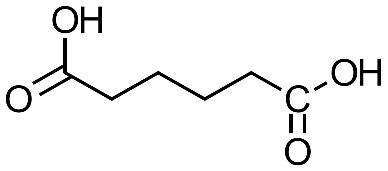


]

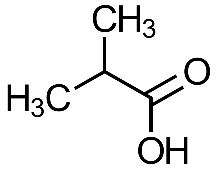
- **C is**

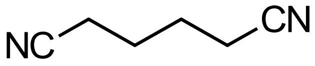


- **D is**

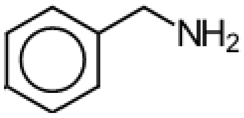


- **E is**

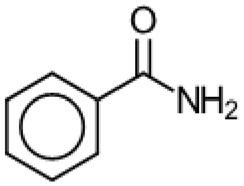


- **F is :** $CN(CH_2)_4CN$ **or** 

(e)

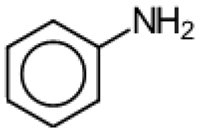


A



B

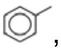
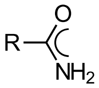
and



C

A, **B** and **C** nitrogen containing compounds. State and explain the relative basicities of these 3 compounds. [3]

Basic strength: B < C < A

- **A is a stronger base than B & C as the benzyl group,**  **, being electron-releasing in nature, increases the electron density on nitrogen atom. The lone pair of electrons on N is more available for dative bonding to a proton.**
- **The lone pair of electrons on the nitrogen atom of C can be delocalised into the benzene ring, making it less available for dative bonding to a proton. Thus C is a weaker base than A.**
- **B is an amide which is neutral because the lone pair electrons on N is delocalised over O-C-N, i.e:**  **(resonance structure), & hence it is not available for donation to a proton.**

[Total:19]

2 This question is about nitrogen compounds and their roles in organic synthesis.

Azide is the anion with the formula N_3^-. Azide is used as a chemical preservative in hospitals and laboratories.

The azide ion in sodium azide (NaN_3) can be oxidised by iodine to form nitrogen gas. To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.
The amount of unreacted iodine is then titrated with standard sodium thiosulfate solution:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm^3 of 0.050 mol dm^{-3} of aqueous iodine. The excess iodine was found to require 23.10 cm^3 of 0.040 mol dm^{-3} aqueous sodium thiosulfate for reaction.

(a) **(i)** Write the equation for the azide ion reacting with iodine. [1]

$2N_3^- \rightarrow 3N_2 + 2e$ (x1)

$I_2 + 2e \rightarrow 2I^-$ (x1)

- $2N_3^- + I_2 \rightarrow 3N_2 + 2I^-$

(ii) Calculate the percentage purity of sodium azide in the sample. [3]

No. of moles of $Na_2S_2O_3 = \frac{23.10}{1000} \times 0.040$ = 9.24×10^{-4} mol

- No. of moles of I_2 reacted with $Na_2S_2O_3$ = $\frac{9.24 \times 10^{-4}}{2}$ = 4.62×10^{-4} mol

No. of moles of I_2 reacted with NaN_3

$$= \left(\frac{25.0}{1000} \times 0.050\right) - 4.62 \times 10^{-4} = 7.88 \times 10^{-4} \text{ mol}$$

$2\ NaN_3 \equiv I_2$

- Mass of $NaN_3 = 2 \times 7.88 \times 10^{-4} \times (23 + 14 \times 3) = 0.102$ g
- Percentage purity of NaN_3 = $\frac{0.102}{0.120} \times 100$ = 85.4 %

(b) A student drew 4 structures **A** to **D** of the linear azide ion in Fig 2.1. His teacher commented one of the structures drawn was incorrect. Determine which is the **incorrect** structure, explaining your answer. [1]

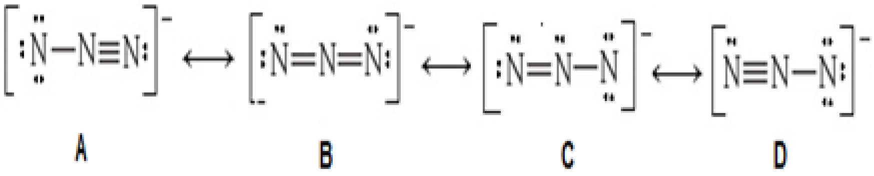


Fig. 2.1

- Structure C is incorrect as it will be bent shape wrt to the central N atom

(c) Azides, being very versatile, can play important roles in organic reactions. An azide ion is called a pseudohalide because it has some properties which are similar to those of chloride ions. As such organic azides, RN_3 have similar chemical properties as chloroalkanes.

One organic reaction scheme, involving sodium azide to form amines is shown in Fig 2.2.

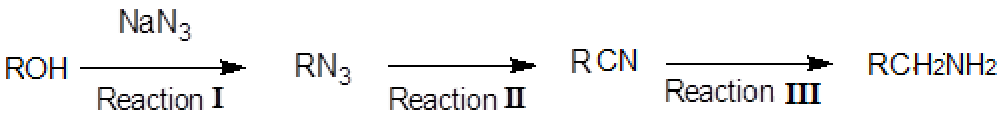
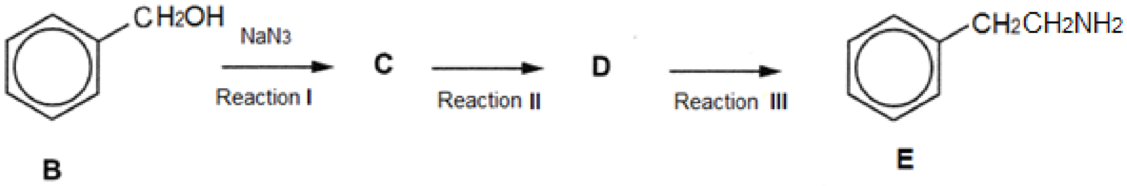


Fig. 2.2

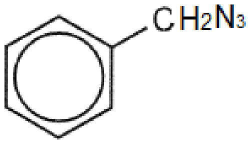
(i) Identify the role of azide ion in Reaction **I**. [1]

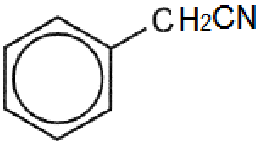
Nucleophile

The 3-stage synthesis of compound **E** from compound **B**, makes use of the reaction scheme shown in Fig. 2.2.



(ii) Suggest structures for intermediates **C** and **D**, and reagents and conditions for reactions **II** and **III**. [3]





- **C** **D**
- **Reaction II: ethanolic KCN, heat**
- **Reaction III: LiA/H4, dry ether as solvent, room temperature.**

(iii) State the *type of reaction* that occur during reaction **III**. [1]

- **Reduction**

A reaction scheme involving compound **B** is shown in Fig.2.3.

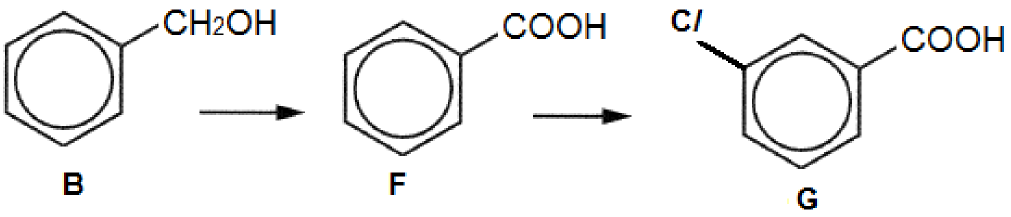


Fig. 2.3

(iv) Suggest the reagents and conditions for the conversion of **B** to **F** and for **F** to **G**. [2]

- **B** to **F: acidified $KMnO_4$, heat**
- **F to G: Cl_2 gas, anhydrous $AlCl_3$ catalyst, room temperature**

(v) Describe and explain how the acidity of **G** would compare to that of **F**. [2]

- **G is a stronger acid than F.**
- ***Cl* being an electronegative atom helps to disperse the negative charge of the anion formed, making it more stable than the anion of F.**

(d) Hydrogen azide, HN_3 has a boiling point of 37°C and ammonia, NH_3 has a boiling point of -33°C.

(i) Suggest a reason for the higher boiling point of hydrogen azide compared to ammonia. [1]

Both compounds have simple molecular structure and hydrogen bonds exist between molecules. However, HN_3 has a larger electron cloud than NH_3, which is more easily polarized, this leads to stronger and more extensive instantaneous-dipole induced-dipole attractions, more energy is needed to overcome the id-id attractions, hence HN_3 has a higher boiling point than NH_3.

(ii) Explain why hydrogen azide is highly soluble in water. [1]

Hydrogen bonds formed between HN_3 and water molecules releases sufficient energy to overcome the hydrogen bonds between HN_3 molecules and hydrogen bonds between water molecules.

(e) Nitride is a compound of nitrogen where nitrogen has a oxidation state of -3. Nitrides are a large class of compounds with a wide range of properties and applications.

(i) State the electronic configuration of the nitride ion, N^{3-}. [1]

$1s^22s^22p^6$

(ii) When a beam of nitride ions, N^{3-} was passed through an electric field, it deflected 63° towards the positive plate. Under identical conditions, a beam of azide ions, N_3^- was passed through the electric field. Determine the angle of deflection of the azide ion beam. [1]

Angle of deflection, $\theta \ \alpha \ q/m$

$\theta m/q$ = constant

$\theta_{azide} m_{azide}/q_{azide} = \theta_{nitride} m_{nitride}/q_{nitride}$

$$\frac{\theta_{azide} \times 42}{1} = \frac{63 \times 14}{3}$$

$$\theta_{azide} = 7°$$

[Total: 18]

3 Oxalic acid is an organic compound with the formula $H_2C_2O_4$. This colourless solid is a dicarboxylic acid. In terms of acid strength, it is about 3,000 times stronger than ethanoic acid. Its conjugate base, known as oxalate ($C_2O_4^{2-}$), is a reducing agent as well as a bidentate ligand for metal cations.

Oxalic acid dissociates in water according to the following equations.

I $HOOC\text{-}COOH + H_2O \rightleftharpoons HOOC\text{-}COO^- + H_3O^+$ $K_{a1} = 5.6 \times 10^{-2}$ mol dm^{-3}

II $HOOC\text{-}COO^- + H_2O \rightleftharpoons {}^-OOC\text{-}COO^- + H_3O^+$ $K_{a2} = 5.4 \times 10^{-5}$ mol dm^{-3}

(a) **(i)** Explain why the value of K_{a1} is larger than K_{a2}. [1]

•The first deprotonation of oxalic acid forms a mono-anion which is stabilised by hydrogen bonding, hence dissociation lies much on the right.

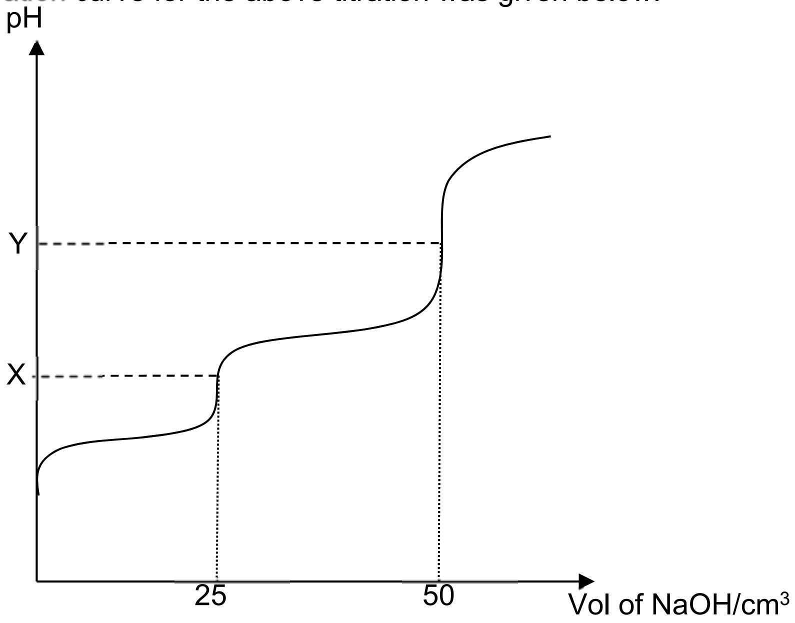
or HOOC-COOH is a stronger acid than HOOC-COO$^-$, as it is more difficult to remove H$^+$ from HOOC-COO$^-$, a negative ion.

(ii) Write expressions for acid dissociation constants for equation **I** and **II** above. [1]

• $K_{a1} = \dfrac{[H_3O^+][HOOC-COO^-]}{[HOOC-COOH]}$ $K_{a2} = \dfrac{[H_3O^+][^-OOC-COO^-]}{[HOOC-COO^-]}$

(b) A 25 cm^3 sample of oxalic acid of concentration 0.100 mol dm^{-3} was titrated with sodium hydroxide of concentration 0.100 mol dm^{-3}.

The titration curve for the above titration was given below.



(i) State the major organic species present at points **X** and **Y.** In your answer, include the equation for the reaction that occurred to produce **each** of these two species. [2]

• Major organic species are $HO_2C–CO_2^-$ and $^-O_2C–CO_2^-$ respectively. The two equations are shown below.

• $HOOC\text{-}COOH + OH^- \rightarrow HOOC\text{-}COO^- + H_2O$ step 1

$HOOC\text{-}COO^- + OH^- \rightarrow {}^-OOC\text{-}COO^- + H_2O$ step 2

(ii) It has been proven that the $[H_3O^+]$ at the first equivalent point, **X**, is given by the expression,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}}$$

Use the given expression to determine the pH value at point **X**. [1]

$[H_3O^+] = \sqrt{5.6x10^{-2}x5.4x10^{-5}} = 1.74 \times 10^{-3}$

• pH =2.76

(iii) Calculate the pH value at the second equivalent point, **Y**, given that the $[OH^-]$ can be assumed to be entirely due to the hydrolysis of the organic species at Y. [2]

$^-OOC\text{-}COO^- + H_2O \rightleftharpoons HOOC\text{-}COO^- + OH^-$

• $[^-OOC\text{-}COO^-] = 25/1000 \times 0.1 \div (25+50)/1000 = 0.0333$ mol dm^{-3}

$$K_{b2} = \frac{[OH^-][HOOC-COO^-]}{[^-OOC-COO^-]} = \frac{[OH^-]^2}{[^-OOC-COO^-]}$$

$K_{b2} = \frac{K_w}{K_{a2}}$ = 10^{-14} ÷ 5.4×10^{-5} = 1.85×10^{-10}

$1.85 \times 10^{-10} = \frac{[OH^-]^2}{0.0333}$

$[OH^-] = 2.48 \times 10^{-6}$ mol dm^{-3} , pOH =5.61

- pH = 8.39

OR $[OH^-] = \sqrt{K_{b2}c}$ where $K_{b2} = \frac{K_w}{K_{a2}}$ = 10^{-14} ÷ 5.4×10^{-5} = 1.85×10^{-10}

$[OH^-] = \sqrt{(1.85 \times 10^{-10} \times 0.0333)} = 2.48 \times 10^{-6}$ mol dm^{-3} , pOH =5.61

- pH = 8.39

(c) Oxalate ions, $C_2O_4^{2-}$, are toxic to the human body. If sufficient amounts are ingested and released into the bloodstream, the high concentration of oxalate ions would cause the precipitation of calcium oxalate in the urine, which can accumulate into painful kidney stones.
Assuming that the body excretes an average of 250 mg of calcium ions per litre of urine, what is the minimum concentration of oxalate ions needed to precipitate calcium oxalate in the urine?
Numerical value of solubility product of calcium oxalate, $CaC_2O_4 = 2.7 \times 10^{-9}$. [2]

- conc of Ca^{2+} in urine = $(250 \times 10^{-3}/40.1) / 1$ mol dm^3 = 6.23×10^{-3} mol dm^{-3}

- Minimum concentration of oxalate = $2.7 \times 10^{-9} / 6.23 \times 10^{-3} = 4.33 \times 10^{-7}$ mol dm^{-3}

(d) Oxalate ions, $C_2O_4^{2-}$, is also able to combine chemically with certain metals commonly found in the human body. It is able to bond chemically, behaving as a *bidentate* ligand, to transition elements, such as iron to form a complex ion.

$$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6H_2O \qquad K_{stab} = 5.00 \times 10^4$$

(i) What do you understand by the term *bidentate* ligand. [1]

- Bidentate ligand is a ligand which can form two dative bonds with the central metal atom or ion.

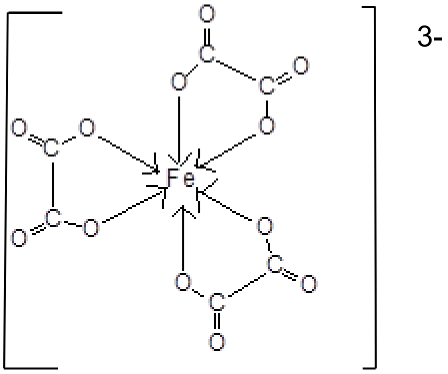
(ii) Suggest a reason why the stability constant, K_{stab} of the above is greater than 1. [1]

- Bidentate or polydentate ligands, bind more strongly with multiple dative bonds and hence form more stable complexes than $Fe(H_2O)_6^{3+}$.

OR

Complexes involving bidentate or polydentate ligands are more likely to be formed due to an increase in entropy as there is an increase in the number of particles.

(iii) Draw the structure of the complex ion, $[Fe(C_2O_4)_3]^{3-}$.Hence suggest the shape for this complex. [2]

- 

- **Shape: octahedral**

(e) Oxalic acid was one of the products formed when an aromatic organic compound, **A,** with molecular formula $C_{10}H_{10}O_2$ undergoes oxidation with acidified manganate(VII) to form another organic product, **B**, with the molecular formula $C_8H_8O_2$. No other organic compound was formed in the oxidation. Compound **B** reacts readily with 2 moles of $Br_2(aq)$ to form compound **E**, $C_8H_6O_2Br_2$. Compounds **A** and **B** are both soluble in NaOH and both **A** and **B** reacts with 2,4-dinitrophenylhydrazine. Compound **A** reacts with acidified dichromate to give an acid, **C**, $C_{10}H_{10}O_3$. Compound **C** reacts with $SOCl_2$ to form a sweet-smelling compound **D**, $C_{10}H_8O_2$.

Suggest structures for **A, B, C, D** and **E** and explain the reactions described. [10]

[Total: 23]

Explanation:

- **A, $C_{10}H_{10}O_2$ undergoes oxidation with acidified $KMnO_4$ to form $H_2C_2O_4$ and B, $C_8H_8O_2$. Thus A has a carbon-carbon double bond in the side chain substituent of the benzene ring.**

- **A and B are both soluble in NaOH ⇒ A and B are both acidic forming soluble salts in the acid-base reaction with NaOH. Hence, A and B is either a carboxylic acid or phenol**

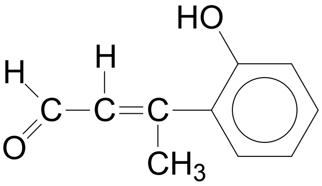
- **B reacts with 2 moles of $Br_2(aq)$ ⇒ Electrophilic substitution has taken place and B is a phenol with another substituent either at 2- or 4- position wrt the phenolic group**

- **A and B reacts with 2,4-DNPH ⇒ Condensation reaction has taken place and both A and B contain the carbonyl functional group.**

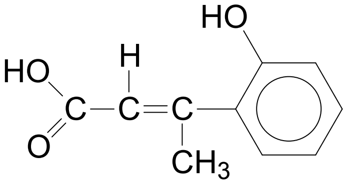
- **A is oxidised by acidified dichromate to form a carboxylic acid, C ⇒ A has an aldehyde group.**

- **C reacts with $SOCl_2$ to form an acid chloride with then reacts with phenol to form a cyclic ester, D. Nucleophilic substitution followed by condensation reaction have taken place.**

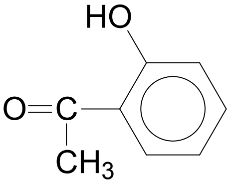
Compound A:



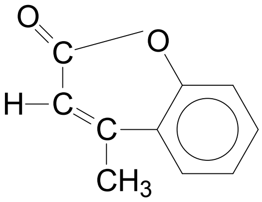
Compound C:



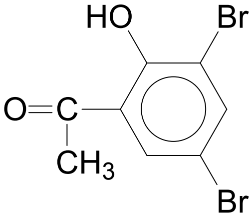
Compound B:



Compound D:



Compound E:



●●●●● for structures A, B, C, D and E

11 points max 10

Turn over for Section B

Section B

Answer **one** question from this section.

4 **(a)** Explain, with reference to relevant E^θ values, the industrial process of the electrolytic purification of a copper alloy consisting of nickel and silver impurities. [4]

$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^\ominus = +0.34\ V$

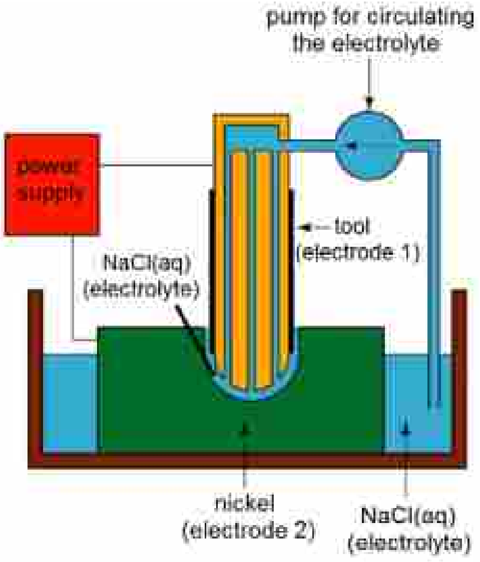
$Ni^{2+} + 2e^- \rightleftharpoons Ni \qquad E^\ominus = -0.25\ V$

$Ag^+ + e^- \rightleftharpoons Ag \qquad E^\ominus = +0.80\ V$

- **Anode (Oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**
  The impure copper is made the anode. Over time, the anode dissolves.
- **Cathode (Reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [pure copper]**
  The electrolyte is made of copper(II) sulfate solution. At the cathode, copper ions are discharged and deposited on the pure copper cathode.
- **Silver has more positive $E^\ominus$ value than $E^\ominus_{Cu^{2+}/Cu}$. It will not undergo oxidation at the crude Cu anode and will dislodge from the anode (since there is no substrate support) and fall off as anode mud.**
- **Nickel has less positive $E^\ominus$ value than $E^\ominus_{Cu^{2+}/Cu}$. Since oxidation occurs at the anode, it will be oxidised together with copper. However, Ni^{2+} will not be reduced at the pure copper cathode as its $E^\ominus$ value is less positive than $E^\ominus_{Cu^{2+}/Cu}$. Only Cu^{2+} ions will be reduced.**

(b) Electrochemical machining is a method used to cut small holes or cavities in metals such as nickel.

The diagram below illustrates the process. The tool (electrode 1) and nickel (electrode 2) are connected to a power supply. The electrodes are in contact with an electrolyte, NaCl(aq), which is being circulated using a pump. Some nickel is then removed by an electrochemical process when the power supply is switched on.



(i) State the polarity of each electrode. Write equation for the reaction occurring at each electrode. [2]

- **Electrode 1: Negative (cathode), $2H_2O + 2e \rightarrow H_2 + 2OH^-$**

- **Electrode 2: Positive (anode), $Ni \rightarrow Ni^{2+} + 2e$**

(ii) As the process takes place, a green solid is observed in the electrolyte. Suggest the identity of the solid. [1]

- **$Ni(OH)_2$**

(c) Magnesium is a Group 2 element that occurs naturally only in combination with other elements. It is the third most abundant element present in seawater, after sodium and chlorine.

(i) Describe and explain, using $E^\ominus$ values, the relative reactivity of Group 2 elements as reducing agents. [2]

- **Group 2 elements have large negative $E^\ominus$ values which become more negative down the Group.**
- **The more negative the $E^\ominus$ value, the stronger the reducing power of the element.**

In China, magnesium is produced by electrolysis of molten magnesium chloride. Anhydrous magnesium chloride is fed continuously into electrolytic cells which are hot enough to melt it. Magnesium is produced at the cathode.

(ii) Determine the mass of magnesium produced when a current of 40.0 A was passed through one such electrolytic cell for 10 hours. [2]

- **Q = I x t = 40 x 10 x 60 x 60 = 1440000 C**
  No. of moles of electrons transferred = 1440000 / 96500 = 14.9 mol
- **Mass of Mg = 14.9 / 2 x 24.3 = 181 g**

The magnesium chloride raw material needed for the electrolysis is obtained from seawater or magnesium chloride-rich brine.

If seawater is used, it is first treated to produce magnesium hydroxide which is then converted to the oxide. The oxide is then heated with carbon in a stream of chlorine at a high temperature as shown in the equation below.

$$2MgO + C + 2Cl_2 \rightarrow 2MgCl_2 + CO_2$$

(iii) Identify the oxdising and reducing agents in the above reaction. [1]

oxidising agent: Cl_2
reducing agent: C

On the other hand, if magnesium chloride-rich brine is used, the solution is treated to remove impurities and concentrated by removing water. Dehydration has to be carried out in the presence of hydrogen chloride gas to avoid the reaction of magnesium chloride with water.

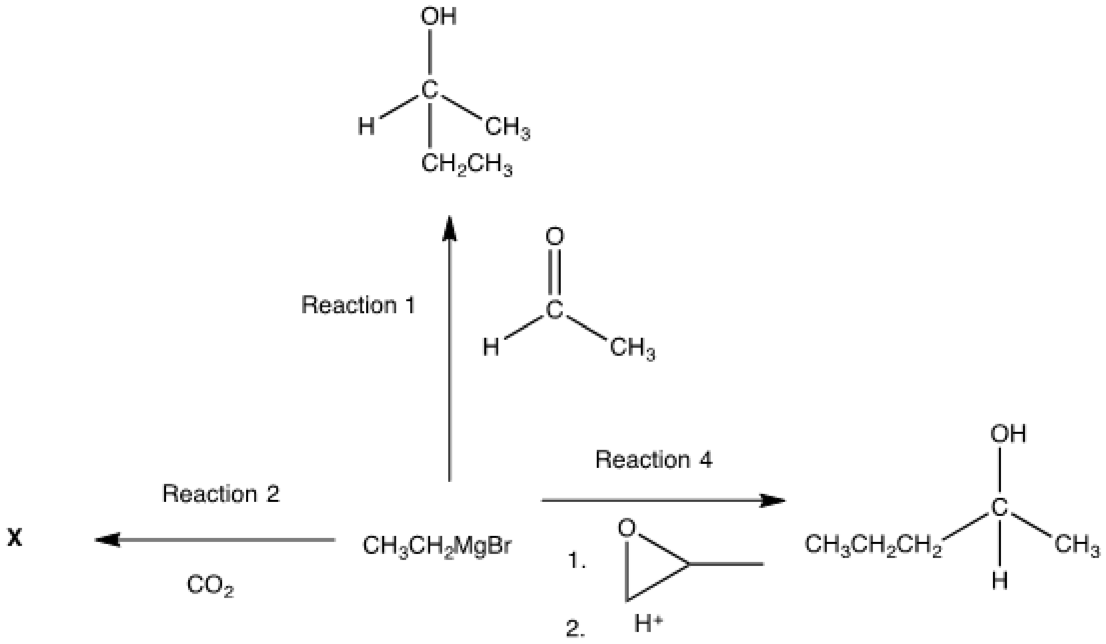
(iv) Describe and explain the reaction of magnesium chloride with water. Write equation where appropriate. [2]

- **$[Mg(H_2O)_6]^{2+}(aq) \rightleftharpoons [Mg(H_2O)_5OH]^{+}(aq) + H^{+}(aq)$**
- **Mg^{2+} has a high charge density hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond. It is easier for a H^+ ion to leave the water molecule. So the resulting solution is slightly acidic.**

Grignard reagents can be formed from the reaction of magnesium metal with an alkyl or aryl bromide as shown below.

R-Br + Mg → RMgBr where R represent an alkyl or aryl group

The following reaction scheme shows some reactions involving the Grignard reagent, CH_3CH_2MgBr. The Grignard reagent produces the carbanion, $^{-}{:}CH_2CH_3$, as the reacting species.



(v) Suggest the type(s) of reaction that occur in reaction 1 and hence explain why the product mixture obtained is optically inactive. [3]

- **Nucleophilic addition (and protonation/acidic hydrolysis)**
- **CH_3CH_2MgBr can attack the trigonal planar carbonyl carbon either from the top of the plane or the bottom of the plane with equal probability.**
- **This leads to the formation of 2 mirror images which are non-superimposable. Since equal amount of each enantiomer is formed, an optically inactive (racemic) mixture is obtained.**

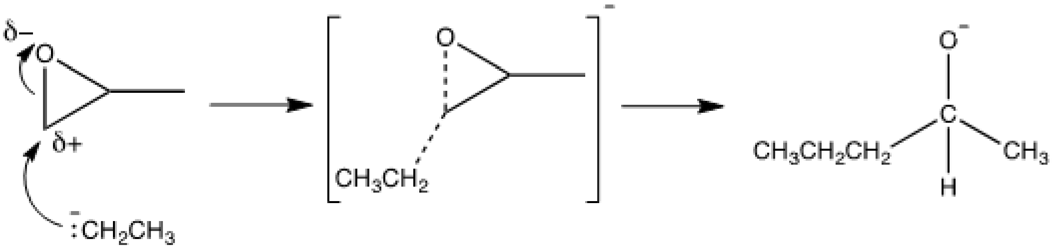
(vi) Reaction 2 occurs in a similar manner to reaction 1. Suggest the structural formula of compound **X**. [1]

- **CH_3CH_2COOH**

(vii) Reaction 3 occurs in two stages.

Stage 1 is a bimolecular nucleophilic substitution reaction.
Stage 2 is a protonation.

Draw the mechanism for stage 1.



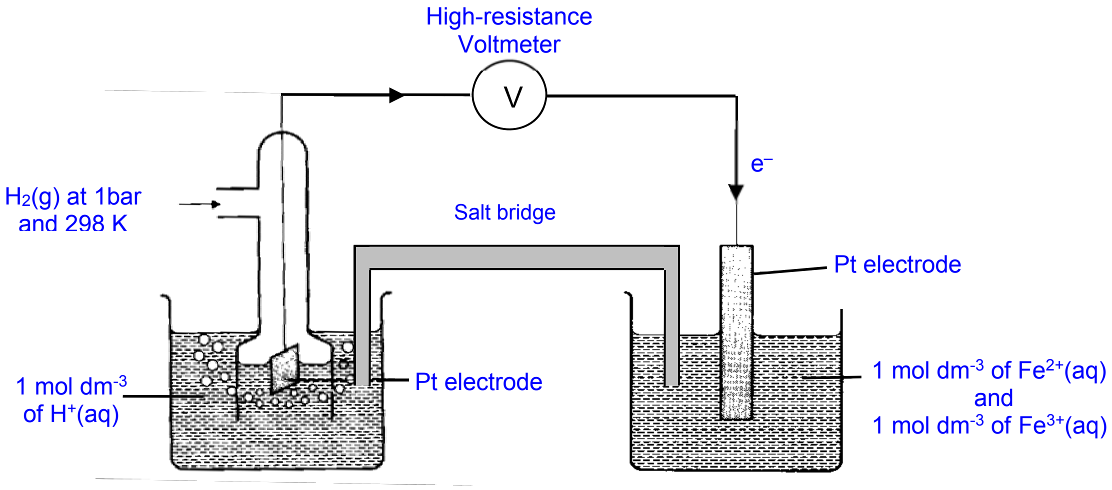
[2]

[Total: 20]

5 This question is about the chemistry of iron-containing compounds.

(a) Iron is the cheapest and one of the most abundant of all metals, comprising nearly 5.6% of the earth's crust and nearly the earth's entire core. It exists in a wide range of oxidation states and undergo redox reactions readily.

(i) By means of a fully labelled diagram, describe how the standard electrode potential of the Fe^{3+}/Fe^{2+} system can be measured. Indicate the direction of electron flow. [3]



[1] – e^- flow [1] – voltmeter, salt bridge + Pt electrodes

[1] – Fe^{3+}/Fe^{2+} electrolyte, hydrogen gas inlet & standard conditions

In Experiment 1, when aqueous iron(III) sulfate is boiled with an excess of potassium cyanide, an orange-red solution is obtained. The solution remains orange-red on addition of aqueous potassium iodide.

In Experiment 2, when aqueous iron(III) sulfate is added to aqueous potassium iodide, a brown solution is obtained.

(ii) State the type of reaction that occurred in each experiment. Write a balanced equation for any reaction that occurred. [3]

- **Experiment 1: Ligand substitution**
  Experiment 2: Redox
- **Expt 1:** $[Fe(H_2O)_6]^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-} + 6H_2O$
- **Expt 2:** $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

(iii) With reference to relevant $E^\ominus$ values, explain the observation in Experiment 1 upon addition of aqueous potassium iodide. [1]

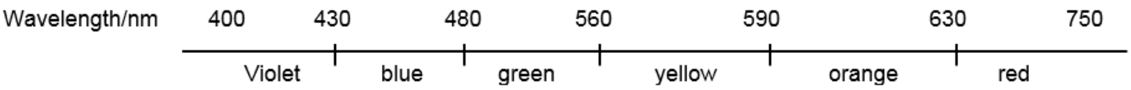
The orange-red solution is due to the presence of the complex ion $[Fe(CN)_6]^{3-}$.

- $E^\ominus_{cell} = +0.36 - (+0.54) = \underline{-0.18\ V < 0}$, **hence $[Fe(CN)_6]^{3-}$ will not be able to oxidise I^- and the solution remains orange-red.**

$Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$ $E^\ominus = +0.36$ V

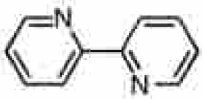
$I_2 + 2e \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

The colour spectrum of the visible region of the electromagnetic spectrum is as shown:



Iron(II) ions form an intense red complex with 2,2'-bipyridine (bipy) according to the following equation:

$$3bipy + Fe^{2+} \rightleftharpoons [Fe(bipy)_3]^{2+}$$



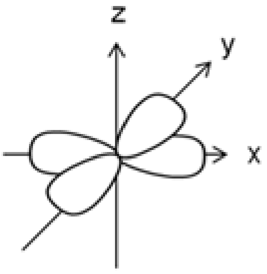
2,2'-bipyridine

The presence of ligands in complexes causes a splitting of the energy of d orbitals into two groups with an energy gap, ΔE, between them.

(iv) Given that aqueous iron(II) ion is green in colour, state and explain which ligand, water or 2,2'-bipyridine, results in a larger ΔE. [2]

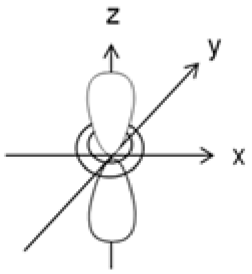
- **2,2'-bipyridine results in a larger ΔE**
- **$[Fe(bipy)_3]^{2+}$ absorbs green light, which has a higher energy/shorter wavelength than the red light absorbed by $[Fe(H_2O)_6]^{2+}$, which correlates to a larger d orbital splitting.**

(v) Draw a labelled diagram of one of the d orbitals at the **higher** energy level in $[Fe(bipy)_3]^{2+}$. [1]



$d_{x^2-y^2}$

or



d_{z^2}

Note: The orbitals drawn should be clearly labelled e.g. d_{x2-y2}, d_{z2}

(b) In the laboratory, iron(II) ions function as a catalyst for the reaction of iodide with hydrogen peroxide.

In an experiment to investigate the kinetics of the reaction, hydrogen peroxide is added to a solution of potassium iodide in the absence of the iron(II) catalyst at 25 °C, and the iodide ions are oxidised according to the equation:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

The following data was obtained.

Expt	**Initial [I^-] / mol dm^{-3}**	**Initial [H_2O_2] / mol dm^{-3}**	**Initial [H^+] / mol dm^{-3}**	**Initial rate of reaction / mol dm^{-3} s^{-1}**
1	0.01	0.01	0.0005	1.15×10^{-6}
2	0.01	0.02	0.0005	2.30×10^{-6}
3	0.02	0.01	0.0005	2.30×10^{-6}
4	0.01	0.01	0.001	1.15×10^{-6}

(i) Use the data above to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction. [3]

Let the rate equation be: Rate = $k[I^-]^x[H_2O_2]^y[H^+]^z$

- **From experiments 1 and 4,**

  When $[I^-]$ and $[H_2O_2]$ are constant and $[H^+]$ is increased by 2 times, initial rate remains unchanged.

Therefore, the order of reaction with respect to H^+ is 0.

- **From experiments 1 and 2,**

  $1.15 = k\,(0.01)^y$ -------(1)

  $2.30 = k\,(0.02)^y$ --------(2)   On solving, $y = 1$

Therefore, the order of reaction with respect to H_2O_2 is 1.

- **From experiments 1 and 3,**

  $1.15 = k\,(0.01)^y$ -------(1)

  $2.30 = k\,(0.02)^y$ --------(2)   On solving, $x = 1$

Therefore, the order of reaction with respect to I^- is 1.

Working (2m):
3 points – 2m
2 points – 1m
1 point – 0m

Rate eqn (1m)

- **Rate = $k[I^-][H_2O_2]$**

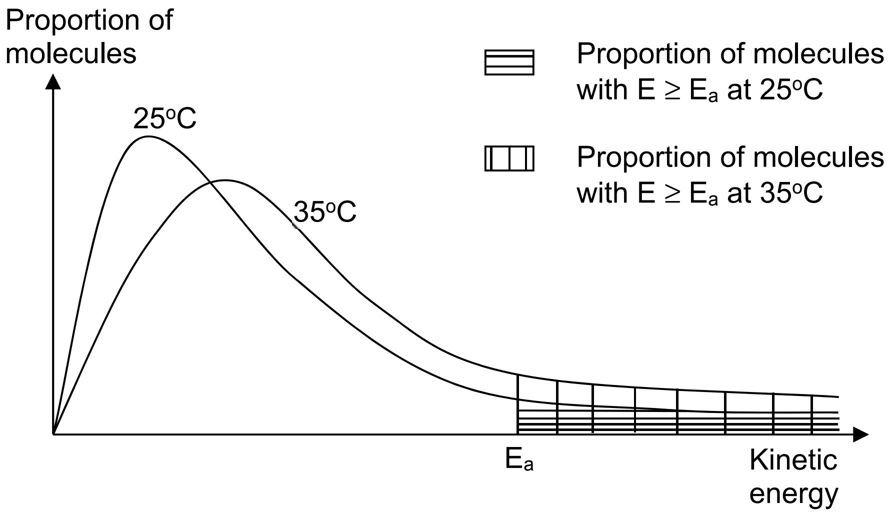
(ii) Calculate a value for the rate constant. Include units in your answer. [1]

Rate = $k[I^-][H_2O_2]$

Using Expt 1 data,

Rate constant, $k = \frac{1.15\times10^{-6}}{(0.01)(0.01)} = 0.0115$ mol^{-1}dm^{3}s^{-1} **(units must be correct)**

(iii) Explain, with the aid of a suitable diagram, why the rate of decomposition of hydrogen peroxide is expected to proceed faster at 35 °C. [2]



- **well labelled diagram**

- **At higher temperature, <u>average kinetic energy of molecules increases</u> and the <u>proportion of molecules with E ≥ E_a increases</u>.**

  Hence <u>frequency of effective collisions increases</u> and rate of reaction increases.

(c) Some protein-built enzymes form complexes with the metal ions at their active site. An example is catalase, which is an enzyme in the liver that breaks down harmful hydrogen peroxide into oxygen and water. It contains four iron-containing heme groups that allow the enzyme to react with the hydrogen peroxide.

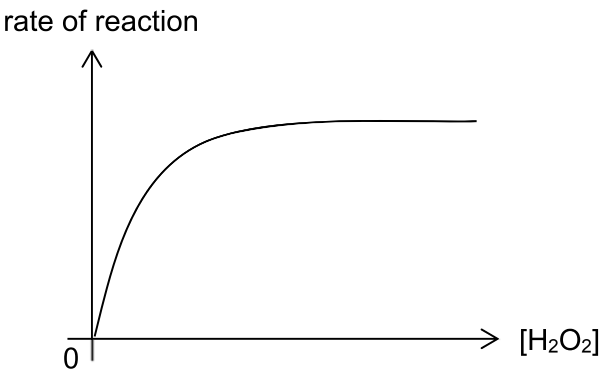
The decomposition of hydrogen peroxide solution to form water and oxygen gas is as shown:

$$2H_2O_2(aq) \xrightarrow{\text{catalase}} 2H_2O(l) + O_2(g)$$

(i) What do you understand by the term *enzyme*? [1]

- **Enzymes are <u>highly specific</u> in the <u>type of reaction(s)</u> which they catalyse, which no other enzymes will catalyse.**

(ii) A series of experiments were carried out to study the effect of hydrogen peroxide concentration on the rate of reaction, by using different concentrations of hydrogen peroxide at 25 °C. The following graph was obtained.



Account for the shape of the graph. [3]

- **At low [H_2O_2], <u>rate of reaction is directly proportional to [H_2O_2] since active sites are not fully occupied</u>. Hence reaction is first order.**
- **As [H_2O_2] increases, <u>the rate increases to a lesser extent and is no longer proportional to [H_2O_2] since more active sites are occupied</u>. Hence reaction is mixed order.**
- **With further increase in [H_2O_2], <u>rate becomes constant as the enzyme is saturated</u>. Hence reaction is zero order.**

[Total: 20]

TEMASEK
JUNIOR COLLEGE

2018 JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME									
CIVICS GROUP			/						
CENTRE NO. / INDEX NO.					/				

CHEMISTRY **9729/04**

Paper 4 Practical **29 August 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 20 and 21.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 24
2	/ 14
3	/ 17
Total	/ 55

This document consists of 21 printed pages and 1 blank page.

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Answer **all** the questions in the spaces provided.

1 Determination of the concentrations of sulfuric acid and potassium hydroxide

FA 1 is a dilute solution of sulfuric acid, H_2SO_4
FA 2 is a dilute solution of potassium hydroxide, KOH
FA 3 is 0.377 mol dm^{-3} aqueous sodium carbonate, Na_2CO_3

You are also provided with thymolphthalein solution.

Both potassium hydroxide and sodium carbonate are bases which will react with sulfuric acid to give a salt and water – a process known as neutralisation.

You will add different volumes of **FA 3** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the volume of sodium carbonate solution you add will only neutralise part of the sulfuric acid. You will then complete the neutralisation of each mixture by titration with dilute potassium hydroxide, **FA 2**.

Analysis of your results using a graph will enable you to determine the concentrations of sulfuric acid and that of potassium hydroxide.

(a) (i) Preparation and titration of reaction mixtures

Prepare four different mixtures of **FA 1** and **FA 3** as described below.

Mixture 1

1. Pipette 25.0 cm^3 of **FA 1** into a conical flask. Label the flask **6.00 cm^3**.
2. Fill a burette with **FA 3.**
3. Add 6.00 cm^3 of **FA 3** into the same conical flask.
4. Thoroughly stir the mixture and set it aside for later use.

Mixture 2

Repeat the procedure used for **Mixture 1** but this time add 25.0 cm^3 of **FA 1** and 20.00 cm^3 of **FA 3** into a second conical flask. Label the flask **20.00 cm^3**.

Mixtures 3 and 4

Repeat the procedure used for **Mixture 1** but with **9.00 cm^3** and **16.00 cm^3** of **FA 3**. In each case, add 25.0 cm^3 of **FA 1** and the respective volume of **FA 3** into a 100 cm^3 beaker. Thoroughly stir the mixture.

Label each 100 cm^3 beaker with the volume of **FA 3** it contains.

Notes: You will perform each titration once only. Great care must be taken that you do not overshoot the end-point.

The end-point of the titration of **Mixture 1** should be at least 25 cm^3 of **FA 2**.

Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Titration

1. Fill the second burette with **FA 2**.
2. Add 3 to 4 drops of thymolphthalein solution to the flask labelled **6.00 cm^3**.
3. Titrate the mixture in the flask with **FA 2** until a blue colour, which lasts for at least 10 s is obtained.
4. Repeat points **1** to **3** above using your remaining mixtures. You should perform your titrations in order of **increasing** volume of **FA 3**.
5. Each of the mixtures stored in beakers should be transferred **completely** to a third conical flask prior to each titration. Rinse this conical flask thoroughly between each titration.

Results

[2]

(ii) Plot on the grid below, your values for the **FA 2** titre (*y-axis*) against the volume of **FA 3** added (*x-axis*).

You should choose scales for the axes which will allow you to determine by extrapolation

- the volume of **FA 3** required, $\boldsymbol{V}_{\mathbf{max}}$**(FA 3)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 2** is added
- the volume of **FA 2** required, $\boldsymbol{V}_{\mathbf{max}}$**(FA 2)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 3** is added

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for $\boldsymbol{V}_{\mathbf{max}}$**(FA 3)** and $\boldsymbol{V}_{\mathbf{max}}$**(FA 2)**.

***V_{max}*(FA 3)** = ………………………… ***V_{max}*(FA 2)** = …………………………

Calculate the gradient of your graph line, showing clearly how you did this.

gradient = ……………………
[8]

(b) **(i)** Explain the gradient obtained in **(a)(ii)** in terms of the chemistry involved.

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……
[1]

(ii) Given that the concentration of aqueous sodium carbonate is 0.377 mol dm^{-3} and using the appropriate data from your graph, calculate the concentration of sulfuric acid in **FA 1.**

concentration of sulfuric acid in **FA 1** = …………………………….
[1]

(iii) Using your answer to **(b)(ii)** and appropriate data from your graph, calculate the concentration of potassium hydroxide in **FA 2.**

concentration of potassium hydroxide in **FA 2** = …………………………….
[2]

(iv) The concentration of potassium hydroxide in **FA 2** can also be calculated using the expression below.

$$[\text{KOH}] = \frac{2[\text{Na}_2\text{CO}_3]}{|\text{gradient}|}$$

A student, Jack, performs this experiment and obtains the concentration of potassium hydroxide using the expression, but he calculated his gradient using two points which are close to each other. His classmate, Jill, used the results from Jack's experiment and calculated the concentration of potassium hydroxide using the method in **(b)(ii)** and **(b)(iii)**, and insists that her calculated value is more accurate.

Suggest whether Jill's claim is correct or wrong, and explain your answer.

Jill's claim is ……………………………………………………………………………………

because ……………………………………………………………………………………………

……

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……

……

[1]

(c) The same experiment was carried out using **FA 3** that was prepared from a sample of solid anhydrous sodium carbonate containing a small amount of inert impurities.

(i) Suggest what effect this would have on the values of **V_{max}(FA 2)** and **V_{max}(FA 3)**. Explain your answer in each case.

effect on **V_{max}(FA 2)**……………………………………………………………………………

explanation………………………………………………………………………………………

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effect on **V_{max}(FA 3)**……………………………………………………………………………

explanation………………………………………………………………………………………

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[2]

(ii) Planning

You are required to write a plan for determining the exact percentage by mass of anhydrous sodium carbonate in the impure sample by collecting and measuring the volume of carbon dioxide gas evolved from its reaction with hydrochloric acid.

You may assume that you are provided with:

- impure solid anhydrous sodium carbonate,
- 0.10 mol dm^{-3} hydrochloric acid,
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include:

- practical details, including a well-labelled diagram of the set-up, of how you would carry out the gas collection when 0.30 g of carbonate was reacted with 80 cm^3 of hydrochloric acid;
- brief, but specific details of how the results would then be used to determine the exact percentage by mass of anhydrous sodium carbonate.

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[7]

[Total: 24]

2 To investigate the effect of concentration changes on the rate of reaction.

Potassium bromate(V) and potassium iodate(V) are powerful oxidising agents. When reacted with reducing agents such as sulfate(IV), SO_3^{2-}, the bromate(V) and iodate(V) ions will be reduced into the respective halogens.

The equation for the overall reaction is shown below:

$$2XO_3^- + 5SO_3^{2-} + 2H^+ \rightarrow X_2 + 5SO_4^{2-} + H_2O \qquad \text{(where X = Br or I)}$$

FA 4 is aqueous potassium iodate(V), KIO_3.
FA 5 is aqueous sodium sulfate(IV), Na_2SO_3.
FA 6 is 0.1 mol dm^{-3} sulfuric acid, H_2SO_4.

You are also provided with starch indicator and deionised water

In this experiment, you will be investigating the effect of the concentration of acid, **FA 6**, on the initial rate of the overall reaction between aqueous potassium iodate(V), KIO_3, **FA 4**, and aqueous sodium sulfate(IV), Na_2SO_3, **FA 5**.

(a) Potassium iodate(V) reacts with sodium sulfate(IV) in acidic solution to produce iodine in solution according to two stages.

In stage 1, iodate(V) and sulfate(IV) react to produce iodide and sulfate(VI) ions.

In stage 2, the iodide ions formed react with iodate ions to give iodine.

Write equations for the 2 stages involved in the reaction of iodate(V) and sulfate(IV) ions.

Stage 1: ……………………………………………………………………………………………

Stage 2: ……………………………………………………………………………………………

[2]

The iodine formed reacts immediately with sulfate(IV) ions to give iodide ions. When sulfate(IV) ions are completely consumed, the liberated iodine would react with starch solution to give the dark blue colour of the starch-iodine complex. Time taken for the dark blue colour to appear depends on the rate of formation of iodine. The effect of the concentration of acid on the initial rate of the overall reaction can be determined by measuring the time taken for dark blue colour to appear.

You are to perform a series of four experiments, in which the concentration of acid, **FA 6**, is varied, and measure the time, ***t***, taken for the dark blue colour to appear.

For each experiment, you will require two solutions, **solution 1** and **solution 2**. **Solution 1** will be prepared using a fixed volume of **FA 4** and deionised water as described in **(b)(i)**. In each experiment, **solution 2** will contain the same volume of **FA 5** but varying volumes of **FA 6**. The total volume of **solution 2** is kept constant at 100 cm^3 by adding deionised water as required.

(b) **(i) Experiment 1**

Preparation of solution 1

Add 15 cm^3 of **FA 4** into the 100 cm^3 measuring cylinder labelled **solution 1**. Make up the volume to 100 cm^3 using deionised water.

Preparation of solution 2

Add 15 cm^3 of **FA 5** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding 85 cm^3 of **FA 6**.

1. Place the 250 cm^3 beaker on the while tile.
2. Transfer **solution 1** into the 250 cm^3 beaker.
3. Using a 10 cm^3 measuring cylinder, measure and add 5 cm^3 of starch indicator into the 250 cm^3 beaker containing **solution 1**.
4. Transfer **solution 2** rapidly into the beaker containing **solution 1**, **starting a stopwatch as you do so.**
5. Stir the mixture gently using a glass rod, and measure the time, ***t***, for a dark blue colour to appear. Record your time, ***t***, to the nearest second.
6. Wash the beaker thoroughly with water and dry it.

(ii) Experiment 2

7. Prepare **solution 1** as described in **(b)(i)**.
8. Prepare **solution 2** by adding 15 cm^3 of **FA 5** and 25 cm^3 of **FA 6** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding deionised water.
9. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken for a dark blue colour to appear.

(iii) Experiments 3 – 4

10. Select **two** other suitable volumes of **FA 6**, between 25 cm^3 and 85 cm^3, for use in the remaining two experiments.
11. Prepare **solution 1** as described earlier.
12. Use your selected volume of **FA 6,** together with 15 cm^3 of **FA 5** and water, to prepare 100 cm^3 of **solution 2** for each experiment. Prepare a table in the space provided in **(c)** for recording purposes.
13. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken in each case for a dark blue colour to appear.

(c) Prepare a table in the space provided below in which to record, for each experiment:

- all volumes used to prepare **solution 2**,
- all values of ***t***,
- calculated values of Vol of **FA 6** x t, (Vol of **FA 6**)^2 x t to 3 significant figures

Results

[4]

(d) **(i)** Explain clearly why the concentration of H^+ in the initial reaction mixture could be represented as the volume of **FA 6** used.

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[1]

(ii) Calculate the concentration, in mol dm^{-3}, of hydrogen ions present in the reaction mixture for **experiment 1** at time *t* = 0 s.

$[H^+]$ = ...
[1]

(iii) Explain the significance of the values of (Vol. of **FA 6)** × time and (Vol. of **FA 6**)^2 × time.

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[2]

(iv) With reference to your answers in **(d)(iii)**, deduce the order of reaction with respect to H^+ ions.

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[1]

(v) Explain the effect on the initial rate of reaction if the concentration of **FA 6** is increased from 0.1 mol dm^{-3} to 0.2 mol dm^{-3}. Assume all other conditions are kept constant.

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[1]

(e) Select, from **experiments 1** to **4**, the experiment which is likely to have the greatest error. Explain your choice.

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[1]

(f) Suggest how the collection of data can be improved so that the order of reaction with respect to acid for this experiment can be accurately determined.

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[1]

[Total: 14]

3 Identification of ions

You are provided with **FA 7** solution, a mixture of two salts.

You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

FA 7 is a solution containing two cations.

		Test	*Observation*
(a)	Test the **FA 7** solution using Universal indicator paper.		
(b)	**(i)**	Place about 2 cm^3 of **FA 7** into a test-tube. Carefully add sodium hydroxide, dropwise with shaking, until no further change are seen. Swirl and filter the mixture, collecting the filtrate in a boiling tube labelled **FA 8**. The filtrate is **FA 8** which should be put to one side for use in **(c)(i).** Wash the residue thoroughly with deionised water. Discard the washings. The residue is **FA 9**. Retain the residue for use in **(b)(ii)**	

	Note: When $KMnO_4$ is added in **(b)(ii) and (c)(ii)**, the end point is permanent pale pink colour. In each case, use the same dropping pipette and record the number of drops of $KMnO_4$ you added to reach the end point.		
	(ii)	Transfer a spatula load of **FA 9** into a clean test-tube. Add hydrochloric acid, a few drops at a time and shaking, until no further changes are seen. Add $KMnO_4$, dropwise with shaking, until the end point is reach	
(c)	**(i)**	Place about 1 cm^3 of **FA 8** in a test-tube. Carefully add hydrochloric acid, dropwise with shaking, until no further change is seen. This solution is **FA 10**. Label this test tube **FA 10**.	
	(ii)	Place about 1 cm^3 of **FA 10** in test-tube. Add $KMnO_4$, dropwise with shaking, until the end point is reached.	
	(iii)	Place about 1 cm^3 of **FA 10** in a test-tube, add aqueous ammonia, dropwise with shaking, until no further change is seen.	

[5]

(d) Conclusions

(i) Identify the **two** cations present in **FA 7.**

Cation 1: ………………………… Cation 2: …………………………

[1]

(ii) Identify the metal-containing complex present in **FA 8**.
Write equations to illustrate the formation of this complex.

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[1]

(iii) Suggest an explanation for the observations in **(b)** and hence deduce the compositions of residue, **FA 9**.

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[2]

(iv) Explain the difference, if any, in the number of drops of $KMnO_4$ required to reach the end point in **(b)(ii)** and **(c)(ii)**.

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[2]

(e) **Planning**

There are four solutions labelled **FB 1**, **FB 2**, **FB 3**, and **FB 4**. Each solution contains one of the following:

- dilute hydrochloric acid
- aqueous sodium carbonate
- aqueous barium nitrate
- aqueous aluminium chloride

The solution names and **FB** codes are not in order.

(i) Without any indicators and using these solutions alone, plan the steps which will enable you to identify these solutions. Write your plan in the space below, showing how you would record your observations in a table.

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[2]

(ii) Describe, with reference to the reactions occurring, how you would use the observations to confirm the identities of **FB 1**, **FB 2**, **FB 3**, and **FB 4**.

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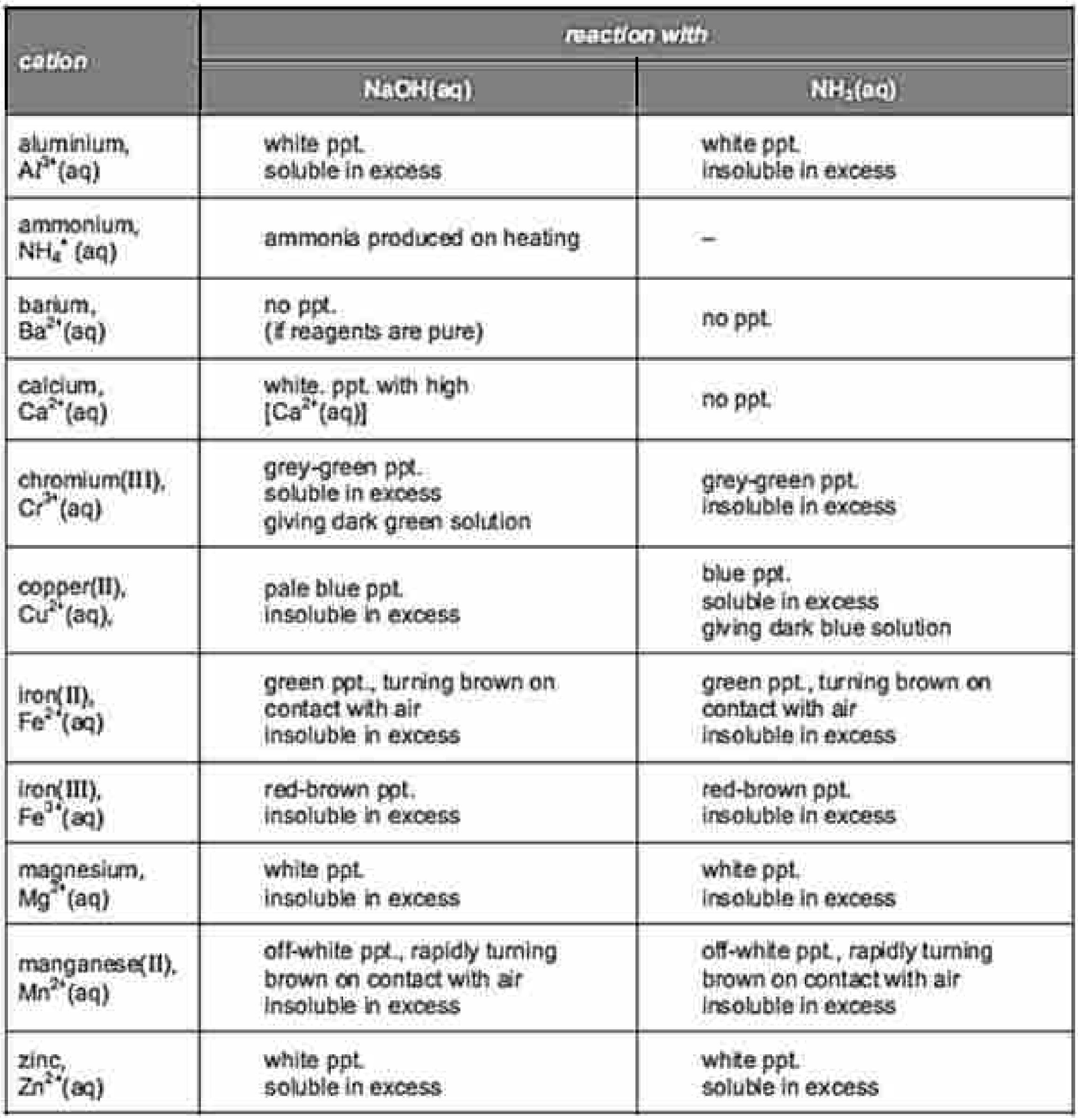
[4]

[Total: 17]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations



cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME								
CIVICS GROUP			/					
CENTRE NO. / INDEX NO.					/			

CHEMISTRY **9729/04**

Paper 4 Practical **29 August 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 20 and 21.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 24
2	/ 14
3	/ 17
Total	/ 55

This document consists of 20 printed pages and 1 blank page.

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Answer **all** the questions in the spaces provided.

1 Determination of the concentrations of sulfuric acid and potassium hydroxide

FA 1	is a dilute solution of sulfuric acid, H_2SO_4
FA 2	is a dilute solution of potassium hydroxide, KOH
FA 3	is 0.377 mol dm^{-3} aqueous sodium carbonate, Na_2CO_3

You are also provided with thymolphthalein solution.

Both potassium hydroxide and sodium carbonate are bases which will react with sulfuric acid to give a salt and water – a process known as neutralisation.

You will add different volumes of **FA 3** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the volume of sodium carbonate solution you add will only neutralise part of the sulfuric acid. You will then complete the neutralisation of each mixture by titration with dilute potassium hydroxide, **FA 2**.

Analysis of your results using a graph will enable you to determine the concentrations of sulfuric acid and that of potassium hydroxide.

(a) (i) Preparation and titration of reaction mixtures

Prepare four different mixtures of **FA 1** and **FA 3** as described below.

Mixture 1

1. Pipette 25.0 cm^3 of **FA 1** into a conical flask. Label the flask **6.00 cm^3**.
2. Fill a burette with **FA 3.**
3. Add 6.00 cm^3 of **FA 3** into the same conical flask.
4. Thoroughly stir the mixture and set it aside for later use.

Mixture 2

Repeat the procedure used for **Mixture 1** but this time add 25.0 cm^3 of **FA 1** and 20.00 cm^3 of **FA 3** into a second conical flask. Label the flask **20.00 cm^3**.

Mixtures 3 and 4

Repeat the procedure used for **Mixture 1** but with **9.00 cm^3** and **16.00 cm^3** of **FA 3**. In each case, add 25.0 cm^3 of **FA 1** and the respective volume of **FA 3** into a 100 cm^3 beaker. Thoroughly stir the mixture.

Label each 100 cm^3 beaker with the volume of **FA 3** it contains.

Notes: You will perform each titration once only. Great care must be taken that you do not overshoot the end-point.

The end-point of the titration of **Mixture 1** should be at least 25 cm^3 of **FA 2**.

Record your results in the space provided. Make certain that your recorded results show the precision of your working.

Titration

1. Fill the second burette with **FA 2**.
2. Add 3 to 4 drops of thymolphthalein solution to the flask labelled **6.00 cm^3**.
3. Titrate the mixture in the flask with **FA 2** until a blue colour, which lasts for at least 10 s is obtained.
4. Repeat points **1** to **3** above using your remaining mixtures. You should perform your titrations in order of **increasing** volume of **FA 3**.
5. Each of the mixtures stored in beakers should be transferred **completely** to a third conical flask prior to each titration. Rinse this conical flask thoroughly between each titration.

Results

Volume of **FA 3** / cm^3	6.00	9.00	16.00	20.00
Final burette reading / cm^3	26.35	47.40	34.85	45.75
Initial burette reading / cm^3	0.00	25.00	19.60	35.00
Volume of **FA 2** / cm^3	26.35	22.40	15.25	10.75

- **correct headers and units + 4 sets of reading present and to nearest 0.05 cm^3**
- **correctly calculate all titre vol of FA2**

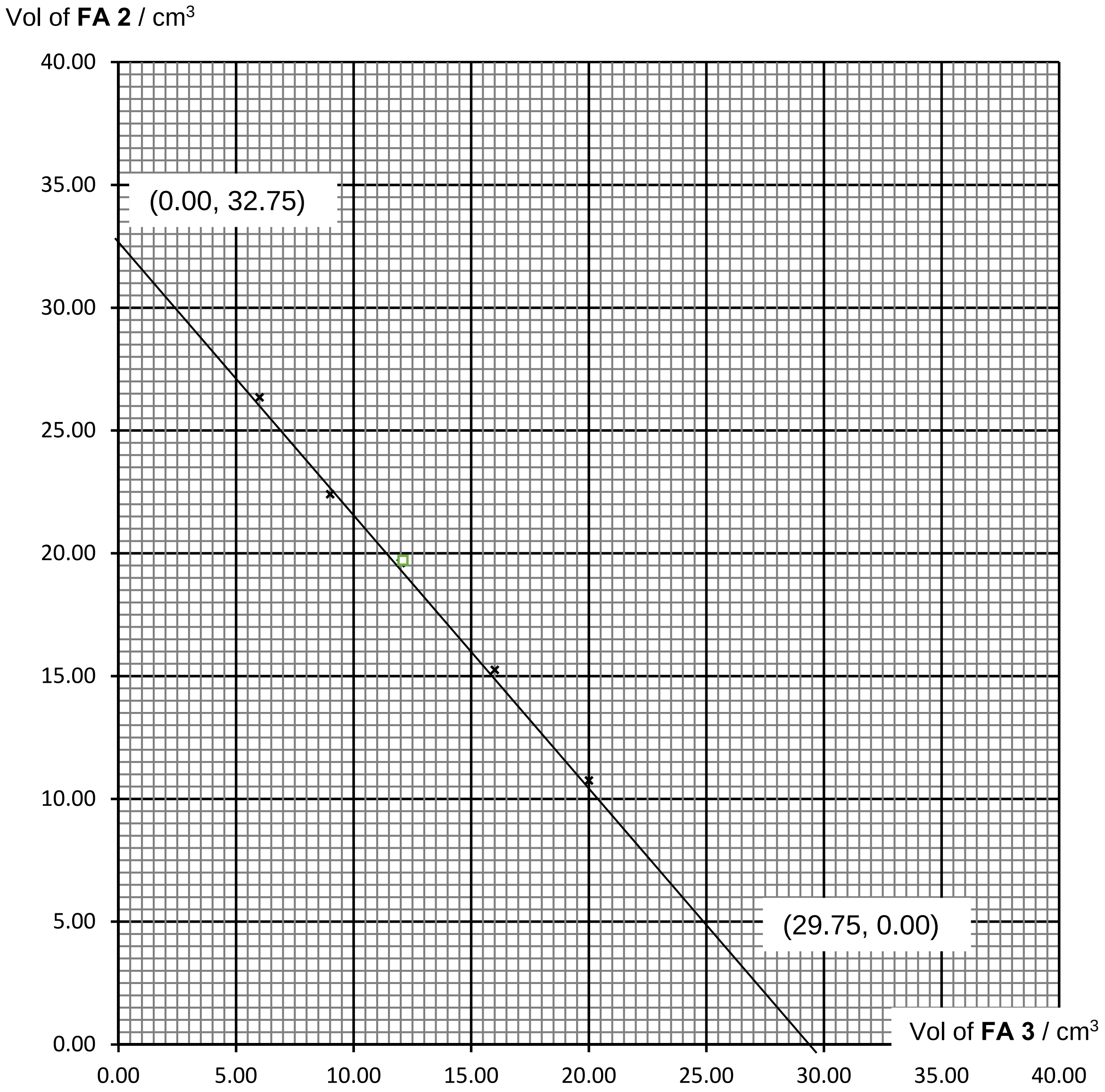
[2]

(ii) Plot on the grid below, your values for the **FA 2** titre (*y-axis*) against the volume of **FA 3** added (*x-axis*).

You should choose scales for the axes which will allow you to determine by extrapolation

- the volume of **FA 3** required, V_{max}**(FA 3)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 2** is added
- the volume of **FA 2** required, V_{max}**(FA 2)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 3** is added

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for V_{max}**(FA 3)** and V_{max}**(FA 2)**.



V_{max}(FA 3) = ……**29.75 cm^3**……… **V_{max}(FA 2)** = ………**32.75 cm^3**………

Calculate the gradient of your graph line, showing clearly how you did this.

Gradient of the graph $= \dfrac{(32.75-0.00)}{(0.0-29.75)} = -1.10$

gradient = ……**-1.10**………

[8]

- **axes correct way round + labels + units + scale**
- **all points plotted correctly based on student table**
- **best-fit straight line + correct extrapolation + no point further than 1 cm^3 away from line in either direction**
- **correctly read both intercept values as V_{max}(FA 3) and V_{max}(FA 2) based on drawn graph**
- •**• accuracy: each titre value within (inclusive) 1.0 cm^3 of supervisor**
- **clearly stated coordinates / or in working + at least 3 large squares in each direction**
- **correctly calculated gradient**

(b) **(i)** Explain the gradient obtained in **(a)(ii)** in terms of the chemistry involved.

When more Na_2CO_3 (FA 3) is added, more H_2SO_4 is neutralised by Na_2CO_3 and less KOH is required to neutralise the remaining/excess H_2SO_4. Hence, the gradient of the graph is negative.

[1]

(ii) Given that the concentration of aqueous sodium carbonate is 0.377 mol dm^{-3} and using the appropriate data from your graph, calculate the concentration of sulfuric acid in **FA 1.**

$Na_2CO_3 \equiv H_2SO_4$

No. of moles of Na_2CO_3 = $0.377 \times \frac{29.75}{1000}$ = 0.0112 mol

No. of moles of H_2SO_4 = 0.0112 mol

Concentration of H_2SO_4 = $0.0112 \times \frac{1000}{25.0}$

= 0.448 mol dm^{-3}

concentration of sulfuric acid in **FA 1** = ……**0.448 mol dm^{-3}**……
[1]

(iii) Using your answer to **(b)(ii)** and appropriate data from your graph, calculate the concentration of potassium hydroxide in **FA 2.**

$2KOH \equiv H_2SO_4$

No. of moles of H_2SO_4 in 25.0 cm^3 of FA1 added = 0.0112 mol

No. of moles of KOH = 0.0112 x 2 = 0.0224 mol

Concentration of KOH = $0.0224 \times \frac{1000}{32.75}$

= 0.684 mol dm^{-3}

concentration of potassium hydroxide in **FA 2** = ……**0.684 mol dm^{-3}**………
[2]

- **appropriate sf + units in Q1 aii, bii & biii**

(iv) The concentration of potassium hydroxide in **FA 2** can also be calculated using the expression below.

$$[KOH] = \frac{2[Na_2CO_3]}{|gradient|}$$

A student, Jack, performs this experiment and obtains the concentration of potassium hydroxide using the expression, but he calculated his gradient using two points which are close to each other. His classmate, Jill, used the results from Jack's experiment and calculated the concentration of potassium hydroxide using the method in **(b)(ii)** and **(b)(iii)**, and insists that her calculated value is more accurate.

Suggest whether Jill's claim is correct or wrong, and explain your answer.

Jill's claim is **correct.**

because **if the two points for calculating gradient are close, any error in reading the coordinates will result in a larger percentage error in the gradient, while the value in (b)(iii) is calculated from intercept coordinates and has a smaller percentage error.**

[1]

(c) The same experiment was carried out using **FA 3** that was prepared from a sample of solid anhydrous sodium carbonate containing a small amount of inert impurities.

(i) Suggest what effect this would have on the values of ***V***

effect on V_{max}**(FA 2)** **V_{max}(FA 2) will be the same.**

explanation **At V_{max}(FA 2), no FA 3 is present and only KOH reacts with the H_2SO_4. (Since the concentration of H_2SO_4 and KOH remained unchanged, the same volume of KOH is needed to react with the H_2SO_4.)**

effect on V_{max}**(FA 3)** **V_{max}(FA 3) will be larger than the actual value.**

explanation **When the Na_2CO_3 with inert impurities is weighed out, the actual mass and, therefore, amount of Na_2CO_3 is smaller. The concentration of FA 3 is lower and a larger volume of FA 3 is needed to react with the HC*l*.**

[2]

(ii) Planning

You are required to write a plan for determining the exact percentage by mass of anhydrous sodium carbonate in the impure sample by collecting and measuring the volume of carbon dioxide gas evolved from its reaction with hydrochloric acid.

You may assume that you are provided with:

- impure solid anhydrous sodium carbonate,
- 0.10 mol dm^{-3} hydrochloric acid,
- the apparatus and chemicals normally found in a school or college laboratory.

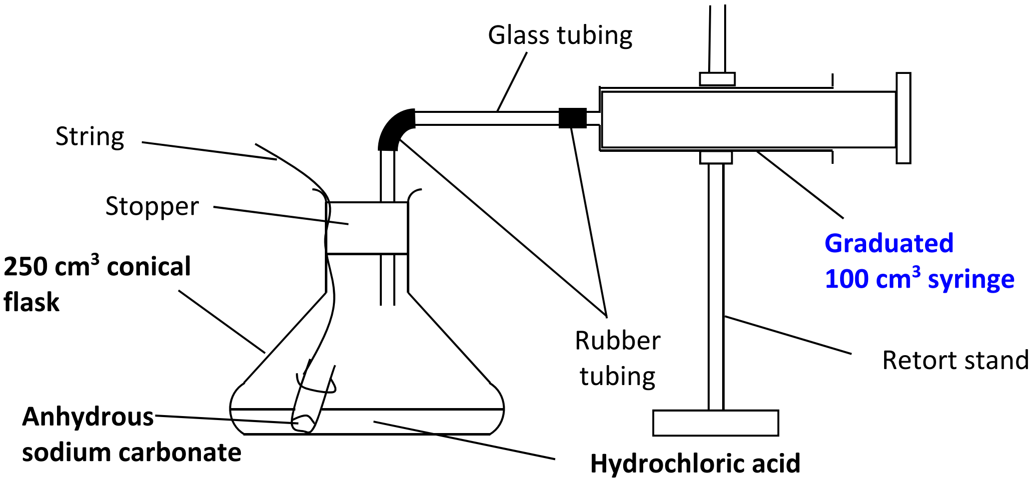
Your plan should include:

- practical details, including a well-labelled diagram of the set-up, of how you would carry out the gas collection when 0.30 g of carbonate was reacted with 80 cm^3 of hydrochloric acid;
- brief, but specific details of how the results would then be used to determine the exact percentage by mass of anhydrous sodium carbonate.

Set-up

• labeling of the capacity of gas syringe

• illustrating a method to add the acid to sodium carbonate or vice versa



Procedure

• measuring mass of sodium carbonate and vol of acid to be added

• recording the initial and final volume reading of the syringe (if thistle funnel is used, vol of gas collected = $V_{after} - V_{before} - V_{acid}$

• final reading taken approx. 20 min after reaction has completed and there is no movement of the plunger in the syringe.

1. **Weigh 0.30 g of anhydrous sodium carbonate into a small test tube / container.**
2. **Measure 80.0 cm^3 of HC*l* using a 100 cm^3 measuring cylinder and transfer it to a 250 cm^3 conical flask.**
3. **Assemble the set-up as shown in the diagram.**

4. **Record the initial volume reading of a 100 cm^3 gas syringe before removing the string to start the reaction.**
5. **Record the final volume reading of the gas syringe 20 minutes after the reaction has completed and there is no movement observed of the plunger in the syringe (to allow the temperature and pressure to equilibrate with the surroundings).**

<u>Calculation</u>

Let y cm^3 be the volume of carbon dioxide evolved.

No of moles of carbon dioxide = $\frac{y}{24000}$ **mol**

• No of moles of Na_2CO_3 present = $\frac{y}{24000}$ **mol**

Mass of anhydrous sodium carbonate present = $\frac{y\ x\ 106}{24000} = \frac{53y}{12000}$ **g**

• % by mass of anhydrous sodium carbonate = $\frac{53y\ x\ 100}{12000\ x\ 0.30} = \frac{53y}{36}$ **%**

[7]
[Total: 24]

2 To investigate the effect of concentration changes on the rate of reaction.

Potassium bromate(V) and potassium iodate(V) are powerful oxidising agents. When reacted with reducing agents such as sulfate(IV), SO_3^{2-}, the bromate(V) and iodate(V) ions will be reduced into the respective halogens.

The equation for the overall reaction is shown below:

$$2XO_3^- + 5SO_3^{2-} + 2H^+ \rightarrow X_2 + 5SO_4^{2-} + H_2O \qquad \text{(where X = Br or I)}$$

FA 4 is aqueous potassium iodate(V), KIO_3.
FA 5 is aqueous sodium sulfate(IV), Na_2SO_3.
FA 6 is 0.1 mol dm^{-3} sulfuric acid, H_2SO_4.

You are also provided with starch indicator and deionised water

In this experiment, you will be investigating the effect of the concentration of acid, **FA 6**, on the initial rate of the overall reaction between aqueous potassium iodate(V), KIO_3, **FA 4**, and aqueous sodium sulfate(IV), Na_2SO_3, **FA 5**.

(a) Potassium iodate(V) reacts with sodium sulfate(IV) in acidic solution to produce iodine in solution according to two stages.

In stage 1, iodate(V) and sulfate(IV) react to produce iodide and sulfate(VI) ions. In stage 2, the iodide ions formed react with iodate ions to give iodine.

Write equations for the 2 stages involved in the reaction of iodate(V) and sulfate(IV) ions.

Stage 1:
- $IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$

Stage 2:
- $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

[2]

The iodine formed reacts immediately with sulfate(IV) ions to give iodide ions. When sulfate(IV) ions are completely consumed, the liberated iodine would react with starch solution to give the dark blue colour of the starch-iodine complex. Time taken for the dark blue colour to appear depends on the rate of formation of iodine. The effect of the concentration of acid on the initial rate of the overall reaction can be determined by measuring the time taken for dark blue colour to appear.

You are to perform a series of four experiments, in which the concentration of acid, **FA 6**, is varied, and measure the time, ***t***, taken for the dark blue colour to appear.

For each experiment, you will require two solutions, **solution 1** and **solution 2**. **Solution 1** will be prepared using a fixed volume of **FA 4** and deionised water as described in **(b)(i)**. In each experiment, **solution 2** will contain the same volume of **FA 5** but varying volumes of **FA 6**. The total volume of **solution 2** is kept constant at 100 cm^3 by adding deionised water as required.

(b) **(i) Experiment 1**

Preparation of solution 1

Add 15 cm^3 of **FA 4** into the 100 cm^3 measuring cylinder labelled **solution 1**. Make up the volume to 100 cm^3 using deionised water.

Preparation of solution 2

Add 15 cm^3 of **FA 5** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding 85 cm^3 of **FA 6**.

1. Place the 250 cm^3 beaker on the while tile.
2. Transfer **solution 1** into the 250 cm^3 beaker.
3. Using a 10 cm^3 measuring cylinder, measure and add 5 cm^3 of starch indicator into the 250 cm^3 beaker containing **solution 1**.
4. Transfer **solution 2** rapidly into the beaker containing **solution 1**, **starting a stopwatch as you do so.**
5. Stir the mixture gently using a glass rod, and measure the time, ***t***, for a dark blue colour to appear. Record your time, ***t***, to the nearest second.
6. Wash the beaker thoroughly with water and dry it.

(ii) Experiment 2

7. Prepare **solution 1** as described in **(b)(i)**.
8. Prepare **solution 2** by adding 15 cm^3 of **FA 5** and 25 cm^3 of **FA 6** into the 100 cm^3 measuring cylinder labelled **solution 2**. Make up the volume to 100 cm^3 by adding deionised water.
9. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken for a dark blue colour to appear.

(iii) Experiments 3 – 4

10. Select **two** other suitable volumes of **FA 6**, between 25 cm^3 and 85 cm^3, for use in the remaining two experiments.
11. Prepare **solution 1** as described earlier.
12. Use your selected volume of **FA 6,** together with 15 cm^3 of **FA 5** and water, to prepare 100 cm^3 of **solution 2** for each experiment. Prepare a table in the space provided in **(c)** for recording purposes.
13. Repeat steps 1 to 6 in **(b)(i)** to determine the time taken in each case for a dark blue colour to appear.

(c) Prepare a table in the space provided below in which to record, for each experiment:

- all volumes used to prepare **solution 2**,
- all values of ***t***,
- calculated values of Vol of **FA 6** x t, (Vol of **FA 6**)^2 x t to 3 significant figures

Table of results

Expt No.	Solution 2			Time, *t* /s	V_{FA6} x t/ cm^3 s	$(V_{FA6})^2$ x t/ cm^6 s
	Volume of FA 5 /cm^3	Volume of FA 6 /cm^3	Volume of water /cm^3			
1	15	85	0	12	1020	86700
2	15	25	60	42	1050	26300
3	15	40	45	25	1000	40000
4	15	50	35	21	1050	52500

- **headers and units**
- **all volumes recorded to 1 cm^3, time to 1s, calculated values to 3 s.f.**
- **4 sets of data recorded, all values of t increase while volume of FA 6 decrease**
- **Correctly calculated values of V_{FA6} x t and $(V_{FA6})^2$ x t**

[4]

(d) **(i)** Explain clearly why the concentration of H^+ in the initial reaction mixture could be represented as the volume of **FA 6** used.

The total volume of the reaction mixture is constant in all experiments. Concentration of H^+ = (Vol of FA 6 x conc of FA 6) / total volume
Since conc of FA 6 is also constant, hence conc of $H^+ \propto$ volume of FA 6

[1]

(ii) Calculate the concentration, in mol dm^{-3}, of hydrogen ions present in the reaction mixture for **experiment 1** at time *t* = 0 s.

Total volume of reaction mixture = 100 + 100 + 5
= 205 cm^3

Concentration of H^+ = $\dfrac{\frac{85}{1000}\times0.1\times2}{\frac{205}{1000}}$

= 0.0829 mol dm^{-3}

$[H^+]$ = **0.0829 mol dm^{-3}** [1]

(iii) Explain the significance of the values of (Vol. of **FA 6)** × time and (Vol. of **FA 6**)^2 × time.

Concentration of FA 6 is directly proportional to the volume of FA 6 (from (d)(i)).

- **The rate of reaction is directly proportional to the reciprocal of the time taken for a fixed amount of iodine to be formed.**

Rate $\propto$ [FA 6]^n where n is the order of reaction with respect to FA 6

- $\frac{1}{t} \propto$ **(Vol. of FA 6)^n**

(Vol. of FA 6)^n × t = constant

If (Vol. of FA 6) × t = constant, n = 1.

- **If (Vol. of FA 6)^2 × t = constant, n = 2.**

3 points = 2 marks
2 points = 1mark

[2]

(iv) With reference to your answers in **(d)(iii)**, deduce the order of reaction with respect to H^+ ions.

From the results obtained, the (Volume of FA 6) × t is approximately constant. Hence, it can be concluded that the order of reaction with respect to H^+ ions is 1.

[1]

(v) Explain the effect on the initial rate of reaction if the concentration of **FA 6** is increased from 0.1 mol dm^{-3} to 0.2 mol dm^{-3}. Assume all other conditions are kept constant.

Since the reaction is first order with respect to H^+, when the concentration of H^+ is increased by two times, the initial rate of reaction should increase by two times.

[1]

(e) Select, from **experiments 1** to **4**, the experiment which is likely to have the greatest error. Explain your choice.

In experiment 1, when time, t is the smallest value and so has the greatest % error.

Or In experiment 2, when the volume of H^+ is the smallest.

[1]

(f) Suggest how the collection of data can be improved so that the order of reaction with respect to acid for this experiment can be accurately determined.

Repeat each experiment and take average of the timings for the dark blue colour to appear.

OR

Plot the rate (1/time) against the volume of acid to more accurately how the rate (1/time) is dependent on the volume or conc. of acid, hence determine order.

[1]

[Total: 14]

3 Identification of ions

You are provided with **FA 7** solution, a mixture of two salts
You are to perform the tests below and record your observations in the spaces provided. Your answers should include

- details of colour changes and precipitates formed;
- the names of any gases evolved **and** details of the test used to identify each one.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated.

You should indicate clearly at what stage in a test a change occurs.

If it appears that no reaction has taken place this should be clearly recorded.

Rinse and reuse test-tubes where possible.

No additional or confirmatory tests for ions present should be attempted.

Candidates are reminded that definite deductions may be made from tests where there appears to be no reaction.

FA 7 is a solution containing two cations.

		Test	*Observation*
(a)		Test the **FA 7** solution using Universal indicator paper.	• **pH 3-4**
(b)	**(i)**	Place about 2 cm^3 of **FA 7** into a test-tube. Carefully add sodium hydroxide, dropwise with shaking, until no further change are seen.	• **white ppt formed** • **then green ppt, insoluble in excess NaOH (turning brown in contact with air)**
		Swirl and filter the mixture, collecting the filtrate in a boiling tube labelled **FA 8**. The filtrate is **FA 8** which should be put to one side for use in **(c)(i).**	• **green residue turns brown in contact with air/ brown residue obtained** • **colourless/pale yellow filtrate**
		Wash the residue thoroughly with deionised water. Discard the washings. The residue is **FA 9**. Retain the residue for use in **(b)(ii)**	
	Note: When $KMnO_4$ is added in **(b)(ii) and (c)(ii)**, the end point is permanent pale pink colour. In each case, use the same dropping pipette and record the number of drops of $KMnO_4$ you added to reach the end point.		
	(ii)	Transfer a spatula load of **FA 9** into a clean test-tube.	
		Add hydrochloric acid, a few drops at a	• **Solid dissolves in acid to form orange to**

		time and shaking, until no further changes are seen. Add $KMnO_4$, dropwise with shaking, until the end point is reach	**form an orange/orange-brown/brown/ yellow solution** • **After > 3 drops (accept any number more than 3), it turns pink/end point is reached**
(c)	**(i)**	Place about 1 cm^3 of **FA 8** in a test-tube. Carefully add hydrochloric acid, dropwise with shaking, until no further change is seen. This solution is **FA 10**. Label this test tube **FA 10**.	• **White ppt forms** • **Ppt solube in excess HCl**
	(ii)	Place about 1 cm^3 of **FA 10** in test-tube. Add $KMnO_4$, dropwise with shaking, until the end point is reached.	• **Instant pink colour/ 1 drop of $KMnO_4$**
	(iii)	Place about 1 cm^3 of **FA 10** in a test-tube, add aqueous ammonia, dropwise with shaking, until no further change is seen.	• **White ppt forms,** • **Ppt insoluble in excess $NH_3(aq)$**

[These points are scaled to 5 MMO/PDO marks as follows.
12-10 = 5
8 - 9 = 4
6 - 7 = 3
5 - 4 = 2
2 – 3 = 1
0 - 1 = 0

[5]

(d) Conclusions

(i) Identify the **two** cations present in **FA 7.** [1]

- **Al^{3+} and Fe^{2+} [both must be correctly identified, reject Fe^{3+}]**

(ii) Identify the metal-containing complex present in **FA 8**.

Write equations to illustrate the formation of this complex.

- **$[Al(OH)_4]^-(aq)$**

$$Al(aq)^{3+} + 4OH^- \rightleftharpoons [Al(OH)_4]^-(aq)$$

OR

$$Al(OH)_3 + OH^- \rightleftharpoons [Al(OH)_4]^-$$

[1]

(iii) Suggest an explanation for the observations in **(b)** and hence deduce the compositions of residue, **FA 9**.

- **Fe^{2+} reacts with OH^- to form green $Fe(OH)_2$ ppt, which is oxidised by oxygen in air to form brown $Fe(OH)_3$ ppt.**

- **Composition: $Fe(OH)_2$ and $Fe(OH)_3$**

[2]

(iv) Explain the difference, if any, in the number of drops of $KMnO_4$ required to reach the end point in **(b)(ii)** and **(c)(ii)**.

- **In (b)(ii), Fe^{2+} is present in the solution. Redox reaction takes place between Fe^{2+} & MnO_4^-/H^+ or Fe^{2+} is the reducing agent that reacts with MnO_4^-/H^+. Hence, more than 3 drops of MnO_4^-/H^+ requires before solution turns pink.**

- **In (c)(ii), Fe^{2+} is not found in the filtrate and no redox reaction takes place. OR Al^{3+}/ other cation identified in the filtrate cannot be oxidised. The solution turns pink immediately with a drop of MnO_4^-/H^+ solution added.**

[2]

(e) **Planning**

There are four solutions labelled **FB 1**, **FB 2**, **FB 3**, and **FB 4**. Each solution contains one of the following:

- dilute hydrochloric acid
- aqueous sodium carbonate
- aqueous barium nitrate
- aqueous aluminium chloride

The solution names and FB codes are not in order.

(i) Without any indicators and using these solutions alone, plan the steps which will enable you to identify these solutions. Write your plan in the space below, showing how you would record your observations in a table.

1. **•Add FB 1 separately to 1 cm^3 solutions of FB 2, FB 3 and FB 4 in a test–tube each.**
2. **Record your observations in the table below.**
3. **Repeat steps 1 to 2 using solutions FB 2, FB 3 and FB 4 separately, adding each solution in turn to all the other solutions.**

FB	**1**	**2**	**3**	**4**
1	▨	🟨	🟧	
2	🟨	▨		
3	🟧		▨	
4				▨

•1 mark for the table

[2]

(ii) Describe, with reference to the reactions occurring, how you would use the observations to confirm the identities of **FB 1**, **FB 2**, **FB 3**, and **FB 4**.

	HCl	**Na_2CO_3**	**$Ba(NO_3)_2$**	**$AlCl_3$**
HCl	▨	**CO_2 evolved**	**No reaction**	**No reaction**
Na_2CO_3		▨	**White ppt**	**White ppt + CO_2 evolved**
$Ba(NO_3)_2$			▨	**No reaction**
$AlCl_3$				▨

•The solution that forms a white ppt with one other solution is aqueous $Ba(NO_3)_2$, as Ba^{2+} will form a precipitate with carbonate.

•The solution that effervescence with one other solution is dilute HCl, as HCl will liberate CO_2 from Na_2CO_3.

•The solution that forms a white ppt with effervescence with one other solution is aqueous $AlCl_3$ as $AlCl_3$ will form a precipitate and liberate CO_2 from Na_2CO_3.

•The solution that forms only a white ppt with one solution, effervescence with another solution, and with the last solution, white ppt with effervescence is Na_2CO_3.

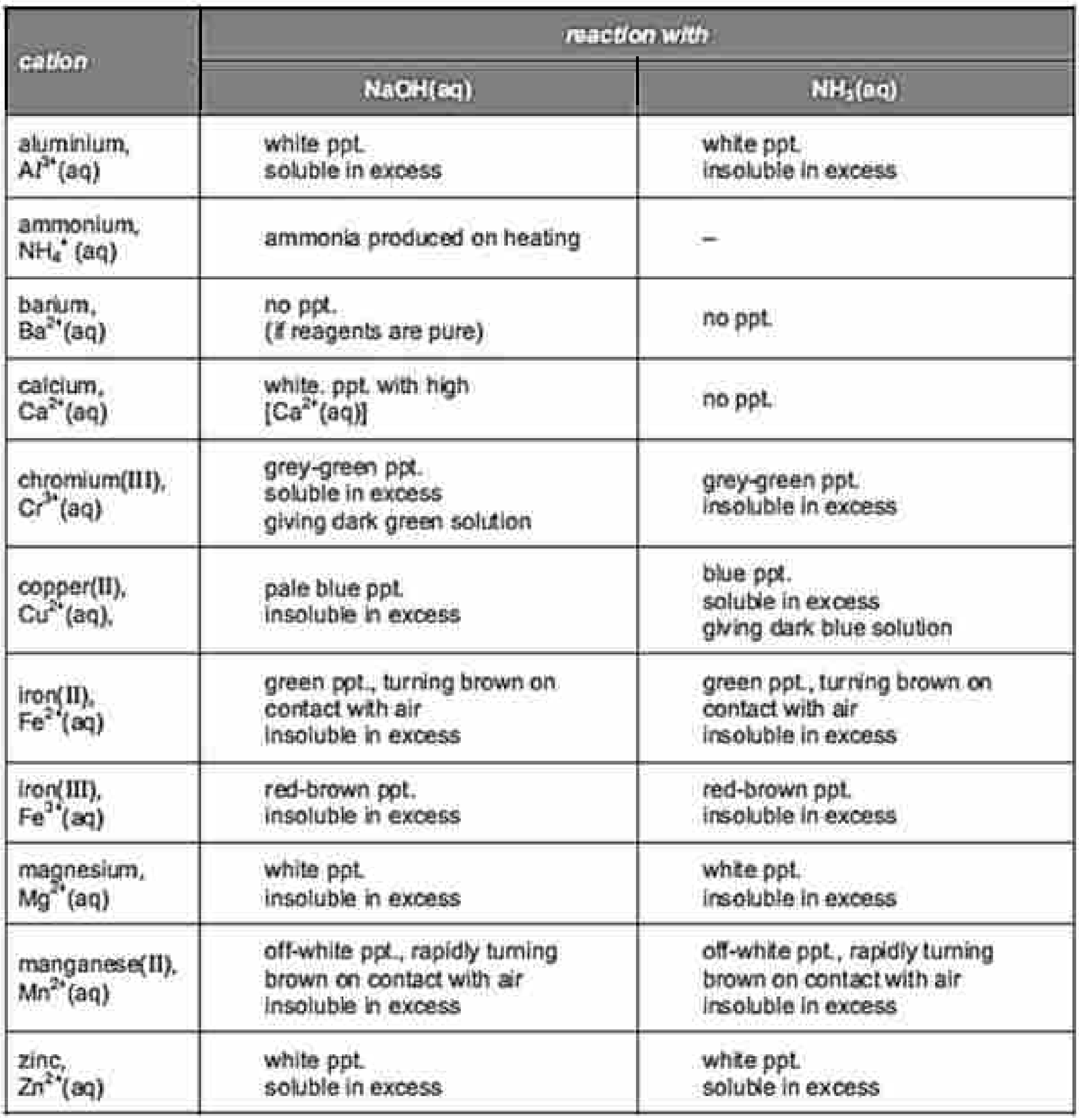
[4]

[Total: 17]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations



cation	reaction with	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

RAFFLES INSTITUTION
2018 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

24 September 2018
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write in **soft pencil**.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, class and index number in the spaces provided on the Answer Sheet.

There are **thirty** questions in this section. Answer **all** questions.

For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in the question booklet.

This document consists of **18** printed pages.

For each question, there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 A sample of iron contains three isotopes: iron-54, iron-56 and iron-58. Its relative atomic mass is 55.849. One of the isotopes has a percentage abundance of 91.8%.

isotope	accurate isotopic mass	percentage abundance
iron-54	53.94	*x*
iron-56	55.94	*y*
iron-58	57.93	*z*

Which row gives the correct values of *x*, *y* and *z*?

	x	*y*	*z*
A	91.8	6.37	1.83
B	1.83	91.8	6.37
C	6.37	91.8	1.83
D	1.83	6.37	91.8

2 S_2Cl_x disproportionates completely in water to give S and SO_2 in the ratio of 3:1.

What is the value of *x*?

A 2

B 4

C 6

D 8

3 Which ion would undergo the greatest deflection in an electric field?

A $^{15}N_2^{+}$

B $^{12}C^{16}O_2^{3+}$

C $^{12}C^{16}O^{2+}$

D $^{16}O^{18}O^{2+}$

4 The radioactive isotope $^{241}_{95}\text{Am}$ is a synthetic isotope used in ionisation smoke detectors.

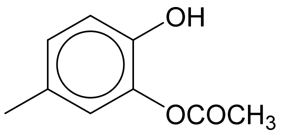
$^{241}_{95}\text{Am}$ decays to give an element **E** and emits a high energy α-particle (which is a helium nucleus, $^{4}_{2}\text{He}$). No other particle is produced.

$$^{241}_{95}\text{Am} \rightarrow \ ^{4}_{2}\text{He} + \textbf{E}$$

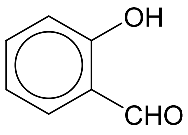
Which row in the table correctly describes the nuclear make-up of element **E**?

	number of protons	number of neutrons
A	91	144
B	91	237
C	93	144
D	93	237

5 Which statement about both molecules shown below is correct?



F



G

A Both can turn hot acidified potassium dichromate(VI) from orange to green.

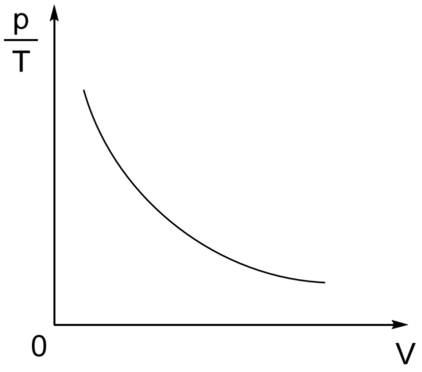
B **G** can form intramolecular hydrogen bonding while **F** cannot.

C Both molecules have the same number of π electrons.

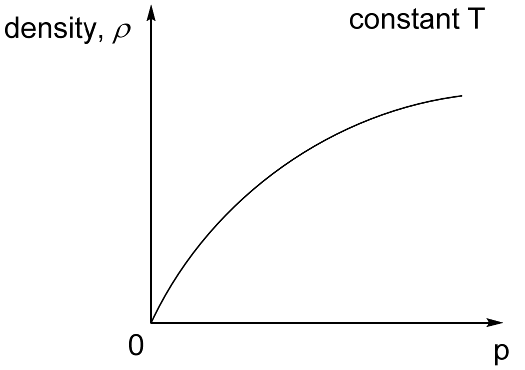
D Both molecules are planar.

6 Which graph represents the correct behaviour for a fixed mass of an ideal gas? (Assume that all temperatures are measured in Kelvin.)

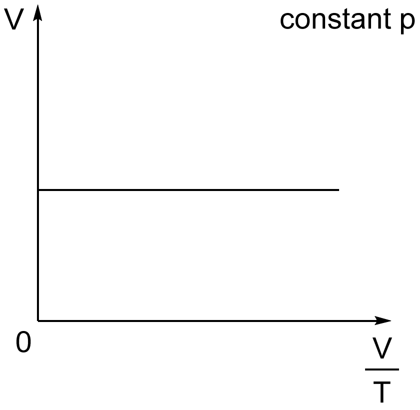
A



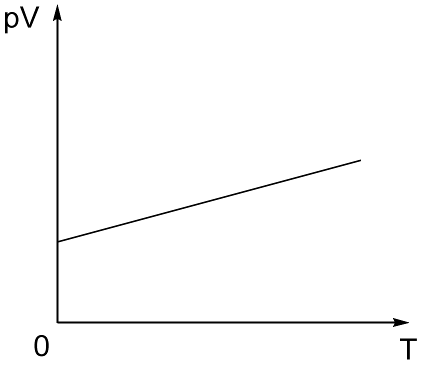
C



B



D

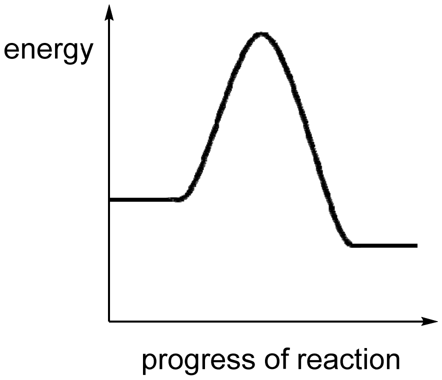


7 *Use of the Data Booklet is relevant to this question.*

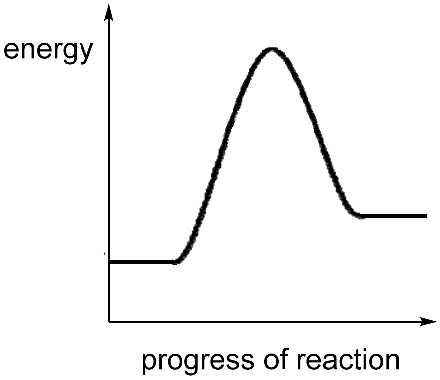
Methane undergoes free radical substitution with bromine in the presence of UV light.

Which energy profile diagram represents the propagation steps that lead to the formation of bromomethane?

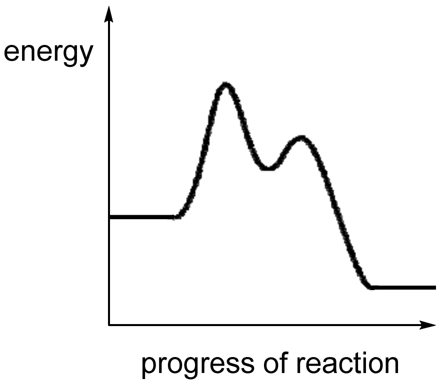
A



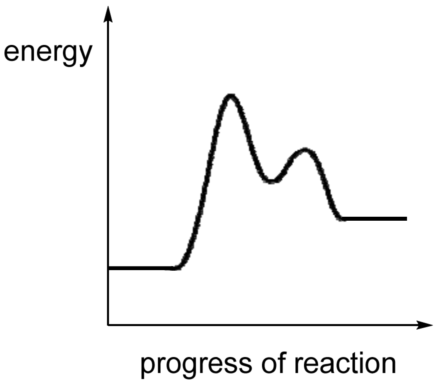
C



B



D



8 Which is **not** a trend from left to right across the elements of the third period of the Periodic Table?

A The maximum oxidation number increases.

B The melting point of the oxides decreases.

C The pH of the aqueous solutions of the chlorides decreases.

D The nature of bonding of the chlorides change from ionic to covalent.

9 Elements **J**, **K** and **L** are elements in Period 3 of the Periodic Table. The melting point of element **J** is higher than that of element **K**. Only the oxide of element **L** is insoluble in water.

Which row in the table gives the correct identities of elements **J**, **K** and **L**?

	J	**K**	**L**
A	C*l*	P	Mg
B	Na	Mg	Si
C	P	S	A*l*
D	S	P	Si

10 The reaction between NO_2 and SO_2 is a key stage in the formation of acid rain.

$$NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$$

A series of experiments was conducted with various concentrations of NO_2 and SO_2 in the absence of air.

experiment	$[NO_2]$ / mol dm^{-3}	$[SO_2]$ / mol dm^{-3}	relative rate
1	0.010	0.20	1
2	0.020	0.20	2
3	0.040	0.40	8

The half-life of NO_2 in experiment 1 was 48 seconds.

Which row gives the correct half-life of NO_2 in experiments 2 and 3?

	half-life in experiment 2	half-life in experiment 3
A	24 s	6 s
B	24 s	24 s
C	48 s	24 s
D	48 s	48 s

11 A pink coloured compound, **M**, reacts with OH^- to give a colourless compound, **N**.

$$\underset{\text{pink}}{\mathbf{M}} + OH^- \longrightarrow \underset{\text{colourless}}{\mathbf{N}}$$

A series of experiments was carried out using different volumes of the 2 reagents, **M**(aq) and NaOH(aq).

The following results were obtained.

experiment	volume of 0.001 mol dm^{-3} **M** / cm^3	volume of 0.1 mol dm^{-3} NaOH / cm^3	volume of water / cm^3	time taken for pink colour to fade / s
1	1	10	4	100
2	2	10	3	100
3	1	5	9	200
4	2	20	8	?

Which conclusions follow from these results?

1 The reaction is first order with respect to **M**.
2 The reaction is first order with respect to OH^-.
3 The time taken for the pink colour to fade in experiment 4 was 50 s.

A 1 and 2
B 2 and 3
C 1 and 3
D 1, 2 and 3

12 Consider the following reversible reaction.

$$\mathbf{Q}(g) + \mathbf{R}(g) \rightleftharpoons \mathbf{S}(g) \qquad \Delta H < 0$$

After equilibrium was reached, the system was disturbed and the changes to the system were monitored. The changes were as follows.

[**S**]	K_p	rate of forward reaction	rate of backward reaction
increased	unchanged	increased	increased

What was the disturbance applied?

A addition of a catalyst

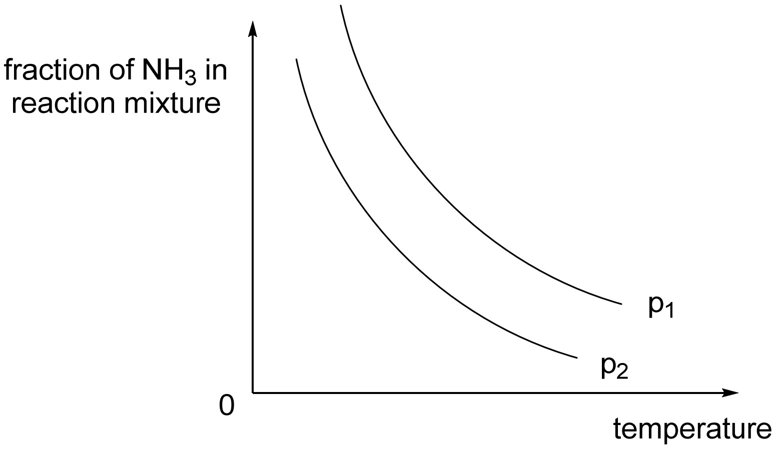
B increase in temperature

C compression of reaction mixture

D addition of an inert gas at constant volume

13 The graph below shows how the fraction of $NH_3(g)$ in the equilibrium mixture of the Haber process varies with temperature at pressures of p_1 and p_2.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H_r = \boldsymbol{x} \text{ kJ mol}^{-1}$$



Which row in the table is correct?

A	$\boldsymbol{x} < 0$	$p_1 > p_2$
B	$\boldsymbol{x} < 0$	$p_1 < p_2$
C	$\boldsymbol{x} > 0$	$p_1 > p_2$
D	$\boldsymbol{x} > 0$	$p_1 < p_2$

14 *Use of the Data Booklet is relevant to this question.*

Which expression gives the pH of a 0.2 mol dm^{-3} NH_3(aq) solution at 25 °C?
(K_a of NH_4^+ = 5.6 × 10^{-10} mol dm^{-3})

A $-\lg\sqrt{0.2 \times 5.6 \times 10^{-10}}$

B $14 + \lg\sqrt{0.2 \times 5.6 \times 10^{-10}}$

C $-\lg\sqrt{0.2 \times \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}}}$

D $14 + \lg\sqrt{0.2 \times \dfrac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}}}$

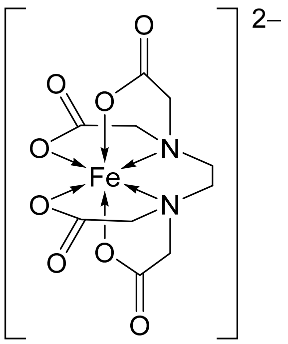
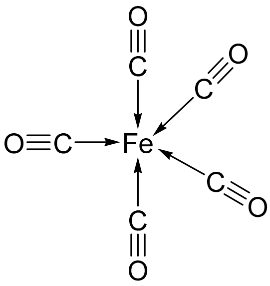
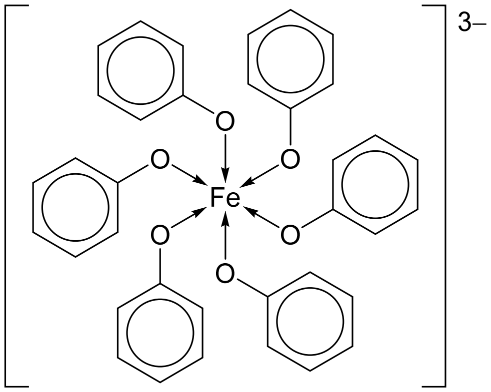
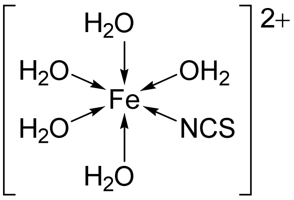
15 Which pairs of substances, when mixed in equal volumes, produce a buffer solution?

1 0.05 mol dm^{-3} HCl(aq) and 0.08 mol dm^{-3} Na_3PO_4(aq)
2 0.05 mol dm^{-3} CH_3CO_2H(aq) and 0.08 mol dm^{-3} NaOH(aq)
3 0.08 mol dm^{-3} $HO_2C–CO_2H$(aq) and 0.05 mol dm^{-3} NaOH(aq)

A 1 only
B 1 and 3
C 2 and 3
D 1, 2 and 3

16 Iron can form complexes with variable oxidation states.

Which row gives the **incorrect** oxidation number of Fe in the iron complex?

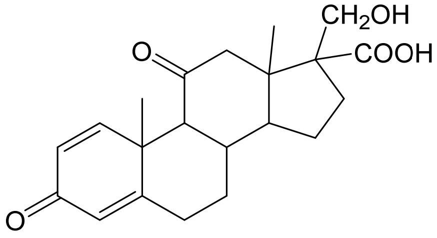
	iron complex	oxidation number of Fe
A		+4
B		0
C		+3
D		+3

17 Adding concentrated HC*l* to $CuSO_4$(aq) causes the colour of the solution to change from blue to green.

Which row best explains this observation?

	number of d-electrons in copper	energy gap between the d-orbitals
A	changes	changes
B	changes	remains the same
C	remains the same	changes
D	remains the same	remains the same

18 Compound **T** is a derivative of a drug used to treat inflammatory and autoimmune diseases.



T

Compound **T** is heated with hydrogen in the presence of a nickel catalyst.

What is the number of stereoisomers for the product formed?

A 2^5

B 2^6

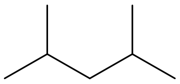
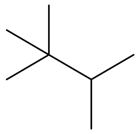
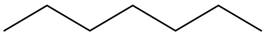
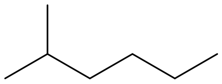
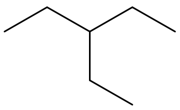
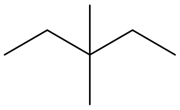
C 2^8

D 2^9

19 **U** and **V** are structural isomers with molecular formula C_7H_{16}.

Both **U** and **V** produce the same number of possible structural isomers upon reaction with chlorine to form monochlorinated compounds with the formula $C_7H_{15}Cl$.

Which pairs are possible structures of **U** and **V**?

	U	**V**
1		
2		
3		

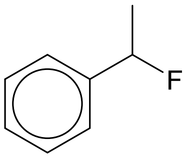
A 1 only

B 1 and 3

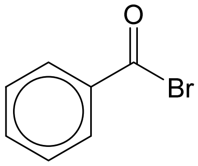
C 2 and 3

D 1, 2 and 3

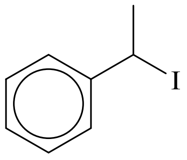
20 Equal amounts of compounds **X**, **Y** and **Z** are added separately to three test-tubes containing equal concentrations of ethanolic silver nitrate solution. The test-tubes are then placed in a heated water bath. No precipitate forms in one of the tubes. In the other two tubes, precipitates form at different rates.



X



Y

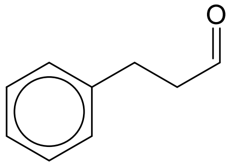


Z

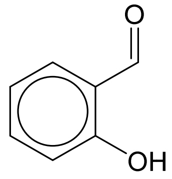
Which row in the table is correct?

	compound which does not form precipitate	colour of precipitate which forms the fastest
A	**Y**	yellow
B	**Z**	pale cream
C	**X**	yellow
D	**X**	pale cream

21 3-phenylpropanal and 2-hydroxybenzaldehyde are used in essential oils.



3-phenylpropanal



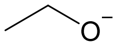
2-hydroxybenzaldehyde

Which reagents could be used to distinguish between the two compounds?

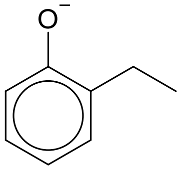
1 Fehling's reagent
2 $[Ag(NH_3)_2]^+$
3 $SOCl_2$

A 1 only
B 1 and 2
C 2 and 3
D 3 only

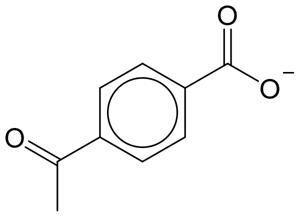
22 Consider the following four compounds.



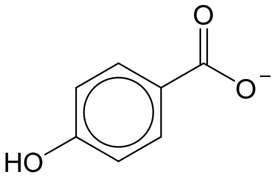
E



F



G

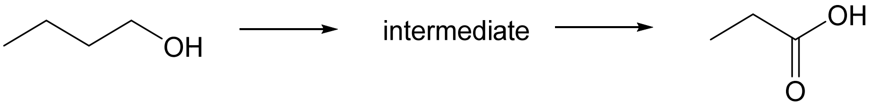


H

What is the relative order, in decreasing basicity, of these compounds?

A **E** > **F** > **H** > **G**
B **G** > **H** > **F** > **E**
C **E** > **F** > **G** > **H**
D **H** > **G** > **F** > **E**

23 Which pair of reactions could have the same reaction intermediate?

1


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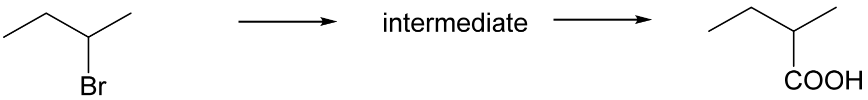


3


4

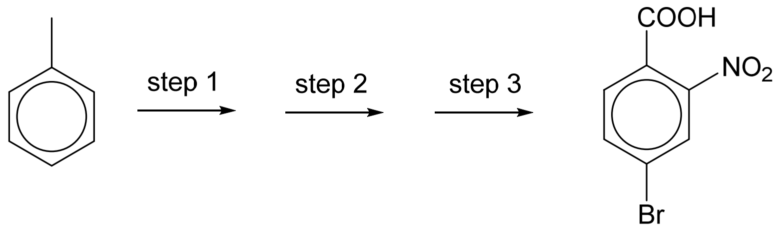

A 1 and 2

B 1 and 4

C 2 and 3

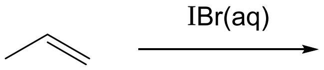
D 3 and 4

24 Which row gives the synthetic route that will lead to the highest yield of the product?

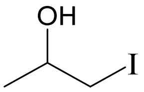


	step 1	step 2	step 3
A	$FeBr_3$, Br_2	$KMnO_4$, H_2SO_4, heat	conc. H_2SO_4, conc. HNO_3, heat
B	$KMnO_4$, H_2SO_4, heat	$FeBr_3$, Br_2	conc. H_2SO_4, conc. HNO_3, heat
C	conc. H_2SO_4, conc. HNO_3, heat	$KMnO_4$, H_2SO_4, heat	$FeBr_3$, Br_2
D	conc. H_2SO_4, conc. HNO_3, heat	$FeBr_3$, Br_2	$KMnO_4$, H_2SO_4, heat

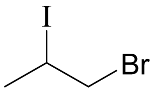
25 Which product will **not** be formed in the following reaction?



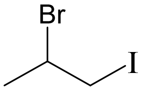
A



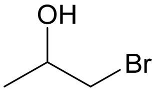
C



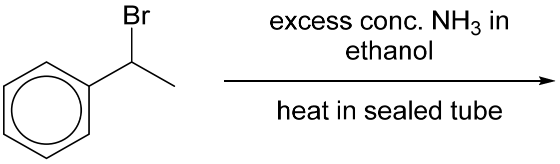
B



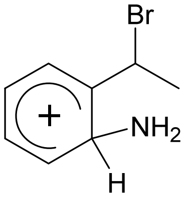
D



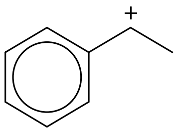
26 Which species could be an intermediate of the following reaction?



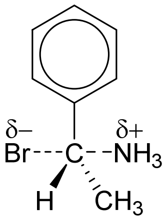
A



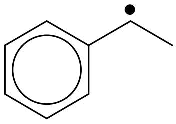
C



B



D



27 A non-cyclic organic compound has the molecular formula $C_4H_5O_2N$. The compound is neutral and does not decolourise Br_2 in CCl_4.

Which pair of functional groups could be present in this molecule?

1 one amide group and one ketone group
2 one ester group and one amine group
3 one ester group and one nitrile group

A 1 only
B 3 only
C 1 and 2
D 2 and 3

28 The solubility products of $ZnCO_3$ and Ag_2CO_3 in water are shown in the table below.

carbonate	solubility product at 25 °C
$ZnCO_3$	1.46×10^{-10} mol^2 dm^{-6}
Ag_2CO_3	8.46×10^{-12} mol^3 dm^{-9}

A solution contains 0.02 mol dm^{-3} $Zn(NO_3)_2$ and 0.02 mol dm^{-3} $AgNO_3$ at 25 °C.
Zn^{2+} and Ag^+ can be separated by adding solid Na_2CO_3 slowly.

Which statement is correct?

A Ag_2CO_3 will be precipitated before $ZnCO_3$.

B The solubility of Ag_2CO_3 in water is 2.04×10^{-4} mol dm^{-3}.

C At any point in time, only one compound, Ag_2CO_3 or $ZnCO_3$, can be precipitated.

D When the more soluble compound first starts to precipitate, the concentration of carbonate ions in the solution is 2.12×10^{-8} mol dm^{-3}.

29 *Use of the Data Booklet is relevant to this question.*

The anodising of aluminium allows highly reactive aluminium to be safely used as a construction material.

A piece of aluminium object was placed in dilute sulfuric acid and anodised with a direct current of 1.4 A. After *t* seconds, the mass of the oxide layer formed is 23.7 g.

Which expression gives the time taken, *t*, for this anodisation?

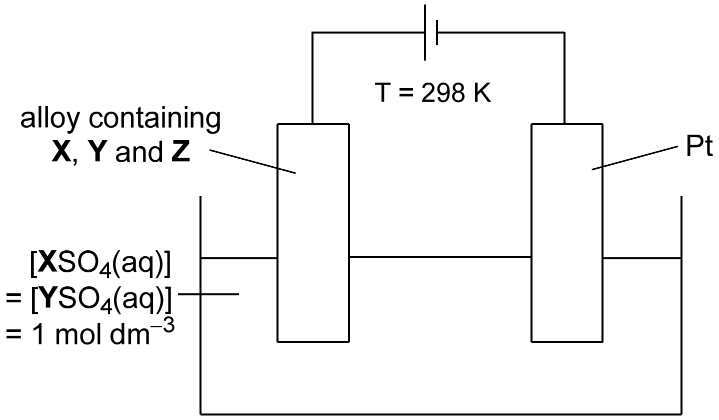
A $\dfrac{23.7 \times 96500}{102 \times 1.4}$

B $\dfrac{3 \times 23.7 \times 96500}{2 \times 102 \times 1.4}$

C $\dfrac{3 \times 102 \times 1.4}{2 \times 23.7 \times 4 \times 96500}$

D $\dfrac{3 \times 23.7 \times 4 \times 96500}{2 \times 102 \times 1.4}$

30 In an electrolysis set-up in a beaker, an alloy containing **X**, **Y** and **Z** was used as an electrode as shown.



After some time, the amounts of **X** and **Y** in the alloy decreased while unreacted **Z** was found at the bottom of the beaker. **X** was also deposited on the platinum electrode.

Based on the information above, which options are correct?

1 $E^\ominus(\mathbf{X}^{2+}/\mathbf{X}) > E^\ominus(H_2O/H_2)$

2 $E^\ominus(\mathbf{Z}^{2+}/\mathbf{Z}) < E^\ominus(\mathbf{X}^{2+}/\mathbf{X}) < E^\ominus(\mathbf{Y}^{2+}/\mathbf{Y})$

3 When the polarity of the battery is reversed, H_2 is produced at the Pt electrode.

A	1 only	**C**	2 and 3
B	1 and 3	**D**	1, 2 and 3

2018 Y6 H2 Chemistry Preliminary Examinations Paper 1 (Suggested Solutions)

Question	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Answer	C	A	C	C	C	A	B	B	D	C	A	C	A	D	B
Question	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Answer	A	C	D	B	D	A	A	B	D	D	C	B	D	D	A

RAFFLES INSTITUTION
2018 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions **11 September 2018**
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided at the top of this page.
Write in dark blue or black pen in the spaces provided.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 8**
2	**/ 13**
3	**/ 16**
4	**/ 13**
5	**/ 10**
6	**/ 15**
Total	**/ 75**

This document consists of **23** printed pages.

Answer **all** the questions in the spaces provided.

1 Gemstones such as amethysts, pearls and malachites contain compounds of main group and transition elements.

Fig. 1.1 shows the logarithm of the ionisation energies, log (IE), for the outermost ten electrons in an atom of an element **X**, which has atomic number smaller than 20.

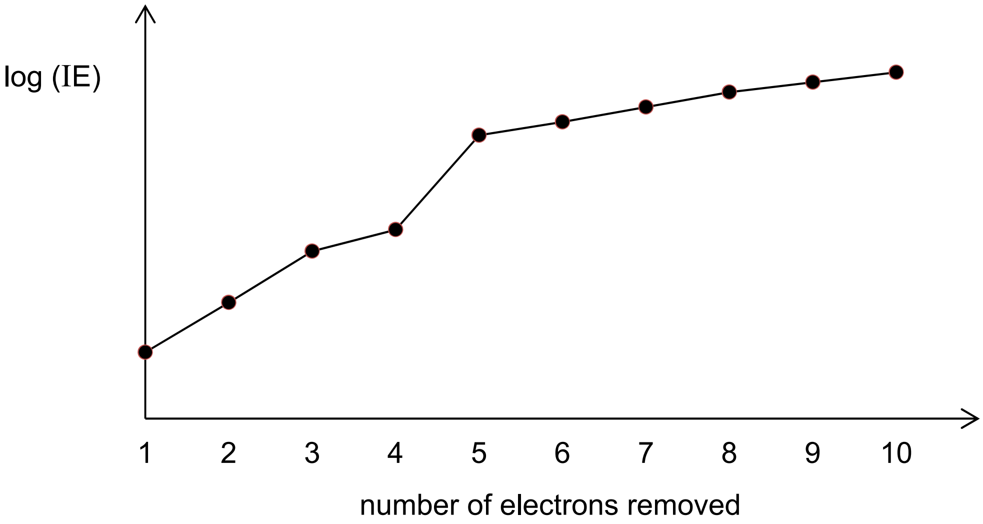


Fig. 1.1

(a) Deduce which Group in the Periodic Table **X** belongs to and state the identity of **X**. Explain your answer.

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……………………………………………………………………………………………………[3]

(b) The colour of amethyst is caused by the presence of compounds containing manganese and iron.

Explain why the first ionisation energies of manganese and iron are similar.

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……………………………………………………………………………………………………[3]

For examiner's use

(c) *Use of the Data Booklet is relevant to this question.*

Malachites contain copper(II) carbonate while pearls contain calcium carbonate. Predict whether calcium carbonate or copper(II) carbonate has a higher decomposition temperature. Explain your answer.

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…………………………………………………………………………………………… [2]

[Total: 8]

2 **(a)** Polycyclic aromatic hydrocarbons (PAHs) are potential carcinogens.

Anthracene is an example of a PAH and its Kekulé structure is shown in Fig. 2.1.

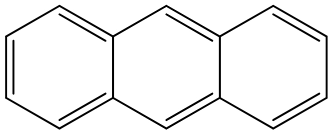

Fig. 2.1

(i) A compound is aromatic if it satisfies the following criteria:

- it is a cyclic planar molecule,
- it has a delocalised π electron system, and
- it has (4n + 2) π electrons, where n is an integer.

By considering the hybridisation of the carbon atoms in anthracene and the criteria for aromaticity, explain why anthracene is aromatic.

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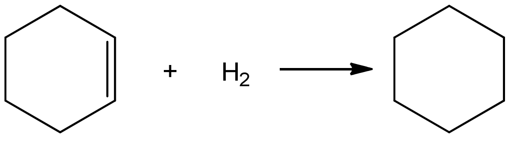
……………………………………………………………………………………………[3]

(ii) The enthalpy change of hydrogenation of cyclohexene to cyclohexane is -118 kJ mol^{-1}.



Using the Kekulé structure given in Fig. 2.1, calculate the enthalpy change of complete hydrogenation of anthracene, ΔH_1.

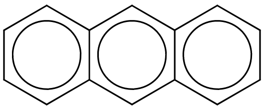
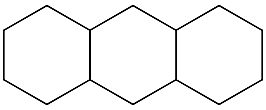
[1]

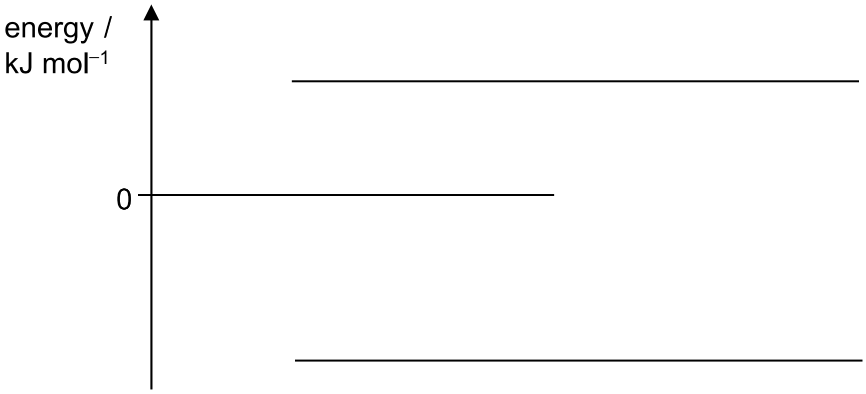
(iii) Fig. 2.2 is the actual representation of anthracene.

Fig. 2.2

Complete the energy level diagram below using the data in Table 2.1.
Hence, calculate the actual value for the enthalpy change of complete hydrogenation of anthracene, ΔH_2.

Table 2.1

compound	formula	enthalpy change of formation / kJ mol^{-1}
 anthracene	$C_{14}H_{10}(s)$	+129
 tetradodecahydroanthracene	$C_{14}H_{24}(s)$	–356



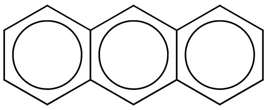
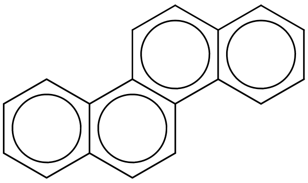
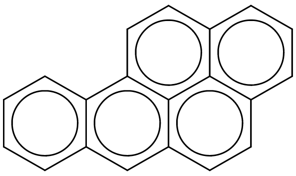
ΔH_2 = ……………………………….. [3]

(iv) Using your answers to **(a)(ii)** and **(a)(iii)**, calculate the resonance energy of anthracene.

[1]

(b) Table 2.2 shows some information on anthracene and other PAHs found in smoked fish.

Table 2.2

PAH	structure	mean concentration (C_m) / ppm	Toxicity Equivalency Factor (TEF)
anthracene $C_{14}H_{10}$		0.029	0.01
chrysene $C_{18}H_{12}$		0.135	0.01
benzo[a]pyrene $C_{20}H_{12}$		0.204	1.00

(i) The carcinogenic toxic equivalent (TEQ) of PAHs in smoked fish can be calculated using equation 2.1.

TEQ = Sum of [C_m (in ppm) $\times$ TEF] ------ equation 2.1

Using equation 2.1 and the data from Table 2.2, calculate the TEQ of smoked fish.

[1]

(ii) For an average person, the excess cancer risk (ECR) resulting from exposure to PAHs through smoked fish consumption can be determined using equation 2.2.

$$\text{ECR} = \frac{\text{TEQ}}{\text{body weight in kg}} \times 1.37 \times 10^{-3} \text{ ------ equation 2.2}$$

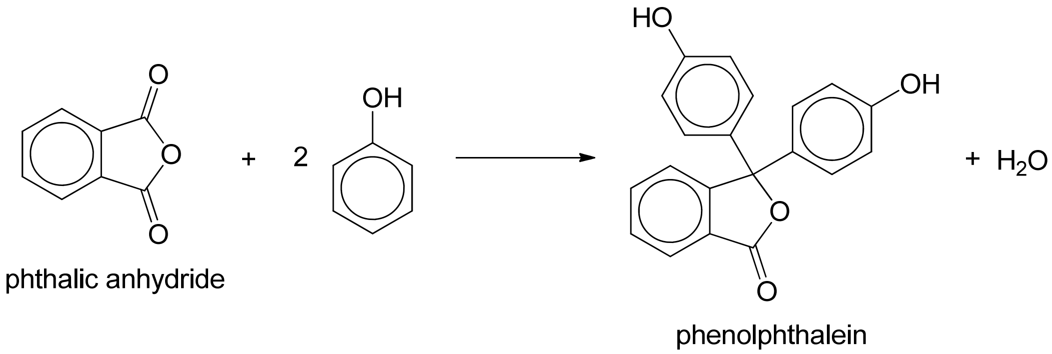
Given that the acceptable ECR value set by United States Environmental Protection Agency is 1.0×10^{-6}, use equation 2.2 to determine the ECR value due to the consumption of smoked fish by a 70 kg person. Hence, state whether the person is at risk of cancer.

[1]

For examiner's use

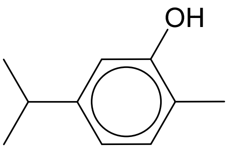
(c) Phenolphthalein is formed when phenol undergoes electrophilic substitution with phthalic anhydride.

The overall equation for the reaction is shown below.



(i) As phenolphthalein is a carcinogen, it has been replaced by thymolphthalein, which can be formed by a similar reaction between thymol and phthalic anhydride.

By using the structure of thymol as shown below, draw the structure of thymolphthalein.



thymol

[1]

(ii) Explain whether thymol or phenol undergoes electrophilic substitution more readily.

……………………………………………………………………………………………………..

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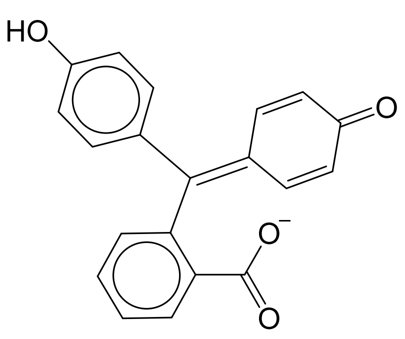
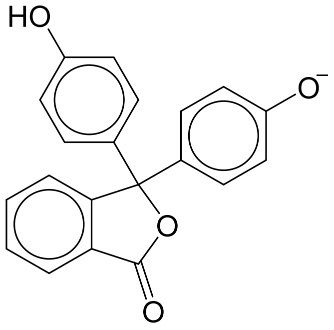
……………………………………………………………………………………………………[1]

(d) Phenolphthalein indicator is colourless. Under basic conditions, phenolphthalein undergoes dissociation to form its conjugate base, which is pink in colour.

The conjugate base of phenolphthalein is found to be **A** and **not B**.



A



B

Explain why the structure of **A** is more stable than that of **B**.

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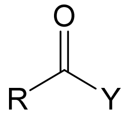
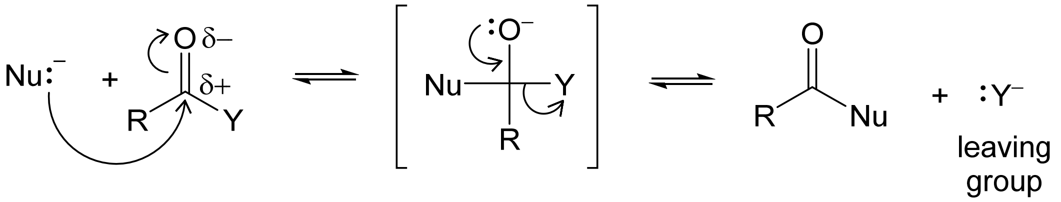
…………………………………………………………………………………………………[1]

[Total: 13]

3 (a) Acid derivatives, RCOY, are compounds formed when the –OH group of carboxylic acid is replaced by a different group (Y). They have the general structure as shown below.



Acid derivatives undergo nucleophilic acyl substitution, with the general mechanism shown below:



The mechanism involves the heterolytic fission of the C−Y bond, resulting in Y leaving with a pair of electrons as Y^-. Y^- is called the leaving group.

When RCOY undergoes nucleophilic acyl substitution, one factor that affects its reactivity is the basicity of Y^-. In general, the stronger Y^- is as a Lewis base, the poorer it is as a leaving group. This results in RCOY being less reactive towards nucleophilic acyl substitution.

(i) Suggest why strong Lewis bases are poor leaving groups.

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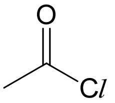
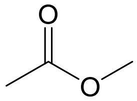
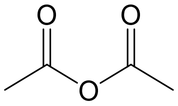
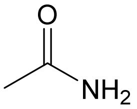
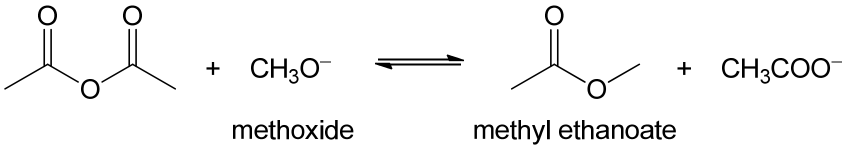
Table 3.1 shows the four most common types of acid derivatives and the pK_b of Y^-.

Table 3.1

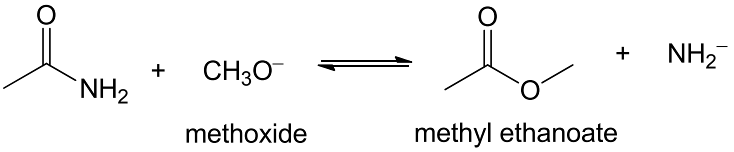
functional group	example of acid derivative	leaving group, Y^-	pK_b of Y^-
acyl chloride	 ethanoyl chloride	Cl^-	21
ester	 methyl ethanoate	CH_3O^-	−2
acid anhydride	 ethanoic anhydride	CH_3COO^-	9
amide	 ethanamide	NH_2^-	−24

(ii) A student proposed two reactions to synthesise methyl ethanoate using methoxide ions.

Reaction **1**



Reaction **2**



With reference to the pK_b values given in Table 3.1, explain why reaction **1** is a better method to synthesise methyl ethanoate than reaction **2**.

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(b) Methyl ethanoate can also be synthesised from methanol and ethanoic acid. The reaction is reversible and does not go to completion.

Reaction **3** $CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$

Table 3.2 shows the densities and molar masses of methanol and ethanoic acid.

Table 3.2

compound	density / g cm^{-3}	molar mass / g mol^{-1}
methanol	0.792	32.0
ethanoic acid	1.05	60.0

To determine the equilibrium constant, K_c, for this reaction, a student mixed 20.0 cm^3 of ethanoic acid with 20.0 cm^3 of methanol, and left the mixture to stand for one week to reach equilibrium.

5.0 cm^3 of the equilibrium mixture was pipetted out and added to 100 cm^3 of ice-cold water in a conical flask. The resultant mixture required 16.80 cm^3 of 0.500 mol dm^{-3} aqueous NaOH for complete reaction.

(i) Calculate the initial amount of methanol used in the reaction.

[1]

(ii) Calculate the amount of ethanoic acid present in the equilibrium mixture. Assume that the total volume of the equilibrium mixture is 40.0 cm^3.

[2]

(iii) Write an expression for the K_c of reaction **3**.

[1]

(iv) Given that the initial amount of ethanoic acid used is 0.350 mol, calculate a value for K_c.

[2]

(v) Explain why 5.0 cm^3 of the equilibrium mixture was added to 100 cm^3 of ice-cold water before it was titrated against aqueous NaOH.

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(c) Methyl ethanoate and ethyl methanoate are isomers. Suggest a simple chemical test which can distinguish between them. Write equations for the reactions that occur for the ester that gives the positive test.

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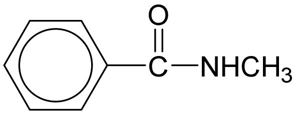
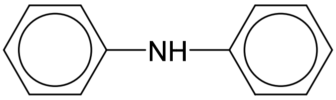
………..[3]

For examiner's use

(d) Compounds **P** and **Q** are solids at room temperature and are insoluble in water. They have the structures shown below.



compound **P**



compound **Q**

A student added some **Q** to **P** by mistake. Outline how **P** can be separated from **Q**. Briefly explain your answer.

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[Total: 16]

4 Magnesium sulfate heptahydrate, $MgSO_4{\cdot}7H_2O$, commonly called Epsom salt, has been traditionally used as a component of bath salts.

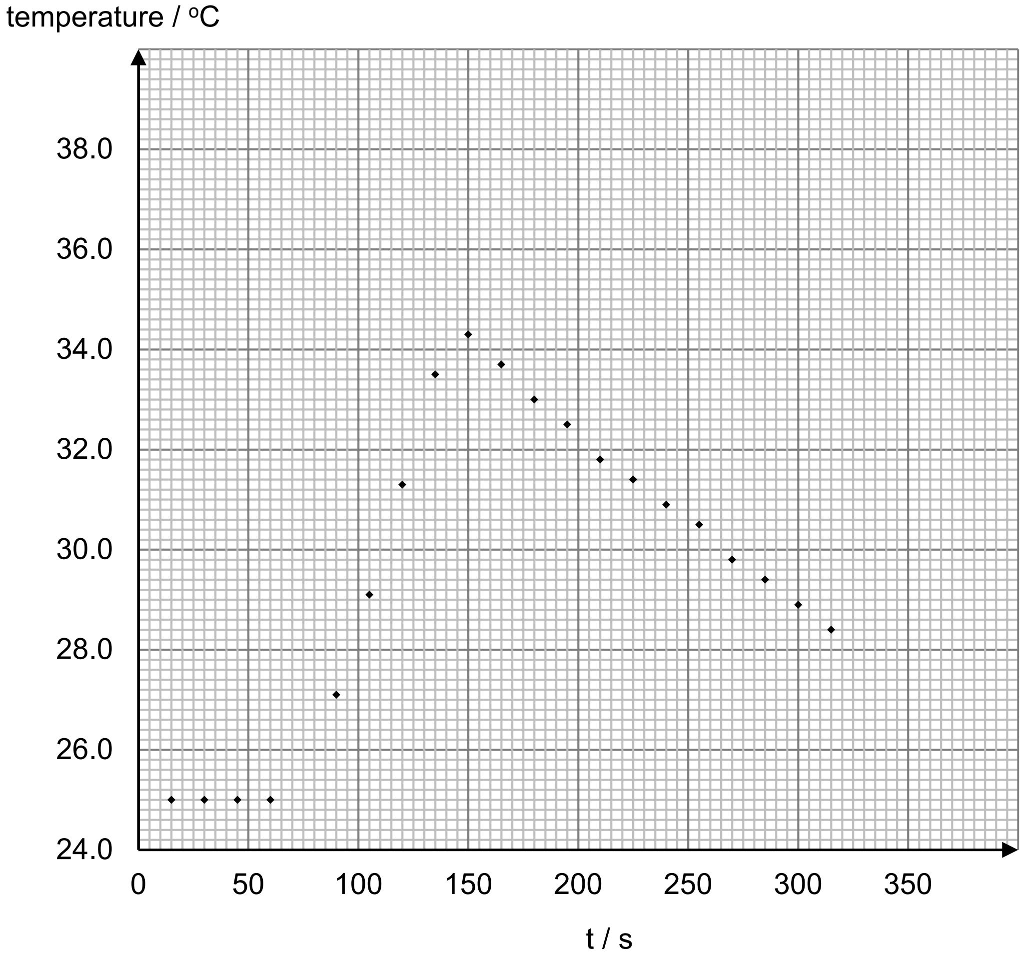
(a) The standard enthalpy change of the following reaction, $\Delta H_r^\ominus$, cannot be determined directly.

$$MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4{\cdot}7H_2O(s) \qquad \Delta H_r^\ominus$$

An experiment was performed to determine the standard enthalpy change of solution, $\Delta H_{sol}^\ominus$, of anhydrous $MgSO_4$ and Hess' Law was then used to calculate $\Delta H_r^\ominus$.

The experimental procedure involved using a data logger to measure the temperature of the mixture when 7.500 g of anhydrous $MgSO_4$ was added to 100 cm^3 of water in a Styrofoam cup at t = 75 s.

A graph of temperature against time was plotted.



(i) Explain what is meant by the term *standard enthalpy change of solution*, $\Delta H_{sol}^\ominus$.

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……………………………………………………………………………………………[2]

(ii) Determine the maximum temperature change of the reaction, ΔT, from the graph. Show all construction lines and working clearly.

[2]

(iii) Using your answer to **(a)(ii)**, calculate the experimental $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$. You may assume that the density of the solution is 1 g cm^{-3} and its specific heat capacity is 4.18 J g^{-1} K^{-1}.

[2]

(iv) The actual value of $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$ is –88.0 kJ mol^{-1}. Other than the assumptions made above, give a reason for the discrepancy between this value and your answer in **(a)(iii)**.

Hence, suggest a possible improvement to the experimental procedure.

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……………………………………………………………………………………………[2]

(v) The $\Delta H_{sol}^{\ominus}$ of hydrated magnesium sulfate, $MgSO_4{\cdot}7H_2O$, is +16.0 kJ mol^{-1}. Using the $\Delta H_{sol}^{\ominus}$ of anhydrous $MgSO_4$ given in **(a)(iv)**, calculate $\Delta H_r^{\ominus}$.

[1]

(b) Using the data in Table 5.1 and relevant data from the *Data Booklet*, construct an energy level diagram to calculate the standard enthalpy change of formation, $\Delta H_f^\ominus$, of $SO_4^{2-}(g)$.

Table 5.1

standard enthalpy change of formation of anhydrous $MgSO_4$, $\Delta H_f^\ominus(MgSO_4(s))$	–1278 kJ mol^{-1}
lattice energy of anhydrous $MgSO_4$	–2705 kJ mol^{-1}
standard enthalpy change of atomisation of Mg(s), $\Delta H_{at}^\ominus(Mg(s))$	+148 kJ mol^{-1}

[4]

[Total: 13]

For examiner's use

5 **(a)** *Use of the Data Booklet is relevant to this question.*

The $Ag^+(aq)/Ag(s)$ half-cell was connected to the $Cu^{2+}(aq)/Cu(s)$ half-cell, and the standard e.m.f. was measured.

(i) Draw a fully labelled diagram to show the set-up for measuring the standard e.m.f. of the above cell.

In your diagram, show clearly the direction of the electron flow in the external circuit.

[3]

(ii) Calculate the $E^\ominus_{cell}$ for this set-up.

[1]

(iii) With the aid of equations, state what is observed in the $Cu^{2+}(aq)/Cu(s)$ half-cell when $NH_3(aq)$ is added slowly to it, until in excess.

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(iv) Predict and explain how the E_{cell} changes after the addition of $NH_3(aq)$.

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(b) The zinc-silver oxide alkaline battery is available in small sizes as button cells and the overall cell reaction is shown below.

$$Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2Ag(s) \qquad E^{\ominus}_{cell} = +1.60\ V$$

Calculate the $\Delta G^{\ominus}$ for the above reaction.

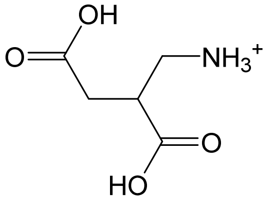
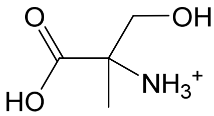
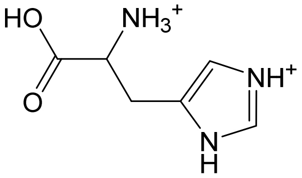
[1]

[Total: 10]

6 In 1969, a large meteorite fell in the village of Murchison, Australia. Over the years, more than 30 different amino acids have been identified in the meteorite by multiple studies. Some of these amino acids are commonly found in proteins, while others are unusual because they are not found in proteins.

The structures of three of the amino acids found in the Murchison meteorite are given in Table 4.1.

Table 4.1

amino acid three letter code	structure of fully protonated amino acid
ams	
msr	
his	

(a) Which two of the three amino acids in Table 4.1 are **not** found in proteins? With reference to their structures, explain your answer.

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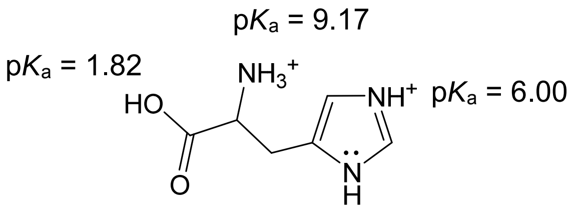
(b) It was suggested that alien organisms could synthesise a dipeptide of the structure *his–msr*. Draw the structure of this dipeptide in the space below.

[1]

The pK_a values of the acidic groups at 25 °C in the fully protonated *his* are labelled below.

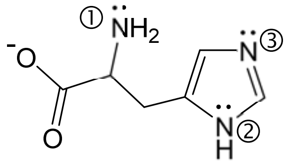


fully protonated *his*

(c) **(i)** Calculate the pK_b values of N① and N③ in the fully **deprotonated** *his* and write them in the boxes below.

[1]

pK_b of N① =



pK_b of N③ =

fully deprotonated *his*

Both N② and N③ in the ring are sp^2 hybridised.

- The lone pair on N② is located in the unhybridised p orbital.
- The lone pair on N③ is located in the sp^2 hybrid orbital.

(ii) State the hybridisation of N①.

……………………………………………………………………………………………[1]

(iii) With reference to your answers in **(c)(i)** and **(c)(ii)**, account for the relative pK_b values of N① and N③.

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……………………………………………………………………………………………[2]

(iv) Explain why N② is **not** basic.

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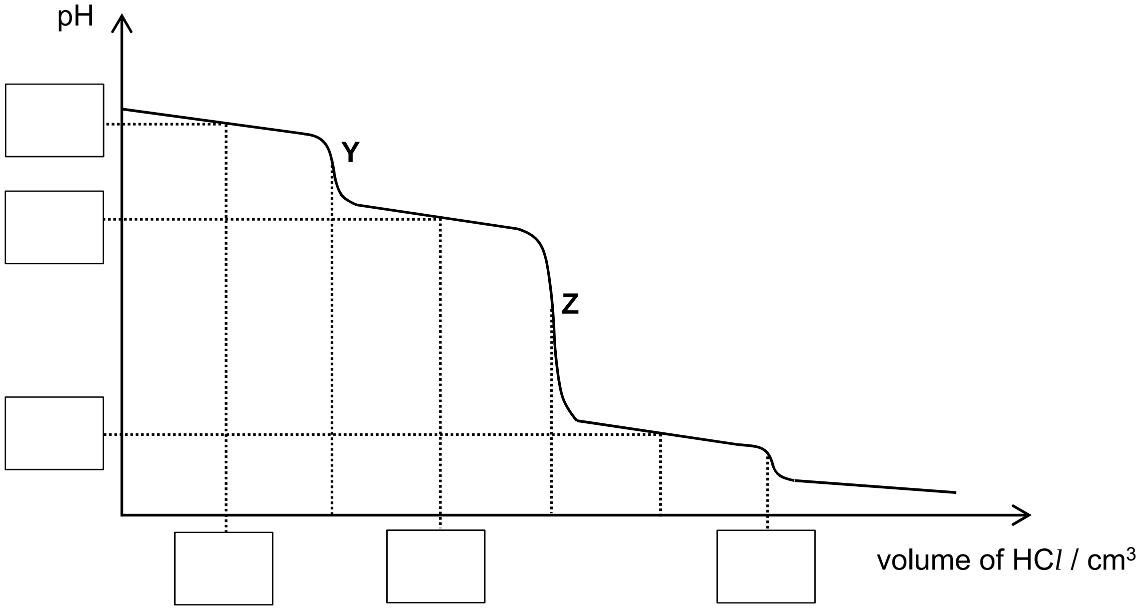
10 cm^3 of 0.1 mol dm^{-3} of the fully **deprotonated** *his* was titrated against 0.1 mol dm^{-3} HC*l*(aq) from a burette. The titration curve is shown below.



(d) Fill in the boxes above with the correct pH values and HC*l* volumes. [2]

(e) Calculate the pH after 6.0 cm^3 of HC*l*(aq) was added from the burette.

[2]

(f) **(i)** Draw the structures of the major species present at points **Y** and **Z** of the titration.

major species at point **Y**	major species at point **Z**

[2]

(ii) The isoelectric point of an amino acid can be defined as the pH at which the amino acid exists predominantly as zwitterions (with no net charge).

By considering your answer in **(f)(i)**, mark the isoelectric point of *his* with an "X" on the titration curve. [1]

[Total: 15]

2018 Y6 H2 Chemistry Preliminary Exams Paper 2 (Suggested Solutions)

1(a) **X** is likely to be in Group 14 as there is a large jump from the 4th to 5th ionisation energies. This shows that the 5^{th} electron is removed from an inner electron shell and requires more energy for removal as it is more strongly attracted to the nucleus. Hence, there are 4 valence electrons in **X**.

Since **X** has at least 10 electrons but fewer than 20 electrons, X is Si.

1(b) Mn and Fe are first-row transition metals. Although Fe has a higher nuclear charge (greater proton number) than Mn, Fe has more 3d electrons which provide more shielding between the nucleus and the outer 4s shell of electrons. This increase in shielding effect offsets the increase in nuclear charge and hence, the increase in effective nuclear charge from Mn to Fe is minimal, resulting in the first ionisation energies of Mn and Fe to be similar.

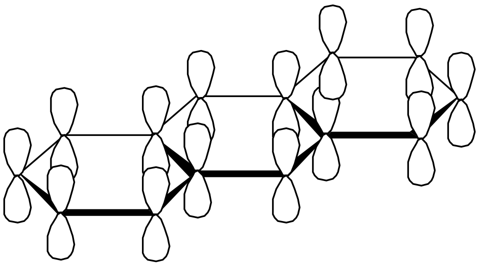
1(c) Ca^{2+} has a larger cationic radius than Cu^{2+}, thus Ca^{2+} has a lower charge density and weaker polarising power.

Consequently, there is lower extent of distortion of the electron cloud of the carbonate anion and hence covalent bonds within the carbonate anion are weakened to a lesser extent. Hence, $CaCO_3$ decomposes at a higher temperature.

2(a)(i) Anthracene is a cyclic molecule. All carbon atoms of anthracene are sp^2 hybridised and are trigonal planar.

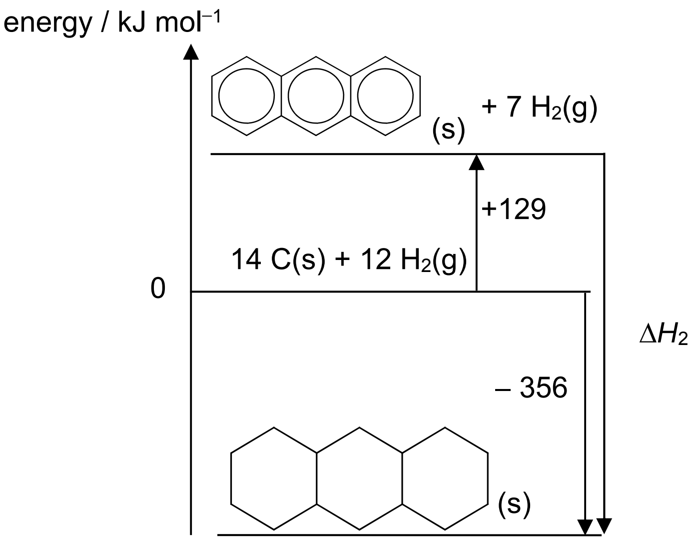
The unhybridised p-orbitals of the carbon atoms in anthracene can form a continuous p-orbital overlap, thus the π electrons are delocalised throughout the molecule.

Anthracene has 4(3) + 2 = 14 π electrons where or n = 3.



2(a)(ii) Enthalpy change of hydrogenation = 7(–118) = –826 kJ mol^{-1}

2(a)(iii)



Enthalpy change of hydrogenation = –356 –129 = $\underline{–485\ \text{kJmol}^{-1}}$

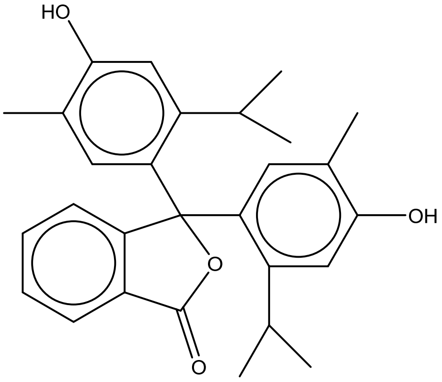
2(a)(iv) Resonance energy = 826 – 485 = $\underline{341\ \text{kJ mol}^{-1}}$

2(b)(i) TEQ = (0.029 x 0.01) + (0.135 x 0.01) + (0.204 x 1.00) = 0.20564 = $\underline{0.206}$

2(b)(ii) ECR = $\frac{0.20564}{70}$ x 1.37 x 10^{-3} = $\underline{4.00 \times 10^{-6}}$

Since the ECR from the consumption of smoked fish exceeds the value set by USEPA, it will be a cancer risk for the 70 kg person.

2(c)(i)



2(c)(ii) Thymol reacts more readily as the alkyl groups of thymol are electron donating and increase the electron density on the benzene ring making it more susceptible to electrophilic substitution.

2(d) The carboxylate anion in **A** is more stable than the phenoxide anion in **B** as the negative charge on oxygen is dispersed over the two highly electronegative oxygen atoms resulting in two equivalent resonance structures in **A** as compared to **B**.

3(a)(i) The stronger the base, the more available is its lone pair of electrons for donation to acid. Hence, a strong Lewis base will readily donate its lone pair to the electron deficient carboxyl C (Lewis acid) to reform the starting acid derivative. Thus, strong Lewis bases are poor leaving groups.

or

Strong Lewis bases donate electron pair more easily and are less likely to accept an electron pair. Thus, it is more difficult to break the C-Y bond to form Y^-.

3(a)(ii) Since pK_b of CH_3COO^- is more positive than NH_2^-, CH_3COO^- is a weaker base and is hence a better leaving group so that the reactivity of $(CH_3CO)_2O$ is higher than that of CH_3CONH_2. Reaction **1** will proceed with a faster rate than reaction **2**.

or

The pK_b of CH_3O^- is less positive than that of CH_3COO^- but more positive than that of NH_2^-. Hence the product CH_3COOCH_3 is less reactive than $(CH_3CO)_2O$ but more reactive than CH_3CONH_2. Thus, reaction **1** is likely to have a higher yield, as the product is less reactive than the reactant so that the backward reaction is less likely to occur, resulting in higher yield.

3(b)(i) Initial amount of $CH_3OH = \dfrac{20 \times 0.792}{32.0} = 0.495$ mol

3(b)(ii) $n_{CH3COOH}$ in 5.00 cm^3 of eqm mixture = $n_{NaOH} = \dfrac{16.80}{1000} \times 0.500 = 0.00840$mol

$n_{CH3COOH}$ in 40.00 cm^3 of eqm mixture = $0.0084 \times \dfrac{40.00}{5.00} = 0.0672$ mol

3(b)(iii) $K_c = \dfrac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

3(b)(iv) $n_{CH3COOH}$ reacted = 0.350 – 0.0672 = 0.2828 mol

	$CH_3OH(l)$ +	$CH_3COOH(l)$ ⇌	$CH_3COOCH_3(l)$ +	$H_2O(l)$
Initial amt/ mol	0.495	0.350	0	0
Change in amt/ mol	–0.2828	–0.2828	+0.2828	+0.2828
Final amt/ mol	0.2122	0.0672	0.2828	0.2828

$$K_c = \frac{\left(\frac{0.2828}{V}\right)\left(\frac{0.2828}{V}\right)}{\left(\frac{0.2122}{V}\right)\left(\frac{0.0672}{V}\right)} = 5.61$$

3(b)(v) The mixture was added to a large amount of ice-cold water to quench it. Cooling and diluting the reaction mixture slows down the reaction so that the equilibrium position would not shift during the titration and the equilibrium concentration of CH_3COOH can be determined.

3(c) Warm the esters separately with aqueous alkaline iodine.
The ester that gives a yellow precipitate of CHI_3 is $HCOOCH_2CH_3$. No yellow precipitate for CH_3COOCH_3.

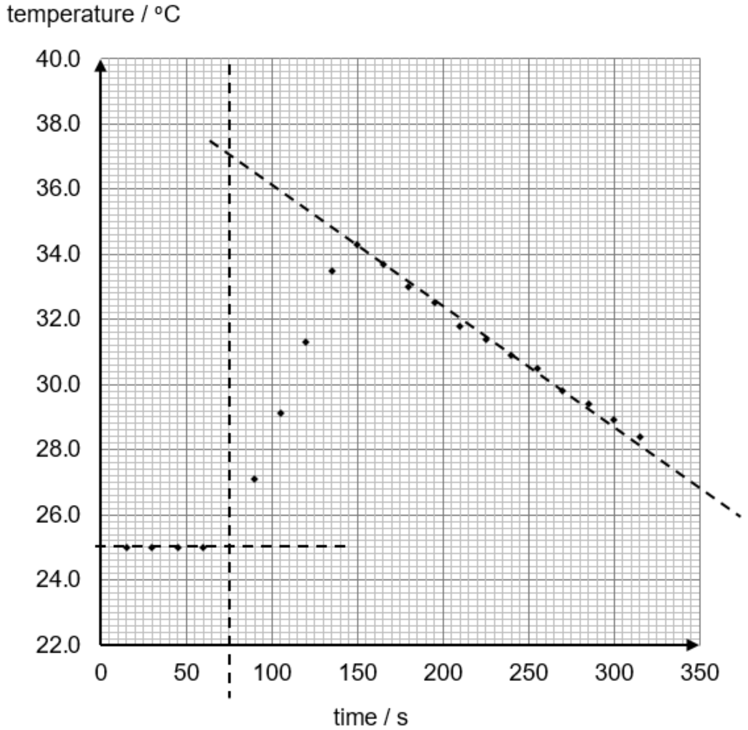
$HCOOCH_2CH_3 + OH^- \longrightarrow HCOO^- + CH_3CH_2OH$
$CH_3CH_2OH + 4I_2 + 6OH^- \longrightarrow HCOO^- + CHI_3 + 5I^- + 5H_2O$
[or $HCOOCH_2CH_3 + 4I_2 + 7OH^- \longrightarrow 2HCOO^- + CHI_3 + 5I^- + 5H_2O$]

3(d) Add dilute hydrochloric acid to the mixture. Stir and filter the mixture. **Q** is obtained as a salt in the filtrate while **P** is obtained as the residue.

Q is an amine and is basic. **Q** reacts with the acid to produce $(C_6H_5)_2NH_2^+$ (or salt) which forms strong ion–dipole interactions with water, resulting in its dissolution. Thus, **Q** dissolves in dilute hydrochloric acid and can be separated from **P** by filtration.

4(a)(i) It is the energy change when one mole of the substance is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 bar.

4(a)(ii) $\Delta T = 37.0 - 25.0 = +12.0\ ^{\circ}C$



4(a)(iii) Heat absorbed by water = $mc\Delta T$ = 100 x 4.18 x (12.0) = 5016 J
Mr of anhydrous $MgSO_4$ = 24.3 + 32.1 + 4(16.0) = 120.4
Amt of anhydrous $MgSO_4$ used = (7.500 / 120.4) = 0.06229 mol
$\Delta H_{sol}^{\ominus} = -(5016 / 0.06229) = -80527\ J\ mol^{-1} = -80.5\ kJ\ mol^{-1}$

4(a)(iv) The experimental value is less exothermic than the actual value.

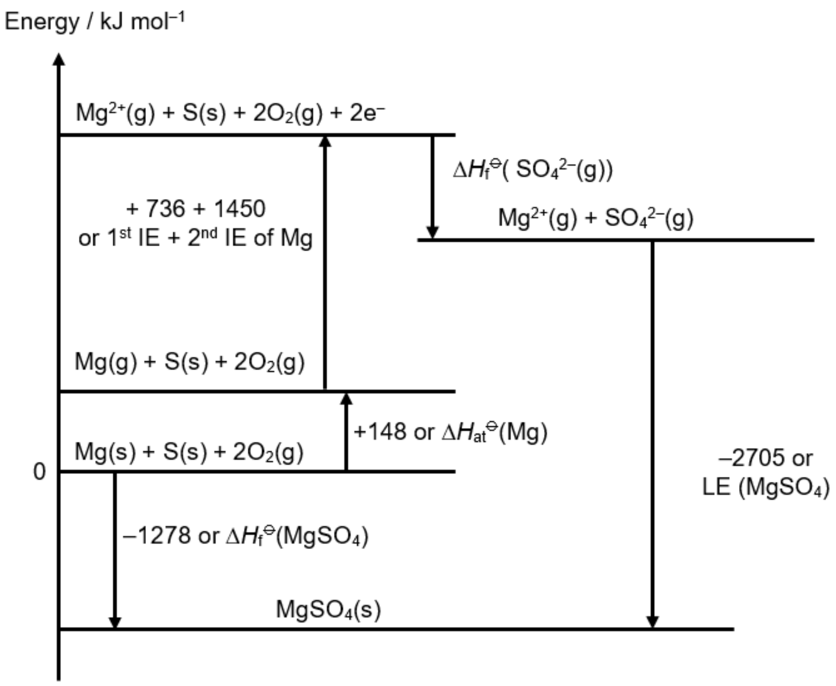
The heat capacity of cup/calorimeter was not taken into consideration. Account for the heat capacity of the cup/calorimeter by calibrating the calorimeter using a sample with known ΔH_{soln}.

or

The solution formed was not sufficiently dilute. Use a larger volume of water or use less solid.

4(a)(v) $\Delta H_r^{\ominus} = -88.0 - (+16.0) = \underline{-104 \text{ kJ mol}^{-1}}$

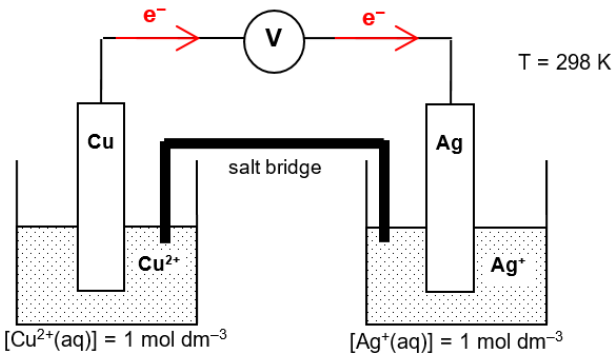
4(b)



$-1278 = +148 + 736 + 1450 + \Delta H_f^{\ominus}(\text{SO}_4^{2-}(g)) - 2705$

$\Delta H_f^{\ominus}(\text{SO}_4^{2-}(g)) = \underline{-907 \text{ kJ mol}^{-1}}$

5(a)(i)



5(a)(ii)
$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{cathode} - E^{\ominus}_{anode} \\ &= +0.80 - (+0.34) \\ &= \underline{+0.46 \text{ V}} \end{aligned}$$

5(a)(iii) Upon addition of NH_3, blue ppt forms.
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$ blue ppt

Upon addition of excess NH_3, ppt dissolves and deep blue solution is formed.
$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ deep blue complex

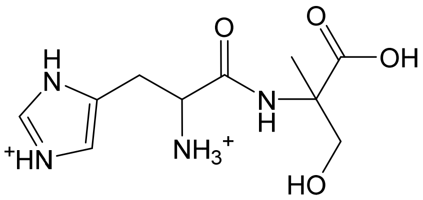
5(a)(iv) Upon addition of NH_3, $[Cu^{2+}]$ decreases such that it becomes less than 1 mol dm^{-3} (i.e. conditions are no longer standard). Position of equilibrium for $Cu^{2+} + 2e^- \rightleftharpoons Cu$ shifts to the left.

E_{anode} in **(a)(ii)** decreases and hence E_{cell} becomes more positive.

5(b) $\Delta G^\ominus = -nFE^\ominus_{cell} = -(2)(96500)(+1.60) = -309$ kJ mol^{-1}

6(a) ams and msr as they do not follow the general formula $NH_2CH(R)COOH$.

6(b)



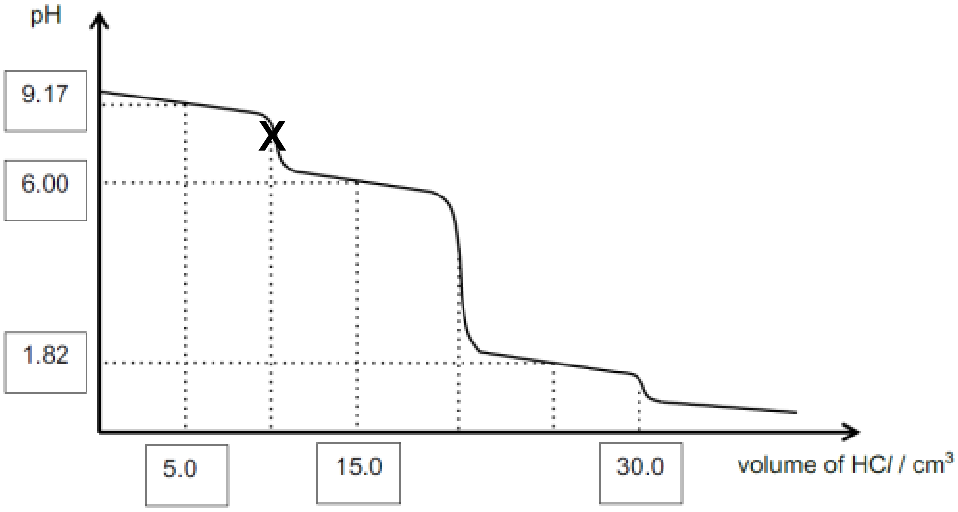
6(c)(i) pK_b of N① = 14 – 9.17 = 4.83
pK_b of N③ = 14 – 6.00 = 8.00

6(c)(ii) sp^3

6(c)(iii) The lone pair on N① is located in the sp^3 hybrid orbital which has less s character than the lone pair on N③ which is located in the sp^2 hybrid orbital. Therefore, N① lone pair is less strongly attracted to the nucleus and is more available for coordination with a proton.

6(c)(iv) The unhybridised p orbital on N② can overlap with the unhybridised p orbitals of the other atoms in the ring. Therefore the lone pair is delocalised and unavailable for coordination with a proton.

6(d) & 6(f)(ii)

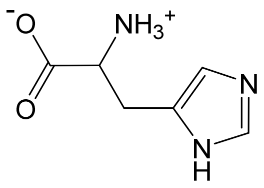


6(e) n(HC*l*) added = n(conjugate acid) formed = 6/1000 x 0.1 = 0.0006 mol
n(fully deprotonated *his*) remaining = (10/1000 x 0.1) – 0.0006 = 0.0004 mol

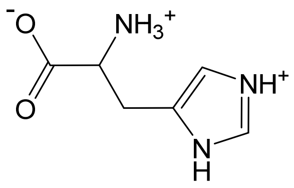
$$\begin{aligned}\text{pH} &= \text{p}K_a + \lg\,([\text{fully deprotonated } his] / [\text{conjugate acid}]) \\ &= 9.17 + \lg\,(0.0004 / 0.0006) \\ &= \underline{8.99}\end{aligned}$$

6(f)(i)

point **Y**



point **Z**



RAFFLES INSTITUTION
2018 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

20 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer all questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together, with the cover page on top. The cover page is found on page 14.

The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **13** printed pages and **1** blank page.

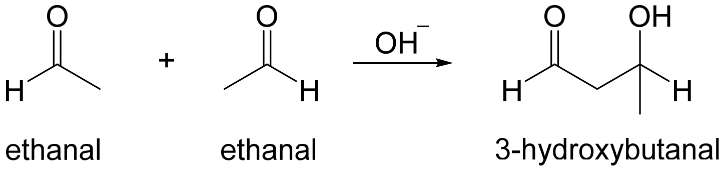
Section A

Answer **all** the questions in this section.

1 **(a)** In the aldol reaction, two carbonyl compounds react with each other in the presence of a base catalyst to form a hydroxy carbonyl compound.

The aldol reaction between two ethanal molecules, in the presence of OH^- ions, is shown below.

Reaction **1**



(i) A mixture of ethanal and propanone was subjected to the aldol reaction. Apart from 3-hydroxybutanal, suggest **three** other possible products formed. Ignore stereoisomers in your answer. [2]

To determine the kinetics of reaction **1**, two experiments, **I** and **II**, were carried out and the graphs of the concentration of ethanal against time were plotted.

The graphs on **page 13** show the results of experiments **I** and **II** with $[OH^-] = 1.0 \text{ mol dm}^{-3}$ and 2.0 mol dm^{-3} respectively. For **(a)(ii)** and **(a)(iii)**, draw clearly any construction lines on the graphs on **page 13**.

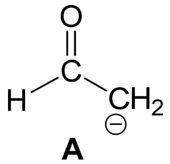
(ii) OH^- ions act as catalyst in the aldol reaction. Using the graph for Experiment **I**, determine the order of reaction with respect to ethanal. Explain your reasoning. [2]

(iii) By finding the initial rates, determine the order of reaction with respect to OH^-. [2]

(iv) Hence, write an overall rate equation for this reaction. [1]

(v) With reference to Experiment **I**, calculate a value for the rate constant and state its units. [2]

(b) **A** is an intermediate formed in reaction **1**.



A

In a separate reaction, **A** was used as a nucleophile to react with an optically active sample of 2-bromobutane. The product formed was found to rotate plane polarised light.

(i) Describe the mechanism of this reaction. In your answer, show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electrons. [3]

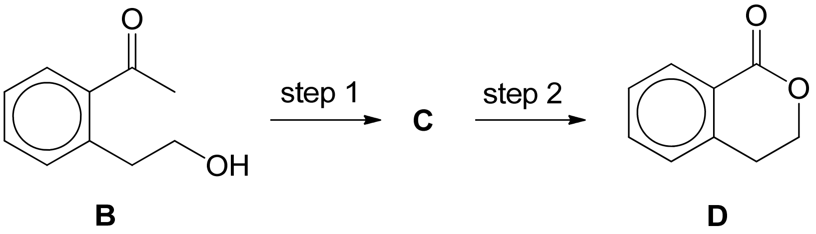
(ii) When conducted at a higher temperature, the same reaction occurred at a higher rate. With the aid of the Boltzmann distribution, explain why this is so. [3]

(iii) In another reaction with **A**, 2-chlorobutane was used instead of 2-bromobutane. With reference to the *Data Booklet*, predict and explain the effect on the rate of reaction. [1]

(iv) Instead of **A**, hydroxide ions were used to react with 2-bromobutane via the same mechanism in **(b)(i)**.

Suggest why the reaction between hydroxide ions and 2-bromobutane is faster than that between **A** and 2-bromobutane. [1]

(c) The following shows a reaction scheme to synthesise an ester **D** from compound **B**.



(i) Suggest the structure of compound **C**. [1]

(ii) Suggest reagents and conditions for steps 1 and 2. [2]

[Total: 20]

2 This question is about the halogens and their compounds.

Halogens react readily with lead to form lead halides. The melting points of some of the lead halides are given in Table 2.1.

Table 2.1

compound	melting point / °C
PbF_2	824
$PbCl_2$	501
$PbBr_2$	373
$PbCl_4$	–15

(a) **(i)** Explain, in terms of structure and bonding, why the melting points of the lead(II) halides decrease from PbF_2 to $PbBr_2$. [2]

(ii) Explain why $PbCl_4$ is a covalent compound and account for its low melting point. [2]

(iii) In an experiment, an excess of solid $PbCl_2$ was added to a solution of 0.050 mol dm^{-3} NaCl and allowed to reach equilibrium at 298 K. The mixture was then filtered. 25.0 cm^3 of the filtrate required the addition of 3.58×10^{-5} mol of NaI for the first trace of PbI_2 precipitate to appear.

Given that the solubility product of PbI_2 is 9.80×10^{-9} mol^3 dm^{-9}, calculate the solubility product of $PbCl_2$. [3]

When concentrated hydrochloric acid is added to a mixture containing the white precipitate of $PbCl_2$, the precipitate dissolves to form a colourless solution containing an ionic compound **E**.

(iv) **E** contains 0.6% H; 59.0% Pb; 40.4% Cl by mass, and has a relative formula mass of 351.0. The ratio of the cation to anion in **E** is 2 : 1.

Suggest the identity of the **complex ion** present in **E**. [2]

(v) Hence, explain the above observation with relevant ionic equations. [2]

(b) Halogens react with hydrogen to form hydrogen halides which may decompose upon heating.

(i) Write an equation for the thermal decomposition of hydrogen iodide. [1]

(ii) In an experiment, three glass jars were filled with hydrogen chloride, hydrogen bromide and hydrogen iodide gases respectively. A red hot wire was inserted into each jar for a fixed period of time. The observations were recorded in Table 2.2.

Table 2.2

gas in glass jar	observations
hydrogen chloride	no observable change
hydrogen bromide	reddish brown vapour formed slowly
hydrogen iodide	purple fumes evolved vigorously

Explain these observations. [2]

(c) Interhalogen species are commonly formed between halogens, where the central atom is the less electronegative of the two halogens.

Draw the dot-and-cross diagram of the IF_4^- ion. In your diagram, use the symbols '•' and '×' to distinguish the electrons from the iodine and fluorine atoms, and the symbol 'o' for any additional electron responsible for the overall negative charge.

State the shape and bond angle in IF_4^- ion. [2]

(d) *Use of the Data Booklet is relevant to this question.*

Halogens are strong oxidising agents which have important industrial applications. Chlorine, for example, is used as a disinfectant.

Show, with appropriate calculations, that manganese(IV) oxide is a product of the redox reaction between chlorine and manganese metal.

Hence, write the overall equation for the reaction. [3]

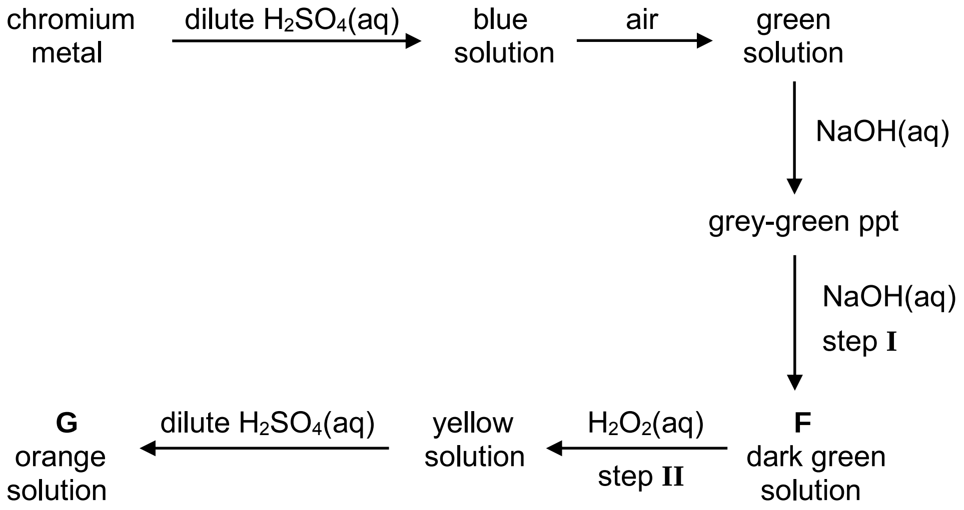
(e) Write a balanced equation for the reaction of PCl_5 with water. [1]

[Total: 20]

3 Chromium is a hard bluish–white metal that is extremely resistant to chemical attack at room temperature. Chromium metal is an important component in stainless steel.

(a) Write the electronic configuration of Cr. [1]

(b) The following sequence of reactions involving chromium illustrates many of the characteristic properties of transition metals.



(i) State the types of reaction in steps **I** and **II**.

Give the formula of the chromium-containing species, **F** and **G**. [3]

(ii) The variety of colours shown by chromium compounds in this reaction scheme is a typical property of transition metals.

State **one other** characteristic property of transition metals that is illustrated by this reaction scheme. Briefly explain why transition metals exhibit this property. [2]

(c) Chromium is said to be a d-block element as it contains d electrons.

(i) Draw the shape of d_{xy} and $d_{x^2-y^2}$ orbitals, showing clearly the axes. [1]

(ii) The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment. Explain why this is so. [2]

(d) The complex ions formed from Cr^{3+}, most of which are octahedral, may exhibit isomerism.

Three compounds having the formula $CrCl_3(H_2O)_6$ are known. All three give a white precipitate when aqueous silver nitrate is added. However, they differ in the fraction of 'free' chloride present and in their electrical conductivities in aqueous solution. In addition, these three compounds exhibit different colours in aqueous solution.

(i) Identify the complex ion in each of the three compounds. [2]

(ii) Explain why aqueous solutions of these three compounds are coloured. [3]

(iii) Suggest why the aqueous solutions of these three compounds exhibit different colours. [2]

(iv) One of the three complex ions in **(d)(i)** can exhibit *cis-trans* isomerism. Draw the *cis* isomer of this complex ion. [1]

(e) Excess ethylenediamine is added to a solution of $[Cr(NH_3)_6]^{3+}(aq)$ ions according to the following equation.

$$[Cr(NH_3)_6]^{3+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons \underset{\text{complex } \mathbf{H}}{[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}(aq)} + 6NH_3(aq)$$

(i) Predict, with reasoning, the sign of ΔS of the forward reaction. [1]

(ii) Suggest a reason why the ΔH value of the forward reaction is close to zero. [1]

(iii) By considering the $\Delta G^\ominus$ value of the forward reaction, suggest whether a higher or lower temperature will increase the yield of complex **H**. [1]

[Total: 20]

Section B

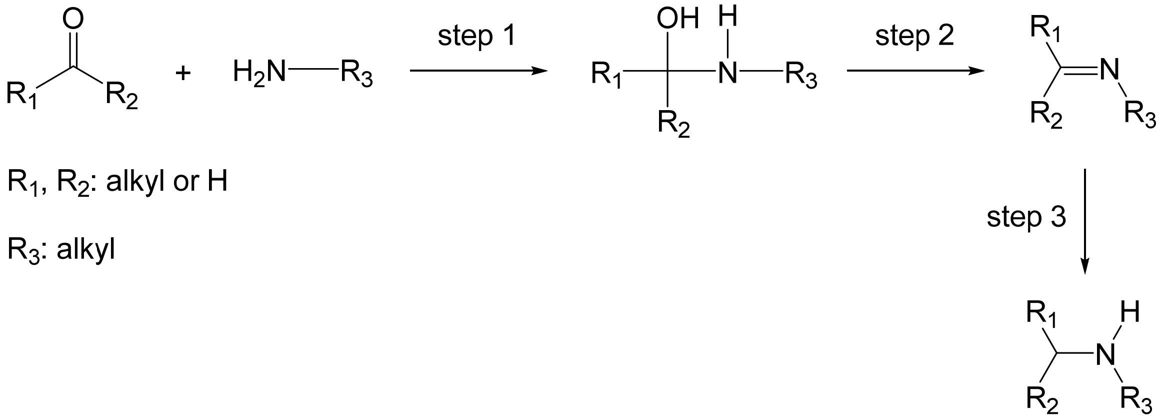
Answer **one** question from this section.

4 **(a)** **(i)** Describe the reactions, if any, of the oxides Na_2O, SiO_2 and P_4O_{10} with water. Write equations for any reactions that occur and include the approximate pH values of the resulting solutions. [5]

(ii) The acid-base behaviour of Al_2O_3 shows similarities to that of MgO and SO_3.

Describe and explain what these similarities are, and why Al_2O_3 occupies this in-between position. Write equations involving Al_2O_3 to illustrate your answer. [3]

In the Leuckart-Wallach reaction shown below, a carbonyl compound reacts with a primary amine to form a secondary amine.



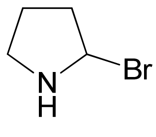
R_1, R_2: alkyl or H

R_3: alkyl

(b) **(i)** State the type of reaction in step 1. [1]

(ii) Unlike primary amines, primary amides cannot be used in the Leuckart-Wallach reaction. With reference to your answer in **(b)(i)**, explain why this is so. [1]

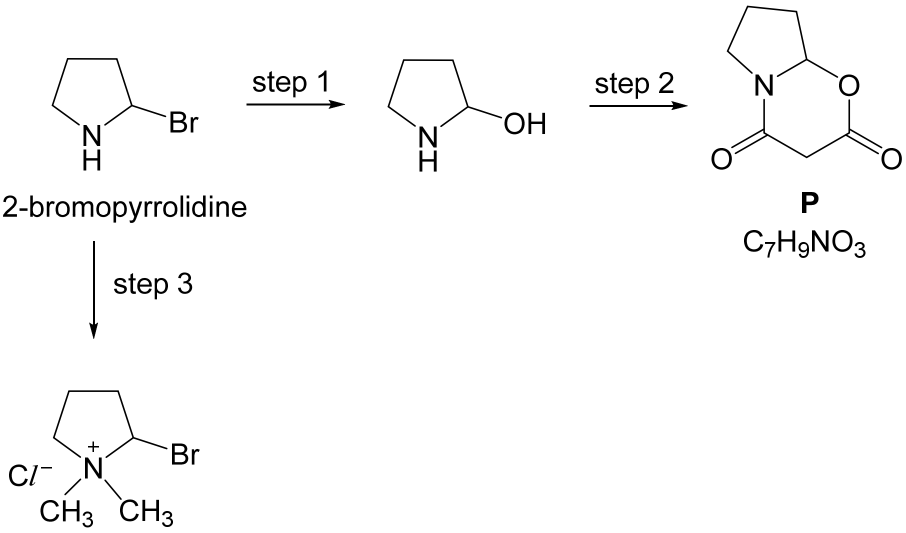
(iii) 2-bromopyrrolidine can be synthesised via the Leuckart-Wallach reaction.



2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]

(c) The following scheme shows the reactions involving 2-bromopyrrolidine.



2-bromopyrrolidine

P
$C_7H_9NO_3$

R
$C_6H_{13}BrN^+Cl^-$

(i) State the reagents and conditions for steps 1, 2 and 3. [3]

(ii) When compound **P** ($C_7H_9NO_3$) is reacted with $LiAlH_4$, compound **Q** ($C_7H_{15}NO_2$) is formed as the only organic product. 1 mole of **Q** reacts with 2 moles of Na but does not react with aqueous Na_2CO_3. Suggest the structure of **Q**. [1]

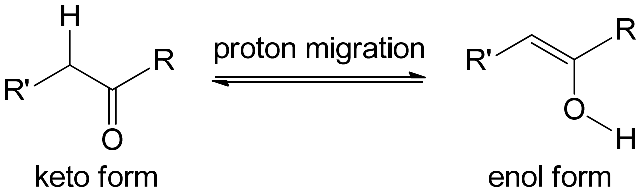
Under suitable conditions, compound **R** can undergo elimination to form two isomers **S** and **T** with the molecular formula $C_6H_{12}BrN$. Both **S** and **T** decolourise aqueous bromine and form salts in dilute acids. However, when heated with ethanolic $AgNO_3$, only **S** gives a pale cream precipitate.

(iii) Suggest the structures of **S** and **T** and state their isomeric relationship. [3]

(iv) Explain why **T** does not form a pale cream precipitate when heated with ethanolic $AgNO_3$. [2]

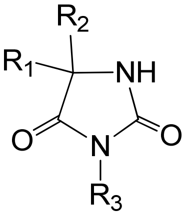
[Total: 20]

5 The stereochemistry of molecules plays a key role in their drug action. The conversion of the keto form to the enol form via proton migration often plays an important part in the orientation and effectiveness of drugs.



(a) State the isomeric relationship between the keto and enol forms. [1]

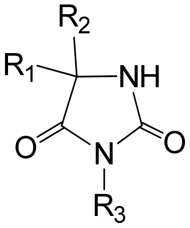
Hydantoins are a class of anti-epileptics that act against convulsions, tremors and seizures. The amide form of hydantoins has the general structure as shown.



(b) Similar to the keto-enol conversion, the molecule above can undergo proton migration to form another isomer under suitable conditions. Draw this isomer. [1]

(c) The most commonly used hydantoins include mephenytoin, phenytoin and derivative **X**.

	substituent		
	R_1	R_2	R_3
mephenytoin	C_6H_5	C_2H_5	CH_3
phenytoin	C_6H_5	C_6H_5	H
derivative **X**	C_6H_5	C_2H_5	C_6H_5



(i) Mephenytoin exists as a pair of stereoisomers.

State the type of stereoisomerism exhibited and draw the isomers. [2]

(ii) Suggest a simple chemical test to distinguish phenytoin from derivative **X**. [2]

(d) Compound **J** ($C_{10}H_{10}N_2O_2$) is neutral and exhibits optical activity. It does not react with 2,4-dinitrophenylhydrazine and does not contain the alkene functional group.

J reacts with H_2(g) in the presence of Ni catalyst at 150 °C and 1 bar to form **K** ($C_{10}H_{14}N_2O_2$). When **J** is heated with dilute sulfuric acid, carbon dioxide gas and NH_4^+ ions were formed. The resultant mixture was then distilled and **L** ($C_3H_6O_3$) was obtained as the distillate. To the residue from the distillation, a base was added and **M** was formed. **M** decolourises aqueous bromine to form a solid **N** ($C_6H_4NBr_3$). **L** reacts with hot alkaline aqueous iodine to give a pale yellow precipitate. **L** also turns hot orange acidified potassium dichromate(VI) green to produce **P**. **P** reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate **Q**.

(i) Calculate the volume of H_2(g) required for the complete reaction of 5.0 g of **J** to form **K**. [2]

(ii) Suggest possible structures for compounds **J** to **N**, **P** and **Q**, explaining the reactions involved. [12]

[Total: 20]

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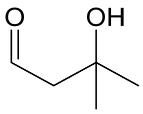
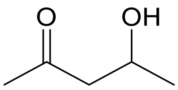
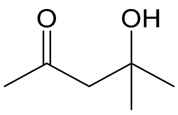
2018 Y6 H2 Chemistry Preliminary Exams Paper 3 (Suggested Solutions)

Section A

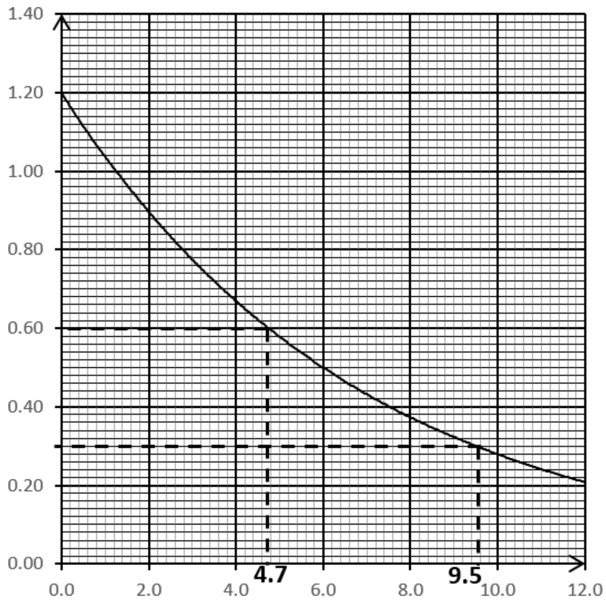
1 **(a)** **(i)**







(ii) Since OH^- is a catalyst, $[OH^-]$ is constant during each experiment and does not affect the reaction rate.



Using Experiment **I**,
First $t_{1/2}$ = <u>4.7 min</u>. Second $t_{1/2}$ = 9.5 – 4.7 = <u>4.8 min</u>.

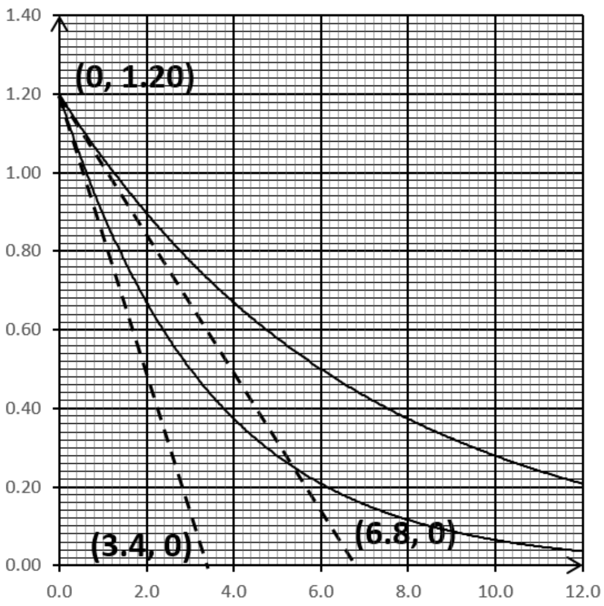
Since both $t_{1/2}$ are approximately the <u>same</u>, the reaction is <u>first order</u> w.r.t. ethanal.

(iii) By drawing tangents at t = 0 min,

For Experiment **I**, initial rate = $\left|\frac{1.20 - 0}{0 - 6.8}\right|$ = <u>0.176 mol dm^{-3} min^{-1}</u>

For Experiment **II**, initial rate = $\left|\frac{1.20 - 0}{0 - 3.4}\right|$ = <u>0.353 mol dm^{-3} min^{-1}</u>

When $[OH^-]$ doubles, rate doubles. Hence, reaction is <u>first order</u> w.r.t. OH^-.



(iv) rate = $k[OH^-][\text{ethanal}]$

(v) <u>Initial rate method</u>
Using Experiment **I**, $0.1765 = k(1.0)(1.2) \rightarrow k =$ <u>$0.147\ mol^{-1}\ dm^3\ min^{-1}$</u>

OR

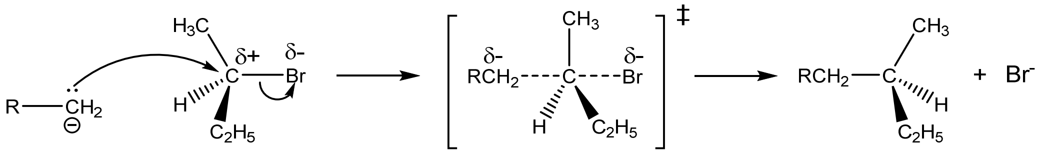
<u>Half-life method</u>

$$t_{½} = \frac{\ln 2}{k\,[OH^-]}$$

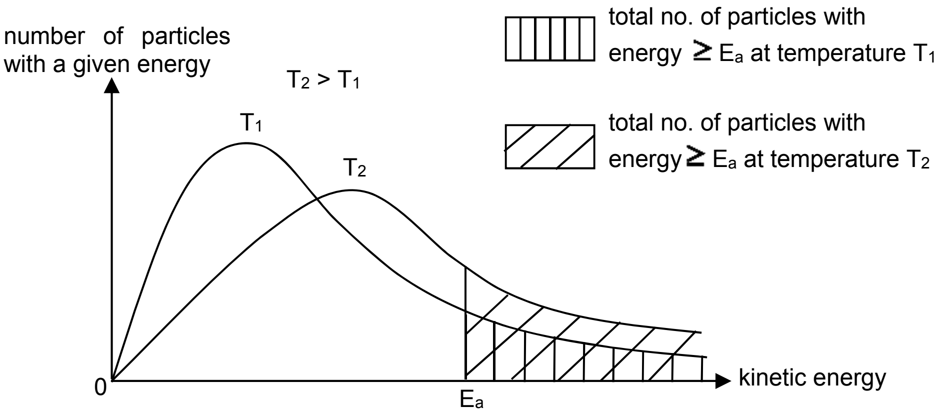
Using Experiment **I**, $4.75 = \frac{\ln 2}{k\,(1.0)} \rightarrow k =$ <u>$0.146\ mol^{-1}\ dm^3\ min^{-1}$</u>

(b) **(i)** Mechanism: <u>S_N2</u> (or bimolecular nucleophilic substitution)

Let RCH_2^- represent **A**.



(ii)



An increase in temperature from T_1 to T_2 increases the average kinetic energy of the reactant particles. More reactant particles have energy greater than or equal to the activation energy of the reaction.

This results in an increase in effective collision frequency and hence an increase in the rate of the reaction.

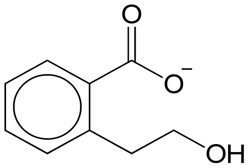
(iii) The C–C*l* bond (BE = 340 kJ mol^{-1}) is stronger than the C–Br bond (BE = 280 kJ mol^{-1}). Hence it is more difficult to break the C–C*l* bond, resulting in a slower reaction for 2-chlorobutane.

(iv) Hydroxide ions are less bulky and will experience less steric hindrance when attacking the electron deficient carbon atom.

OR

In **A**, the negative charge is delocalised into the adjacent C=O group. Hence, lone pair on **A** is less available, resulting in a slower reaction.

(c) (i)



(ii) Step 1: I_2(aq) with NaOH(aq), heat or warm
Step 2: (catalytic) conc H_2SO_4, heat

2 (a) (i) PbF_2, $PbCl_2$ and $PbBr_2$ have giant ionic structure with strong ionic bonds.

PbF_2, $PbCl_2$ and $PbBr_2$ have the same cation and the anions have the same charge. Since the ionic radius increases from F^- to Br^-, the interionic distance increases from PbF_2 to $PbBr_2$. Hence the strength of ionic bond and melting point decreases from PbF_2 to $PbBr_2$.

Or since $|LE| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$ and the ionic radius increases from F^- to Br^-, the LE become less exothermic, less energy is required to overcome the ionic bond and melting point decreases from PbF_2 to $PbBr_2$.

(ii) Due to its high charge and small size, Pb^{4+} has a high charge density and high polarising power, which causes it to distort the electron cloud of Cl^- to such an extent that $PbCl_4$ is predominantly a covalent compound.

Hence, $PbCl_4$, having a simple covalent/molecular structure, consists of discrete molecules held together by weak instantaneous dipole-induced dipole interactions which requires a small amount of energy to overcome. Thus, it has a low melting point.

(iii) $[I^-] = \dfrac{3.58 \times 10^{-5}}{25.0/1000} = 1.432 \times 10^{-3}\ \text{mol dm}^{-3}$

$[Pb^{2+}]$ in filtrate $= \dfrac{9.80 \times 10^{-9}}{(1.431 \times 10^{-3})^2} = 4.779 \times 10^{-3}\ \text{mol dm}^{-3}$

$[Cl^-]$ from $PbCl_2$ in filtrate $= 4.779 \times 10^{-3} \times 2 = 9.558 \times 10^{-3}\ \text{mol dm}^{-3}$

Total $[Cl^-]$ in filtrate $= 9.558 \times 10^{-3} + 0.050 = 0.05956\ \text{mol dm}^{-3}$

$K_{sp} = [Pb^{2+}][Cl^-]^2 = (4.779 \times 10^{-3})(0.05956)^2 = 1.70 \times 10^{-5}\ \text{mol}^3\ \text{dm}^{-9}$

(iv)

	H	Pb	Cl
mass	0.6	59.0	40.4
mole	0.6/1.0	59.0/207	40.4/35.5
	= 0.6	= 0.285	= 1.138
	≈ 2	≈ 1	≈ 4

Empirical formula = H_2PbCl_4
Actual formula = H_2PbCl_4
Complex ion = $[PbCl_4]^{2-}$

(v) The following equilibrium is established in the saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \text{ -----(1)}$$

When concentrated hydrochloric acid is added and the mixture shaken, $[Cl^-]$ is greatly increased. Pb^{2+} ions react with Cl^- to form the soluble complex, $[PbCl_4]^{2-}$, as shown below.

$$Pb^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [PbCl_4]^{2-}(aq) \text{ -----(2)}$$

The formation of $[PbCl_4]^{2-}$ decreases the $[Pb^{2+}]$ in the solution.
To counteract the decrease in $[Pb^{2+}]$, the equilibrium position of reaction (1) shifts to the right i.e. $PbCl_2$ dissolves.
or

$[Pb^{2+}]$ decreases due to the formation of $[PbCl_4]^{2-}$. When ionic product, $[Pb^{2+}][Cl^-]^2$ becomes less than the K_{sp} , all the $PbCl_2$ dissolves.

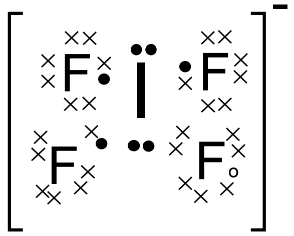
(b) **(i)** $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(ii) The thermal stabilities of HCl to HI, which is related to the H-X bond strength, increase in the order: HI < HBr < HC*l*

The stronger the H-X bond, the more thermally stable HX is. Since the bond strength of HI < HBr < HC*l*, the thermal stability of HI < HBr < HC*l*.

The energy supplied by the red hot wire was insufficient to decompose HC*l*, hence there is no observable change; was able to decompose some HBr, resulting in reddish-brown vapour of Br_2 formed slowly; and was able to decompose HI readily to result in purple fumes of I_2 evolved vigorously.

(c)



Square planar, 90˚

(d) $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\qquad E^\ominus = +1.36$ V
$Mn^{2+} + 2e^- \rightleftharpoons Mn$ $\qquad E^\ominus = -1.18$ V
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ $\qquad E^\ominus = +1.23$ V
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$ $\qquad E^\ominus = +1.67$ V

Considering the reaction between Cl_2 and Mn, $E^\ominus_{cell} = +1.36 - (-1.18)$
$= +2.54$ V (spontaneous)
Considering the reaction between Cl_2 and Mn^{2+}, $E^\ominus_{cell} = +1.36 - 1.23$
$= +0.13$ V (spontaneous)

Considering the reaction between Cl_2 and MnO_2, $E^\ominus_{cell} = +1.36 - 1.67$
$= -0.31$ V (not spontaneous)

Thus, Cl_2 will oxidise Mn to Mn^{2+} and further oxidise Mn^{2+} to MnO_2. (proven)

Overall eqn: $2Cl_2 + Mn + 2H_2O \longrightarrow 4Cl^- + MnO_2 + 4H^+$

(e) $PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$

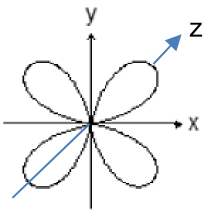
3 **(a)** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

(b) **(i)** Step **I**: acid-base (or complexation or complex formation)
Step **II**: oxidation / redox reaction
F: $[Cr(OH)_6]^{3-}(aq)$ or $[Cr(OH)_4]^-(aq)$
G: $Cr_2O_7^{2-}(aq)$

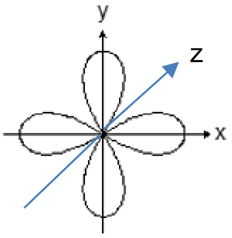
(ii) The ability to display variable oxidation states in their compounds. This is due to the close similarity in energy between the 3d and 4s electrons, which thus allows for different number of these electrons to participate in chemical bonding.

OR Ability to form complexes due to availability of low lying vacant orbitals.

(c) **(i)**



3d xy



3d $_{x^2-y^2}$

(ii) In an octahedral environment, lone pairs on the ligands approach the central metal ion along the x, y and z axes.

$3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals have their greatest electron density along the co-ordinate axes on which the ligands are situated. Hence electrons in these orbitals are pointing towards the lone pairs of ligands, and will be repelled by them.

$3d_{xy}$, $3d_{yz}$, $3d_{xz}$ orbitals have their greatest electron density in between the co-ordinate axes. Hence the repulsion between electrons in these orbitals and those of the approaching ligands will be less compared to electrons in $3d_{x^2-y^2}$ or $3d_{z^2}$ orbitals.

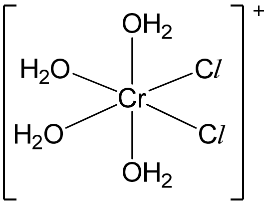
Hence the d-orbitals are split into two different energy levels.

(d) **(i)** $[Cr(H_2O)_4Cl_2]^+$
$[Cr(H_2O)_5Cl]^{2+}$
$[Cr(H_2O)_6]^{3+}$

(ii) The presence of ligands causes the splitting of the five 3d orbitals in Cr^{3+} into two sets of slightly different energy levels. Since the 3d subshell in Cr^{3+} are partially filled, electrons from the lower-energy d orbitals can absorb energy and get promoted to the higher-energy d orbitals (d-d transition). The energy absorbed corresponds to certain wavelength from the visible light spectrum and the colour observed is the complement of the colour absorbed.

(iii) Chloride and water are ligands of different strength. Different proportions of these ligands cause the d orbitals to be split to different extents, creating different energy gaps for different complexes, which in turn absorb energies of different wavelengths from the visible light spectrum, thus displaying different colours.

(iv)



cis-$[Cr(H_2O)_4Cl_2]^+$

(e) **(i)** Positive ($\Delta S > 0$). There is increase in disorder/entropy due to increase in number of particles / molecules / species formed.

(ii) ΔH value of the forward reaction is close to zero as the type (N→Cr coordinate bond) and the number of dative covalent bonds broken and formed are about the same.

(iii) $\Delta G = \Delta H - T\Delta S$
Since ΔH is close to zero and ΔS is positive, ΔG (for the forward reaction) will be more negative at a higher temperature, hence increasing the yield of complex **H**.

Section B

4 **(a)** **(i)** Na_2O reacts with water to form a strongly alkaline solution (pH ≈ 13 – 14).
$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$

SiO_2 does not dissolve in water because of the strong Si–O covalent bonds in the giant molecular structure. Solution remains neutral (pH = 7).

P_4O_{10} reacts with water to form an acidic solution (pH ≈ 2).
$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$
(Note: H_3PO_4 is a weak acid)

(ii) (MgO is an ionic oxide which is basic and react with acids. SO_3 is a covalent oxide which is acidic and reacts with bases.)

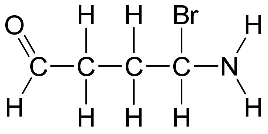
Al_2O_3 (an amphoteric oxide) reacts with both acids and bases as it is an ionic oxide with covalent character. The covalent character is due to the high charge density/polarising power of Al^{3+} that polarise and distort the electron cloud of O^{2-}.

With acid: $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
With base: $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq)$

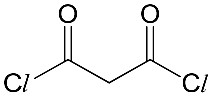
(b) **(i)** Step 1: nucleophilic addition

(ii) In primary amides, the lone pair of electrons on the nitrogen atom interacts with the π electron cloud of the adjacent C=O bond and is delocalised. Hence, the lone pair of electrons is not available for donation to the electrophilic carbonyl carbon atom /unable to act as a nucleophile in step 1.

(iii)

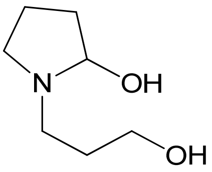


(c) **(i)** Step 1: NaOH(aq), heat

Step 2:  (anhydrous, rtp)

Step 3: excess CH_3Cl, heat

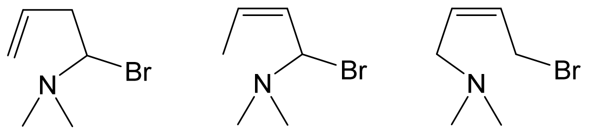
(ii)



Q

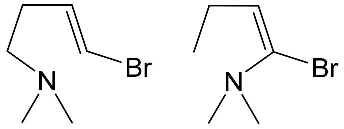
$C_7H_{15}NO_2$

(iii) Possible structures for **S** ($C_6H_{12}BrN$):



(or the trans isomers)

Possible structures for **T** ($C_6H_{12}BrN$):



(or corresponding cis-trans isomer)

S and **T** are constitutional / structural / positional isomers.

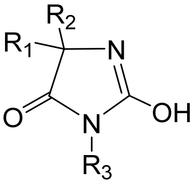
(iv) In **T**, the p orbital of Br overlaps with the π electron cloud of the adjacent C=C bond and the lone pair of electrons in the p orbital of Br delocalises into the C=C bond and results in partial double bond character in the C–Br bond.

Hence, **T** does not undergo nucleophilic substitution and no Br^- are present to react with Ag^+ to form pale cream ppt of AgBr.

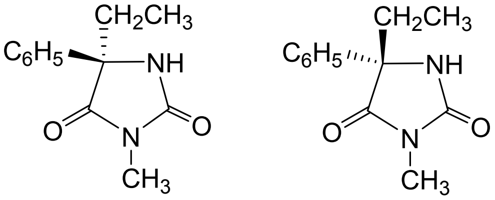
(**S** is an alkyl bromide that can undergo nucleophilic substitution when heated with ethanolic $AgNO_3$ to form alcohol and Br^-. Br^- then forms the pale cream ppt of AgBr with Ag^+.)

5 **(a)** Constitutional / Structural / Functional group isomerism

(b)



(c) **(i)** Enantiomerism



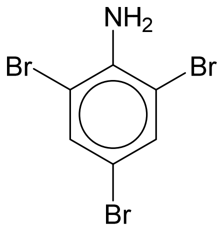
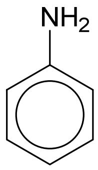
(ii) Test: To separate samples of **X** and phenytoin, add NaOH(aq) and heat strongly.

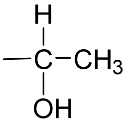
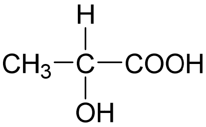
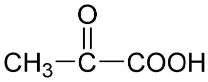
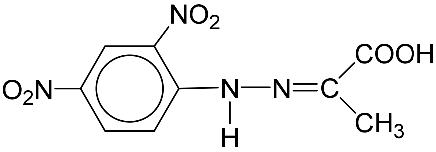
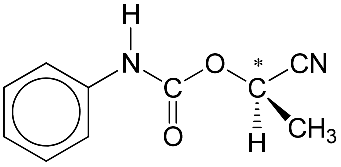
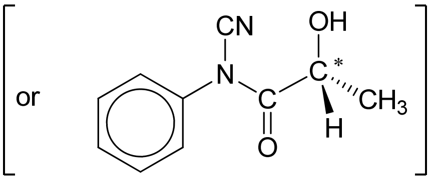
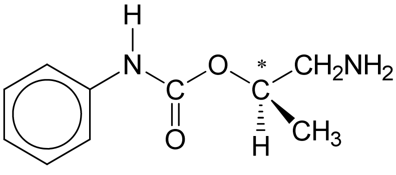
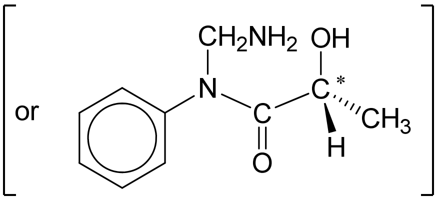
Observation: Pungent gas (NH_3) that turns moist red litmus blue is evolved for the sample containing phenytoin but no pungent gas is evolved for the sample containing **X**.

(d) **(i)** M_r (**J**) = 190
n(**J**) = 5/190 = 0.02632 mol; n(H_2) = 2(0.02632) = 0.05264 mol

$pV_{H2} = nRT$
$(1.0 \times 10^5)\ V_{H2} = (0.05264)(8.31)(273 + 150)$
$V_{H2} = 1.85 \times 10^{-3}\ m^3 = 1.85\ dm^3$

(ii)

Information / Reaction	**Deduction / Explanation**
J has molecular formula, $C_{10}H_{10}N_2O_2$	**J** is likely to contain a benzene ring due to the relatively high C to H ratio.
J exhibits optical activity	**J** contains a chiral centre and/or no plane of symmetry.
J is neutral**.**	**J** contains amide and/or –CN group. Or **J** is not carboxylic acid or amine or phenol.
J has no reaction with 2,4-DNPH	**J** is not aldehyde & ketone / carbonyl
$\mathbf{J} \xrightarrow[150\ ^{o}C]{H_2(g)\ /\ Ni} \mathbf{K}$	Reduction of nitrile. Since C=C is absent and there is increase of 4 H atoms from **J** to **K**, **J** contains –CN group.
$\mathbf{J} \xrightarrow[heat]{H_2SO_4(aq)} CO_2$ + resultant mixture distillation ↓ residue + distillate **L** residue $\xrightarrow{base}$ **M**	**J** contains amide/ester/nitrile and undergoes acidic hydrolysis. Residue is an ionic salt. (**M** is a base.)
$\mathbf{M} \xrightarrow{Br_2(aq)} \mathbf{N}$ ($C_6H_4NBr_3$)	**M** undergoes electrophilic substitution. **N** is  Hence **M** is 

L $\xrightarrow{\text{hot alkaline } I_2(aq)}$ yellow ppt	**L** contains the  $-\overset{H}{\underset{OH}{C}}-CH_3$ group
L decolourises acidified KMnO4(aq) to form **P**	**L** undergoes oxidation to form **P**. Hence, **P** is a methyl ketone / carbonyl compound. **(L** cannot be a methyl ketone since **J** is not carbonyl compound and **L** is oxidised by $KMnO_4$ to form **P.)**
P $\xrightarrow{\text{2,4-DNPH}}$ **Q** (orange ppt)	Hence, **L** ($C_3H_6O_3$) is  $CH_3-\overset{H}{\underset{OH}{C}}-COOH$ **P** is  $CH_3-\overset{O}{\overset{\|}{C}}-COOH$ <u>Condensation</u> **Q** is 
Combining the above deductions, **J** can be:  or  **K** can be:  or 	

CANDIDATE NAME	( )	CLASS	18S0		

H

RAFFLES INSTITUTION
2018 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY

9729/04

Paper 4 Practical

29 August 2018
2 hours 30 minutes

Do NOT turn over the Question Booklet until you are told to do so.

READ THESE INSTRUCTIONS FIRST

Write your name and class on the space provided when instructed to do so.
Give details of the practical shift and laboratory, where appropriate, in the space provided.

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift	
Laboratory	
Bench Number	

For Examiner's Use	
Question	**Marks**
1	**/ 14**
2	**/ 25**
3	**/ 16**
Total	**/ 55**

This document consists of **17** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 Determination of the concentration of $CuSO_4$ in FA 2

You are provided with the following solutions:

FA 1 0.0500 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$
FA 2 aqueous $CuSO_4$ solution of unknown concentration
FA 3 100 g dm^{-3} solution of sodium iodide, NaI
Starch solution

Copper(II) ions react with iodide ions according to the following equation.

$$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$$

The iodine produced in this reaction may be titrated against **FA 1** using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Estimating the required dilution factor for FA 2

(a) The solution of **FA 2** provided is too concentrated to be used directly for reaction with **FA 3** to produce iodine for titration against **FA 1**.

A preliminary experiment was carried out to estimate a dilution factor for the **FA 2** solution, so that 25 cm^3 of this diluted solution would require approximately 25 cm^3 of **FA 1** for complete reaction. It was found that 30 drops of **FA 1** were needed to react completely with the iodine produced from the reaction between 5 drops of **FA 2** and excess **FA 3**.

Use the information above to calculate the volume of **FA 2** needed to make 250 cm^3 of the diluted $CuSO_4$ solution, **FA 4**.

[1]

Preparation of FA 4 by dilution of FA 2

(b) You will now follow the instructions given below to prepare **FA 4**, a diluted solution of **FA 2**.

1. Using a burette, measure between 40.00 and 42.00 cm^3 of **FA 2** into a 250 cm^3 graduated flask.

2. Record in the space below, your burette readings and the volume of **FA 2** transferred to the flask.

[2]

3. Fill the graduated flask to the 250 cm^3 mark with deionised water, stopper and mix thoroughly by inverting the flask a number of times.

   The diluted $CuSO_4$ solution you have prepared is **FA 4**.

Titration

1. Fill the second burette with **FA 1**.
2. Pipette 25.0 cm^3 of **FA 4** into a conical flask.
3. Use the measuring cylinder provided to add 10 cm^3 of **FA 3** to the conical flask.

   *As described earlier, the Cu^{2+} ions in **FA 4** react with I^- ions from **FA 3** to produce I_2, which can be titrated with **FA 1**. The reaction also produces a cream precipitate of CuI.*
4. Titrate the iodine in the conical flask with **FA 1** until the brown colour of the iodine becomes pale brown.
5. Add about 10 drops of starch solution to the flask and continue adding **FA 1** until the blue-black colour just disappears.
6. Repeat the titration as many times as you think necessary to obtain consistent results. Record your titration results in the space below.

Results

[5]

(c) Indicate clearly which results you have used, and show with calculation the volume of **FA 1** used.

……….....… cm^3 of **FA 4** produced an amount of iodine which required ……….....… cm^3 of **FA 1** for complete reaction.

[1]

(d) Calculate the number of moles of $S_2O_3^{2-}$ in the volume of **FA 1** recorded in **(c)**, and hence determine the molar concentration of Cu^{2+} ions in **FA 4**.

number of moles of $S_2O_3^{2-}$ = ……………………….……

concentration of Cu^{2+} in **FA 4** = ………………………………
[2]

(e) Using the volume of **FA 2** recorded in **(b)**, calculate the molar concentration of $CuSO_4$ in **FA 2**.

concentration of $CuSO_4$ in **FA 2** = ……………………………….[1]

(f) A student repeated the experiment using 50 g dm^{-3} sodium iodide solution instead. Predict, using calculations, if the titre volumes obtained would differ when the new solution of iodide ions is used.
(A_r: Na = 23.0; I = 126.9)

[2]

[Total: 14]

2 Determination of the concentration of NaC*l*O and a value for an enthalpy change of reaction, ΔH_{rxn}

You are provided with the following solutions:

FA 5 is an aqueous solution containing sodium chlorate(I), NaC*l*O.
FA 6 is an aqueous solution of 0.100 mol dm^{-3} sodium thiosulfate in aqueous sodium hydroxide.

You are to perform a series of experiments using different volumes of **FA 5** and **FA 6** which together give a total volume of **40.0 cm^3**. The temperature change, ΔT, for each experiment will be determined and you will plot a graph of ΔT against the volume of **FA 5** used.

You will then use data from your graph to determine the concentration of sodium chlorate(I) in **FA 5**. You will also use data from your graph to determine a value for the enthalpy change of reaction, ΔH_1, for the reaction between aqueous sodium chlorate(I) and sodium thiosulfate.

$$4NaClO(aq) + Na_2S_2O_3(aq) + 2NaOH(aq) \xrightarrow{\Delta H_1} 4NaCl(aq) + 2Na_2SO_4(aq) + H_2O(l) \text{ --- Reaction } \mathbf{1}$$

(a) Procedure

Follow the steps below to determine the temperature changes when different volumes of **FA 5** and **FA 6** are reacted together.

1. Use a 50 cm^3 measuring cylinder to transfer 10.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup containing **FA 5** inside a second Styrofoam cup which is placed in a 250 cm^3 glass beaker to prevent it from tipping over.

2. Place a thermometer into the cup containing **FA 5**. Stir gently, measure and record the temperature of the **FA 5** solution, T_1.

3. Using another 50 cm^3 measuring cylinder, transfer 30.0 cm^3 of **FA 6** into the cup containing **FA 5**. Use the thermometer to stir the mixture gently. Measure and record the highest temperature, T_2, of the mixture.

4. Empty, wash and carefully dry the Styroform cup.

5. Repeat steps 1 to 4 using 20.0 cm^3, 30.0 cm^3 and 35.0 cm^3 of **FA 5**, each time using the appropriate volume of **FA 6** so that the total volume of the mixture is 40.0 cm^3.

6. Record all measurements of volume, temperature and temperature change, ΔT, in an appropriate format in the spaces provided on the next page. The data for these four experiments should be recorded together with the two or three additional experiments described in **(b)(ii)**.

(b) (i) Results

[4]

(ii) Plot the points of temperature change, ΔT, against volume of **FA 5** using the four experimental results that you have obtained.

By considering your plotted points, perform two or three additional experiments to identify the volume of **FA 5** needed to produce the maximum temperature change, ΔT_{max}. In each experiment, ensure that the total volume of the reaction mixture is 40.0 cm^3. You may find it helpful to plot the results from each experiment before choosing the volumes to use in the next experiment. [4]

(iii) Draw two lines of best fit for the points plotted and extrapolate both lines to find the maximum temperature change, ΔT_{max}, and the volume of **FA 5** required to completely react with the amount of **FA 6** used, V_{rxn}.

Record these values in the spaces provided below.

From the graph,

maximum temperature change of reaction mixture, ΔT_{max} = …………………

volume of **FA 5** required for complete reaction, V_{rxn} = ………………… [2]

(c) Use your results from part **(b)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of sodium chlorate(I), NaC*l*O, in **FA 5**.

concentration of NaC*l*O in **FA 5** = ………………………………….[2]

(ii) the enthalpy change of reaction, ΔH_1, in kJ mol^{-1}, for the reaction between **FA 5** and **FA 6** in reaction **1**.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

ΔH_1 = …………………………………..[2]

(d) Predict and explain if ΔT_{max} will be affected when the volumes of **FA 5** and **FA 6** used in the reaction are doubled.

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………………………………………………………………………..………..………[1]

(e) Planning

FA 6 is an aqueous solution of 0.100 mol dm^{-3} sodium thiosulfate in aqueous NaOH.

FA 7 is an impure sample of solid sodium chlorate(I), NaC*l*O, with a percentage purity of about 80%.

The percentage purity of NaC*l*O in **FA 7** and the enthalpy change of reaction, ΔH_2, of the following reaction is to be determined.

$$4NaClO(s) + Na_2S_2O_3(aq) + 2NaOH(aq) \xrightarrow{\Delta H_2} 4NaCl(aq) + 2Na_2SO_4(aq) + H_2O(l) \text{ -- Reaction } \mathbf{2}$$

This can be done by performing experiments to find the maximum temperature rise when known masses of **FA 7** are **separately** added to 30 cm^3 of **FA 6** and plotting the graph of maximum temperature rise against mass of **FA 7** used.

You may assume that the impurity present in **FA 7** does not react with **FA 6** and does not cause a change in temperature when dissolved in water.

(i) Calculate the mass of NaC*l*O required to react completely with 30 cm^3 of **FA 6**.
(A_r: Na = 23.0; C*l* = 35.5; O = 16.0)

[1]

(ii) Hence, calculate the mass of **FA 7** required to react completely with 30 cm^3 of **FA 6**, assuming that the percentage purity of NaC*l*O in **FA 7** is 80%.

[1]

(iii) Plan an investigation, based on the description outlined above, to determine the percentage purity of NaC*l*O in **FA 7** and the enthalpy change of reaction, ΔH_2, of reaction **2**.

You may assume that you are provided with
- **FA 6** and **FA 7**,
- an analytical balance,
- a weighing bottle,
- the equipment normally found in a school or college laboratory.

Your plan should include the following:
- an outline of how the mass of **FA 7** used is determined,
- brief details of the apparatus that you would use, the procedure that you would follow and the measurements that you would take,
- a sketch of the graph you would expect to obtain,
- how the data obtained from your graph would be used to determine
  - the percentage purity of NaC*l*O in **FA 7**,
  - the enthalpy change of reaction, ΔH_2, of reaction **2**.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1} and that its density is 1.00 g cm^{-3}.

……………………………………………………………………………………………………[6]

(iv) With the aid of a suitable energy cycle, derive an expression for the enthalpy change of dissolution of NaC*l*O, ΔH_{sol}, in terms of ΔH_1 and ΔH_2.

[2]

[Total: 25]

3 Inorganic and Organic Analysis

(a) **FA 2** is an aqueous solution of $CuSO_4$.
FA 8 is a reducing agent.
FA 9 is a solution of ammonium vanadate(V), NH_4VO_3.

You are to perform the tests described in Table 3.1 and record your observations in the table.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests. Your answers should include

- details of colour changes and precipitates formed
- the identities of gases evolved and details of the test used to identify each gas

Table 3.1

	tests	observations
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 2** into a boiling tube. Add 4 spatulas of **FA 8**. Warm the mixture cautiously till boiling. Leave to cool for 5 minutes. Filter the mixture and keep the filtrate for tests **(ii)** and **(iii)**.	
(ii)	To 1 cm depth of the filtrate, add aqueous ammonia.	

Table 3.1

	tests	observations
(iii)	To another 1 cm depth of the filtrate, add 2 spatulas of solid ammonium chloride, followed by aqueous ammonia.	
(iv)	Using a measuring cylinder, transfer 2 cm^3 of **FA 9** into a boiling tube. Add 10 cm^3 of dilute sulfuric acid and swirl the mixture gently. The resultant yellow solution is **FA 10**, which is an acidified solution of VO_2^+.	
(v)	Using a spatula, add a **very small quantity** of **FA 8** to the boiling tube containing **FA 10** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 8** in small quantities with swirling, until no further colour change is observed. Record all colour changes observed.	
	Filter the mixture and retain the filtrate for test **(vi)**.	
(vi)	To 1 cm depth of the filtrate from test **(v)**, add an equal volume of aqueous hydrogen peroxide.	

[6]

(b) **(i)** Complete Table 3.2 below, using the observations in Table 3.1**.**
In your answer, identify any gas and/or precipitate formed.

Table 3.2

identity of **FA 8**	evidence

[2]

(ii) With the aid of equation(s), explain your observation in test **(a)(iii)**.

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………………………………………………………………………………………………[2]

(iii) The half equations that represent the stepwise reduction of VO_2^+ ions are shown below.

Electrode reaction	$E^\ominus$ / V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20

When excess aqueous ammonia is added to 1 cm depth of the filtrate in test **(a)(v)**, a grey precipitate is observed.

Given that the $E^\ominus$ value for **FA 8** is between −1.00 V to –0.50 V, state the identity of the grey precipitate.

………………………………………………………………………………………………[1]

(c) Planning

The labels of four bottles of solutions in your school chemistry laboratory are found to be missing. They are aqueous solutions of Na_2CO_3, $Al_2(SO_4)_3$, CH_3COOH and CH_3CH_2CHO.

To identify the solutions in the unlabelled bottles, the following reagents are provided:

- **FA 2** which is an aqueous solution of $CuSO_4$,
- solution **X** which contains alkaline tartrate ions.

Fehling's solution can be prepared by mixing equal volumes of solution **X** and **FA 2**.

Using only the four unlabelled solutions, **FA 2** and solution **X**, you are to describe a detailed sequence of steps to identify each of the four solutions. Each of the solutions should be identified by at least one positive test.

Your plan should also state the expected observations, identities of any gas and/or precipitate formed and solutions identified at each step.

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…………………………………………………………………………………………………[5]

[Total: 16]

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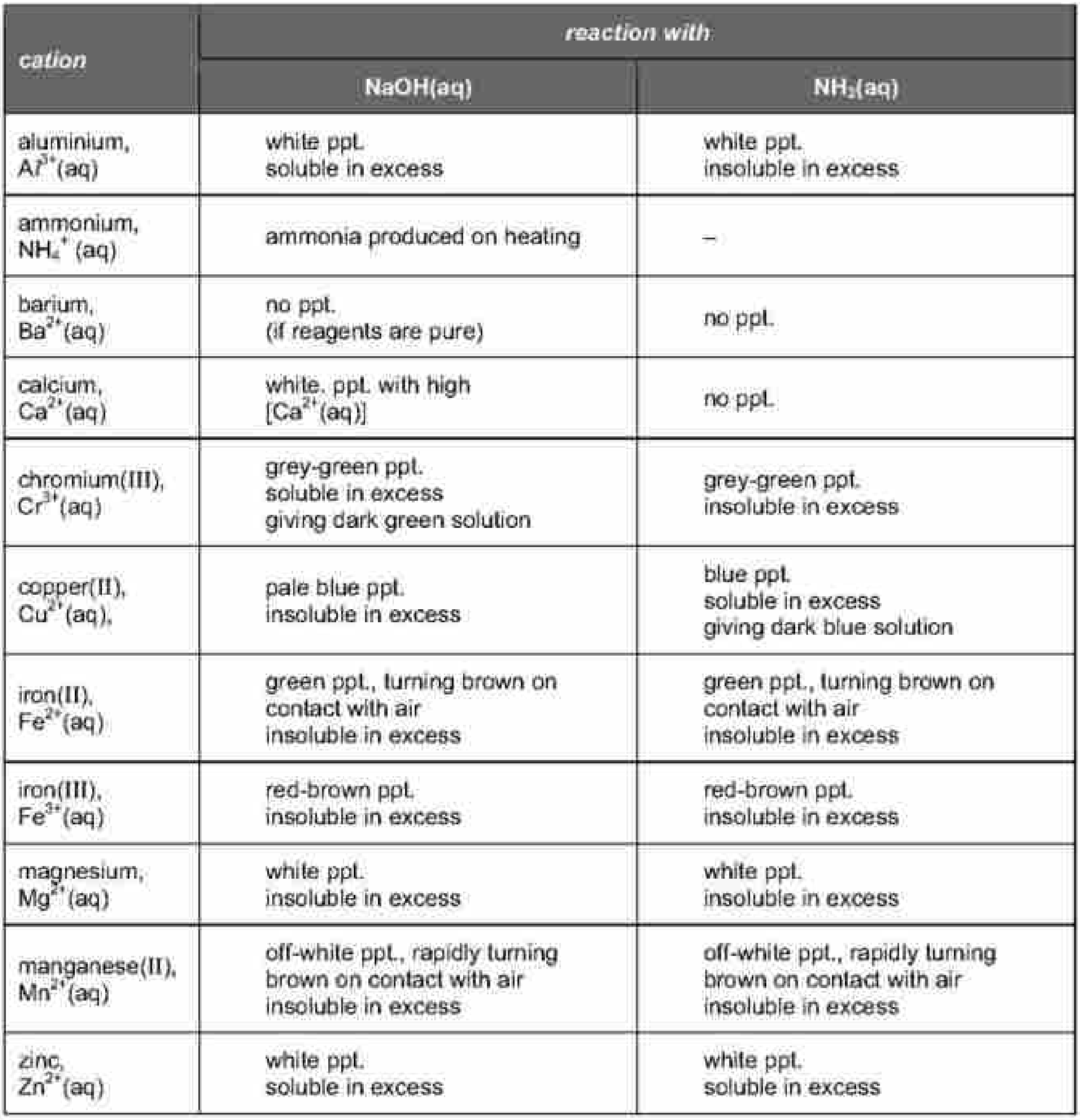
Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations



cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Test for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colours of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 RI H2 Chemistry Preliminary Examinations Paper 4 – Preparation List

Apparatus list (per student)

s/n	Apparatus	Quantity	Question Number
1	50 cm^3 burette	2	1
2	Filter funnel	2 (1 glass, 1 plastic)	1 and 3
3	25 cm^3 Pipette	1	1
4	Pipette filler	1	1
5	White tile	1	1
6	250 cm^3 conical flask	2	1
7	250 cm^3 volumetric flask	1	1
8	10 cm^3 measuring cylinder	1	1 and 3
9	Deionised water bottle	1	1, 2 and 3
10	100 cm^3 beaker	1	1
11	250 cm^3 beaker	1	2
12	50 cm^3 measuring cylinder	2	2
13	Polystyrene cup	2	2
14	Thermometer	1	2
15	Test-tube rack	1	3
16	Test-tubes Boiling tube Droppers	4 2 4	3 2 1,2 and 3
17	Bunsen burner, shield and rubber mat	1	3
18	Lighter	1	3
19	Glass rod	1	3
20	Wooden splint, litmus papers and filter paper	—	3

Chemical List (per student)

Code	Identity of reagent	Question	Quantity required
FA 1	0.05 mol dm^{-3} $Na_2S_2O_3$	1	120 cm^3
FA 2	0.276 mol dm^{-3} $CuSO_4$	1,3	80 cm^3
FA 3	10% KI	1	40 cm^3
Starch	2% starch solution	1	5 cm^3
FA 5	**0.25 mol dm^{-3} sodium chlorate(I), NaClO** 10% NaClO, Density = 1.10g.ml MW=74.44g/mol **Molarity =** (10%/100)x1.10x(1/74.4)(1000) = 1.478 mol/L **m1v1=m2v2** v1 = (1000x0.25)/1.478 **= 169.15 ml/L**	2	160 cm^3
FA 6	0.100 mol dm^{-3} $Na_2S_2O_3$ in **0.08 mol dm^{-3} NaOH** Weigh the salts and mixed. Make-up to 1 dm^3.	2	160 cm^3
FA 8	Zn powder	3	B155 and spoon
FA 9	0.5 mol dm^{-3} ammonium vanadate(V), NH_4VO_3(aq) Weigh the chemical and dissolves into 2M NaOH per each dm^3.	3	10 cm^3

Bench reagents

1. 1 mol dm^{-3} H_2SO_4
2. 2M NH_3
3. $Ca(OH)_2(aq)$
4. NH_4Cl solid (8g each)
5. Aq. H_2O_2 3% solute

2018 Y6 H2 Chemistry Preliminary Exams Paper 4 (Suggested Solutions)

1(a) Volume of **FA 2** needed = $\frac{5}{30}$ x 250 = $\underline{41.67\text{ cm}^3}$

1(b) Dilution of **FA 2**:

Final burette reading / cm^3	41.00
Initial burette reading / cm^3	0.00
Volume of **FA 2** used / cm^3	41.00

Titration Results:

Titration number	**1**	**2**
Final burette reading / cm^3	24.80	24.80
Initial burette reading / cm^3	0.00	0.00
Volume of **FA 1** used / cm^3	24.80	24.80
Values used	✓	✓

1(c) Average volume of **FA 1** used = $\frac{24.80 + 24.80}{2}$

= $\underline{24.80\text{ cm}^3}$

$\underline{25.0}$ cm^3 of **FA 4** produced an amount of iodine which required $\underline{24.80}$ cm^3 of **FA 1**.

1(d) Amount of thiosulfate ions = $0.0500 \times \frac{24.80}{1000}$ = $\underline{1.24 \times 10^{-3}\text{ mol}}$

Mole ratio of Cu^{2+} : I_2 : $S_2O_3^{2-}$ = 2 : 1 : 2

Amount of Cu^{2+} in 25.0 cm^3 of **FA 4** = amount of $S_2O_3^{2-}$

= 1.24×10^{-3} mol

[Cu^{2+}] in **FA 4** = $\frac{1.24\times10^{-3}}{25.0\times10^{-3}}$ = $\underline{0.0496\text{ mol dm}^{-3}}$

1(e) [Cu^{2+}] in **FA 2** = 0.0496 x $\frac{250}{41}$ = $\underline{0.302\text{ mol dm}^{-3}}$

1(f) Amount of NaI in 10 cm^3 of 50 g dm^{-3} sodium iodide

= $\frac{50}{23.0 + 126.9}$ x 0.010 = $\underline{0.00334\text{ mol}}$

Amount of NaI required to react with Cu^{2+} in 25.0 cm^3 of **FA 4**

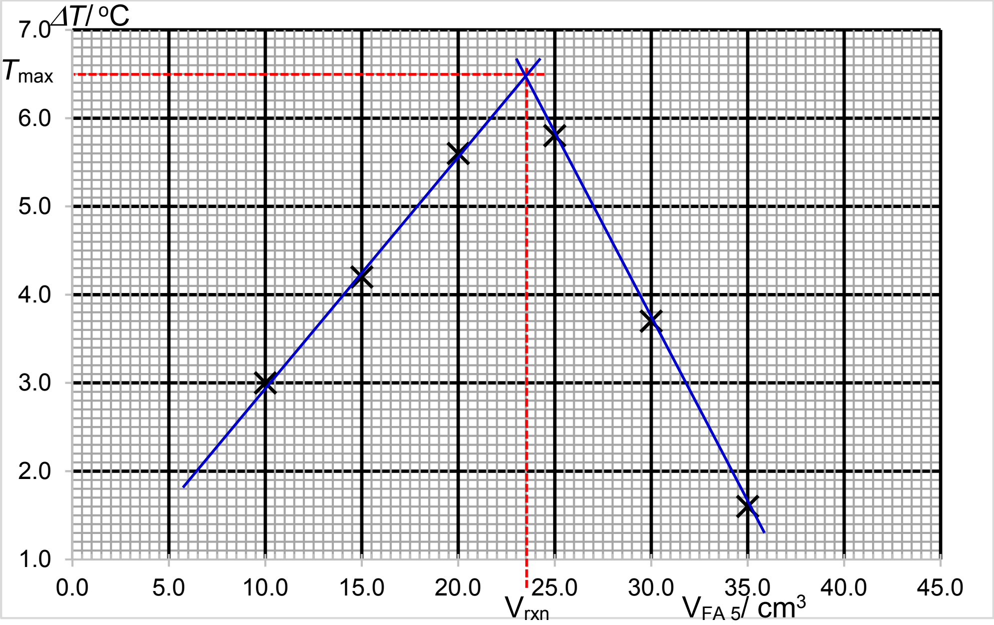
= 2 x 25.0 x 10^{-3} x 0.0496 = 0.00248 mol

When using 50 g dm^{-3} sodium iodide, amount of <u>iodide is still in excess</u>. Hence there is <u>no effect</u> on the titre volume as the same amount of I_2 will be produced.

2(b)(i) Results:

No	V_{FA5}/ cm^3	V_{FA6}/ cm^3	T_1/ °C	T_2/ °C	ΔT/ °C
1	10.0	30.0	29.0	32.0	3.0
2	20.0	20.0	29.6	35.2	5.6
3	30.0	10.0	29.6	33.3	3.7
4	35.0	5.0	30.0	31.6	1.6
5	25.0	15.0	29.6	35.4	5.8
6	15.0	25.0	29.0	33.2	4.2

2(b)(ii)



2(b)(iii) maximum temperature change of reaction mixture, ΔT_{max} = <u>6.5</u> °C
volume of **FA 5** required for complete reaction, V_{rxn} = <u>23.5</u> cm^3

2(c)(i) To obtain ΔT_{max}, $V_{FA6} = 40.0 - 23.5 = 16.5\ cm^3$

Amount of $S_2O_3^{2-} = \frac{16.5}{1000} \times 0.100 = \underline{0.00165\ mol}$

Amount of NaClO in 23.5 cm^3 of **FA 5**

= 4 x amount of $S_2O_3^{2-}$ = 0.00660 mol

Concentration of NaClO in **FA 5** $= \frac{0.00660}{0.0235} = \underline{0.281\ mol\ dm^{-3}}$

2(c)(ii) Heat given out = 40.0 x 4.18 x 6.5 = <u>1086.8 J</u>

$\Delta H_1 = -\frac{1086.8}{0.00165}\ J\ mol^{-1} = \underline{-659\ kJ\ mol^{-1}}$

2(d) $q = mc\Delta T_{max} = n \times \Delta H_1 \Rightarrow \Delta T_{max} = \frac{n \times \Delta H_1}{m \times c}$

When $\mathbf{V_{FA5}}$ and $\mathbf{V_{FA6}}$ are doubled, <u>both n and m are doubled</u> (ΔH_1 and c remain constant).
Hence <u>ΔT_{max} is unaffected</u>.

2(e)(i) Amount of $S_2O_3^{2-} = 0.030 \times 0.100 = 3.00 \times 10^{-3}$ mol
Amount of $ClO^- = 4 \times$ amount of $S_2O_3^{2-}$ = 0.0120 mol
Mass of NaClO = 0.0120 x (23.0 + 35.5 + 16.0) = <u>0.894 g</u>

2(e)(ii) Assuming a percentage purity of 80 % NaC*l*O,

Mass of **FA 7** required $= \dfrac{0.894}{0.80} = \underline{1.12\ \text{g}}$

2(e)(iii) **<u>Using an analytical balance</u>**, weigh accurately about 0.400 g of **FA 7. Record the mass of the weighing bottle and the mass of FA 7,** m_1.

Using a burette, add 30.00 cm^3 of FA 6 in a clean and dry Styrofoam cup. Place the cup inside a second Styrofoam cup which is placed in a 250 cm^3 glass beaker to prevent it from tipping over.

Place a thermometer into the cup containing FA 6. Stir gently, measure and record the initial temperature of FA 6, T_1.

Pour **FA 7** from the weighing bottle into the cup containing **FA 6.** Using the thermometer, **stir to dissolve FA 7, measure and record the highest temperature of the mixture**, T_2.

Weigh and record the mass of the emptied weighing bottle, m_2.

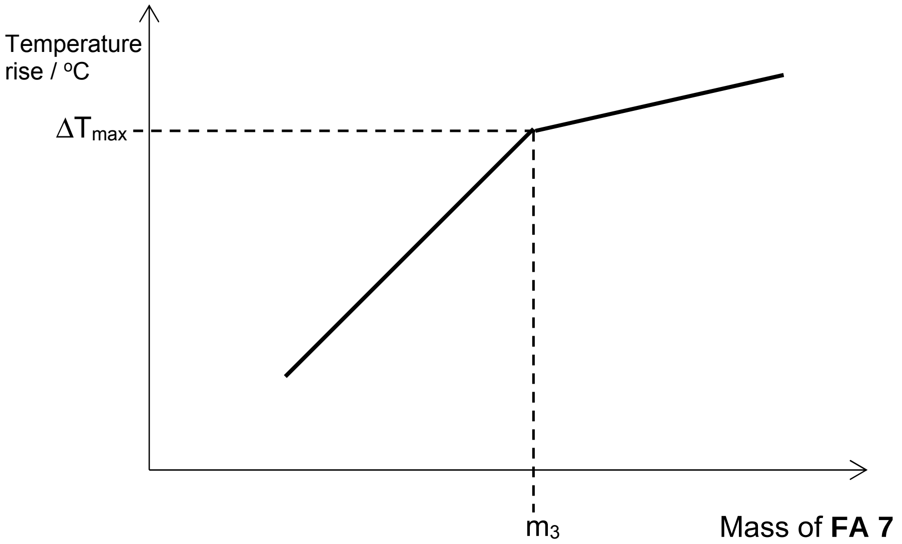
Mass of **FA 7** used = $m_1 - m_2$.

Maximum temperature change = $T_2 - T_1$.

Repeat the experiment using 0.600 g, 0.800 g, 1.200 g, 1.400 g and 1.600 g of **FA 7.**

Plot graph of maximum temperature change against mass of FA 7 used.

A graph similar to the following graph would be obtained:



m_3 and $\Delta T_{\max}$ may be obtained.

Percentage purity of NaC*l*O in **FA 7** $= \dfrac{0.894}{m_3} \times 100\ \%$

Heat change, $q = 30.00 \times 4.18 \times \Delta T_{\max}$

Enthalpy change of reaction 2, $\Delta H_2 = -\dfrac{30.00 \times 4.18 \times \Delta T_{\max}}{\text{amount of } S_2O_3^{2-}} = -\dfrac{30.00 \times 4.18 \times \Delta T_{\max}}{0.003}$

$= \underline{-41800\ \Delta T_{max}\ \text{J mol}^{-1}}$

2(e)(iii)

$$\begin{tikzcd}
4NaClO(s) + Na_2S_2O_3(aq) + 2NaOH(aq) \arrow[rr, "\Delta H_2"] \arrow[dr, "4\Delta H_{sol}"'] & & 4NaCl(aq) + 2Na_2SO_4(aq) + H_2O(l) \\
& 4NaClO(aq) + Na_2S_2O_3(aq) + 2NaOH(aq) \arrow[ur, "\Delta H_1"'] &
\end{tikzcd}$$

$\Delta H_{sol} = \frac{1}{4}(\Delta H_2 - \Delta H_1)$

3(a)

	Test	**Observations**
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 2** into a boiling tube. Add 4 spatulas of **FA 8**. Warm the mixture cautiously till boiling. Leave to cool for 5 minutes. Filter the mixture and keep the filtrate for tests **(ii)** and **(iii)**.	Blue **FA 2** turns colourless. Red-brown/brown/black residue colourless filtrate
(ii)	To 1 cm depth of the filtrate, add aqueous ammonia.	White ppt formed, soluble in excess NH_3 to give a colourless solution.
(iii)	To another 1 cm depth of the filtrate, add 2 spatulas of solid ammonium chloride, followed by aqueous ammonia.	No ppt formed.
(v)	Using a spatula, add a **very small quantity** of **FA 8** to the boiling tube containing **FA 10** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 8** in small quantities with swirling, until no further colour change is observed. Record all colour changes observed.	Yellow solution turns green Green solution turns blue Blue solution turns green Green solution turns violet/purple Effervescence of H_2 gas extinguished lighted splint with a 'pop sound.
(vi)	To 1 cm depth of the filtrate from test **(v)**, add an equal volume of aqueous hydrogen peroxide.	Violet solution turns red brown/brown/ orange/orange-brown. Effervescence of O_2 gas relighted glowing splint.

3(b)(i)

Identity of FA 8	**Evidence**
Zn	In test (i), Zn was oxidised to Zn^{2+} by Cu^{2+} in **FA 2**. In test (ii) The Zn^{2+} formed a white ppt of $Zn(OH)_2$, soluble in excess NH_3 to give a colourless solution.

3(b)(ii)

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ----(1)

In the presence of NH_4^+ from the full dissociation of ammonium chloride, the dissociation of NH_3 is suppressed (or position of equilibrium of (1) lies to the left).

The concentration of OH^- is too low for the ionic product to exceed K_{sp} or for ppt to form.

3(b)(iii) The grey ppt was $V(OH)_2$.

3(c) Add **FA 2** to the four unknown solutions. The solution that produces a bluish green ppt of $CuCO_3$ is Na_2CO_3.

To the three remaining solutions that did not give a blue–green ppt, add an equal volume of Solution **X** and warm.
The solution that produces a reddish brown ppt of Cu_2O is CH_3CH_2CHO.

The two remaining solutions that did not produce any ppt are $Al_2(SO_4)_3$ and CH_3COOH.

To the two remaining solutions, add the unknown that was identified as Na_2CO_3.

The solution that produces effervescence of CO_2 is CH_3COOH.

The solution that produces effervescence of CO_2 and a white ppt of $Al(OH)_3$ is $Al_2(SO_4)_3$.

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

29 August 2018
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **18** printed pages.

[Turn over

1 The Basic Oxygen steel-making process is a method of preparing steel from carbon-rich molten pig iron. The process is basic because chemical bases are added to remove impurities. One such impurity is phosphorus pentoxide, P_4O_{10}. Calcium oxide, CaO, is added to remove it and the only product of the reaction is the salt, calcium phosphate, $Ca_3(PO_4)_2$.

How many moles of CaO reacted with one mole of P_4O_{10} in this reaction?

A 1

B 1.5

C 3

D 6

2 Two moles of an oxidising agent, XO_4^- in the presence of excess acid oxidised 96 dm^3 of nitrogen dioxide gas at room temperature and pressure to NO_3^-.

What is the number of moles of electrons accepted by one mole of XO_4^-?

A 1 **B** 2 **C** 3 **D** 4

3 *Use of the Data Booklet is relevant to this question.*

The ion **T**$^+$ contains 28 electrons and 35 neutrons.

Which of the following statements about **T**$^+$ or **T** is correct?

A **T** and Ga^{3+} are isoelectronic species.

B The elemental form of **T** can be oxidised by chlorine.

C The electronic configuration of **T**$^+$ ion is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^1$.

D The angle of deflection of $^{27}Al^{3+}$ is approximately three times that of **T**$^+$ in an electric field.

4 Which of the following species has a different bond angle from the rest?

A ICl_3 **B** SF_3^+ **C** ClO_3^- **D** N_2H_4

5 What will happen to the volume of a bubble of air submerged in water under a lake at 10.0 °C and 2.00 atm if it rises to the surface where the temperature is 20.0 °C and the pressure is 1.00 atm?

A The volume will increase by a factor of 2.00.

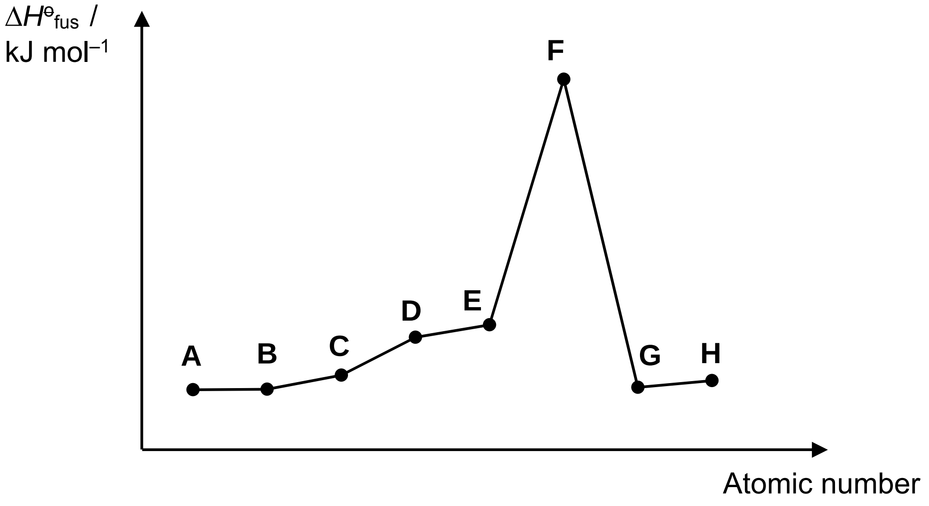
B The volume will increase by a factor of 2.07.

C The volume will decrease by a factor of 2.00.

D The volume will decrease by a factor of 1.93.

6 The graph below shows the variation in the standard enthalpy change of fusion, $\Delta H^{\ominus}_{fus}$ for 8 consecutive elements from period 2 to 3 in the periodic table.

Standard enthalpy change of fusion is the heat absorbed when one mole of a substance changes its state from solid to liquid under standard conditions.



Which of the following statements is true based on the information deduced from the above graph?

A The chlorides become more acidic from **A** to **C**.

B An oxide of **E** dissolves in water to form an alkaline solution.

C Element **G** has a higher first ionisation energy than element **F** and **H**.

D Element **D** has a lower electrical conductivity as compared to element **F**.

7 Some enthalpy changes of combustion are given below.

	ΔH_c / kJ mol^{-1}
$CO(g)$	–283
$H_2(g)$	–286
$CH_3OH(l)$	–715

What is the enthalpy change of the following reaction, in kJ mol^{-1}?

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

A –146

B +146

C –140

D +140

8 The reaction of nitrogen monoxide and hydrogen gas

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

is thought to involve the following steps:

I $NO + NO \rightleftharpoons N_2O_2$ (fast)

II $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

Which of the following about the reaction is true?

A H_2 acts as the catalyst.

B The rate equation for the reaction is rate = $k[N_2O_2][H_2]$.

C The overall order of the reaction is 3.

D Increasing the concentration of NO does not change the rate of reaction.

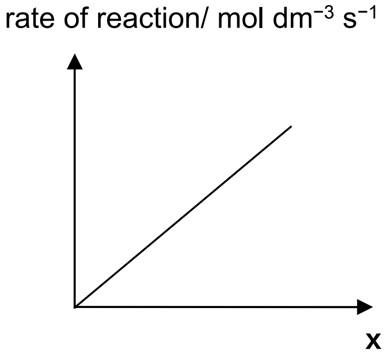
9 Hydrogen peroxide reacts with acidified iodide ions liberating iodine according to the equation below:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

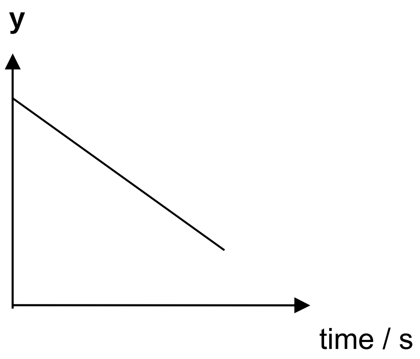
The kinetics of this reaction was investigated and it was found to have the following rate equation: rate = $k[H_2O_2][I^-]$

Two series of experiments were conducted, giving rise to **Graph A** and **Graph B**.

Graph A



Graph B

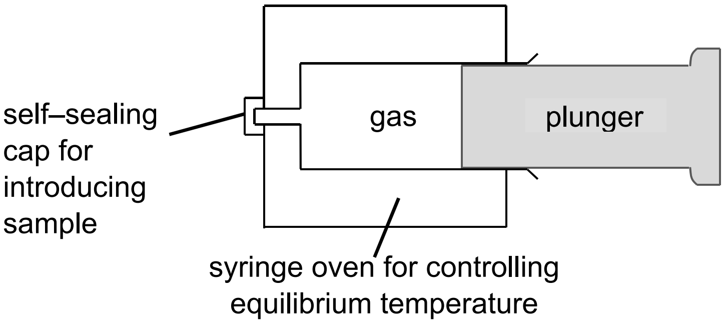


Which of the following shows the correct labelling of the x-axis for **Graph A** and y-axis for **Graph B**?

	x-axis	y-axis
A	$[H_2O_2][I^-]$ / mol^2 dm^{-6}	$[H^+]$ / mol dm^{-3}
B	$[H^+]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}
C	$[H_2O_2][I^-]$ / mol^2 dm^{-6}	$[I^-]$ / mol dm^{-3}
D	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}

10 A gaseous dimer, **Z**, is introduced into an empty gas syringe which has a movable, tightly–fitting plunger. The gas is allowed to expand until equilibrium is reached at a controlled temperature at which 20 % of **Z** dissociates into its monomer **W**.

$$\mathbf{Z}(g) \rightleftharpoons 2\mathbf{W}(g)$$



Which of the following statements is correct?

A The forward reaction is exothermic.

B The value of the equilibrium constant, K_p is 0.167 atm.

C The pressure inside the syringe at equilibrium will be higher than the atmospheric pressure.

D The dissociation of dimer **Z** will be favoured when the plunger is pushed back into the equilibrium mixture.

11 The acid dissociation constants for the diprotic acid, malonic acid $H_2C_3H_2O_4$ are $K_{a1} = 1.5 \times 10^{-3}$ and $K_{a2} = 2.0 \times 10^{-6}$.

What is the K_b for $HC_3H_2O_4^-$?

A $K_w \times K_{a1}$

B $K_w \times K_{a2}$

C K_w / K_{a1}

D K_w / K_{a2}

12 Hardness in tap water can be determined by titrating a sample against a reagent which forms complex ions with dissolved metal ions. The indicator for this titration requires the pH to be maintained at about 10.

Which of the following, in aqueous solution, could be used to maintain the pH at about 10?

A 10 cm^3 of 2.0 g dm^{-3} of sodium hydroxide neutralised by 10 cm^3 of 0.025 mol dm^{-3} of ethanoic acid

B 5 cm^3 of 1.7 g dm^{-3} of ammonia neutralised by 10 cm^3 of 0.025 mol dm^{-3} hydrochloric acid

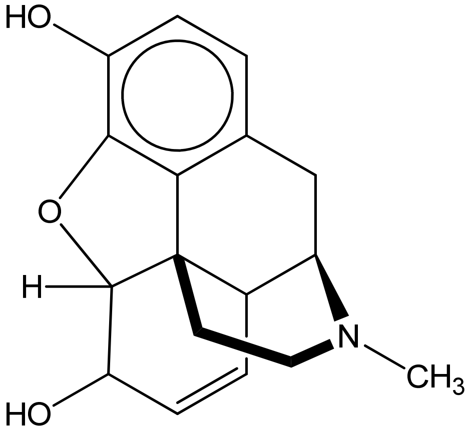
C 20 cm^3 of 0.05 mol dm^{-3} of hydrochloric acid neutralised by 5 cm^3 of 1.7 g dm^{-3} ammonia

D 10 cm^3 of 0.05 mol dm^{-3} of ethanoic acid neutralised by 5 cm^3 of 2.0 g dm^{-3} of sodium hydroxide

13 The solubility product of some sparingly soluble lead compounds are shown below. Which compound will have the lowest concentration of $Pb^{2+}(aq)$ ions in a saturated solution?

	compound	numerical value of solubility product (at 25 °C)
A	lead(II) fluoride	2.7×10^{-8}
B	lead(II) bromide	4.0×10^{-5}
C	lead(II) iodide	7.1×10^{-9}
D	lead(II) sulfate	1.6×10^{-8}

14 Morphine is a powerful narcotic painkiller which could be isolated from opium poppy. Though it relieves pain effectively, it can cause addiction so readily that it should only be used in the cases where other pain medications are inadequate.



morphine

Which of the following claims about morphine is true?

1 There are 5 chiral carbons present in the molecule.

2 There are 7 C–C bonds formed by $sp^3 - sp^3$ overlap.

3 The molecule cannot exhibit cis-trans isomerism at the C=C double bond.

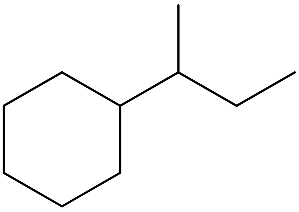
A 1 only

B 2 only

C 2 and 3 only

D 1, 2 and 3

15 Compound **L** reacts with limited chlorine gas in the presence of sunlight.



compound **L**, $C_{10}H_{20}$

Assuming that only mono-chlorination takes place and ignoring the relative rates of abstraction of the different type of hydrogen atom, which of the following statements is **incorrect**?

A The maximum number of chlorinated products formed is 8.

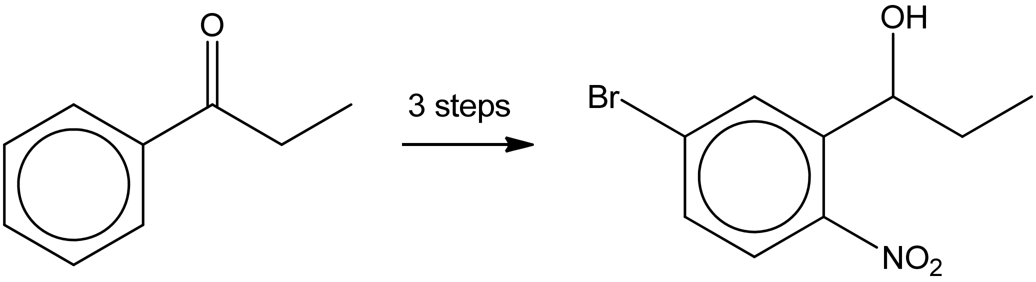
B $C_{20}H_{38}$ is present in small quantities in the products.

C Homolytic fission occurs in both initiation and propagation step.

D The ratio of primary to secondary to tertiary chloroalkanes formed is 3:6:2.

16 *Use of the Data Booklet is relevant to this question.*

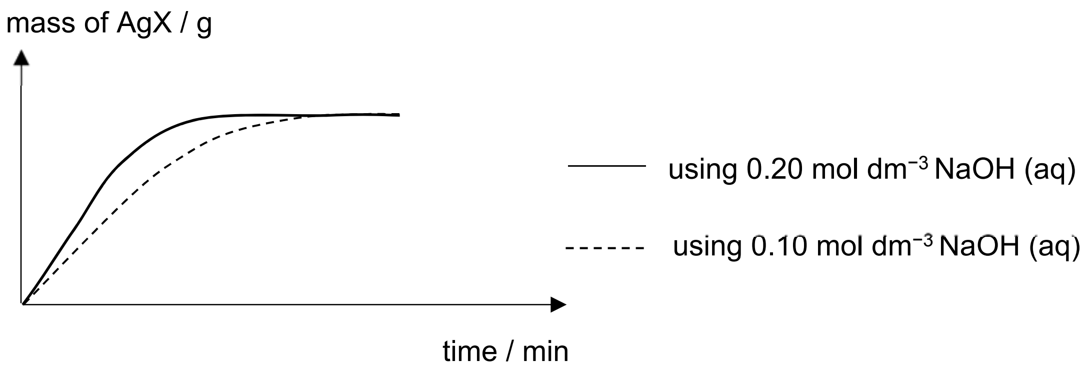
The following transformation takes place in three steps.



Which of the following shows the best choice of reagents and conditions to carry out the transformation?

	step 1	step 2	step 3
A	H_2, Pt	conc HNO_3, conc H_2SO_4	Br_2, $FeBr_3$
B	Br_2, $FeBr_3$	H_2, Pt	conc HNO_3, conc H_2SO_4
C	H_2, Pt	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4
D	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4	H_2, Pt

17 A halogen-containing compound, **U**, is heated with 2 different concentrations of aqueous sodium hydroxide. After acidifying the mixture and adding excess aqueous silver nitrate, the mass of silver halide formed is analysed over a period of time. The following graph for the mass of silver halide precipitate against time was obtained.



Which of the following is the likely structure of **U**?

A

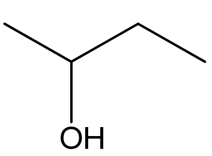
B

C

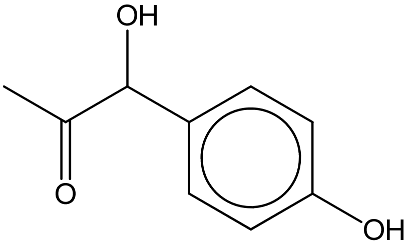
D

18 The following two compounds react with alkaline aqueous iodine to form yellow precipitate of tri-iodomethane as one of the products.

What is the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively?



compound **V**



compound **W**

	compound **V**	compound **W**
A	4	4
B	4	6
C	6	4
D	6	5

19 A fresh salad with tomatoes may contain compound $CH_3CH_2CH_2CH{=}CHCHO$ which provides an aroma for tomatoes. What will be the final product, **P** in this sequence of reactions?

$$CH_3CH_2CH_2CH{=}CHCHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \mathbf{O} \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} \mathbf{P}$$

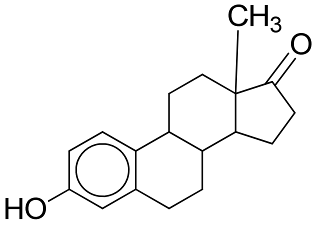
A $CH_3CH_2CH_2CH{=}CHCOOH$

B $CH_3CH_2CH_2CH_2CH_2COOH$

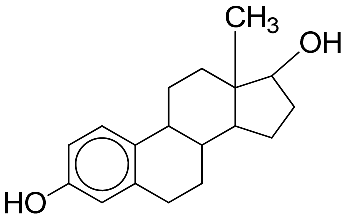
C $CH_3CH_2CH_2CH{=}CHCH_2OH$

D $CH_3CH_2CH_2COOH$

20 Two female sex hormones are oestrone and oestradiol.



oestrone



oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

1 $SOCl_2$

2 $KMnO_4/H^+$

3 $LiAlH_4$ in dry ether

A 1, 2 and 3

B 1 and 2 only

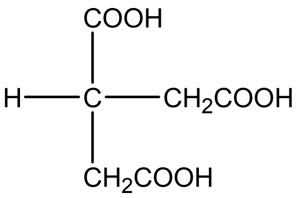
C 2 and 3 only

D 1 only

21 Ethanoic acid can be made by direct carbonylation of methanol, in presence of a rhodium catalyst.

$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

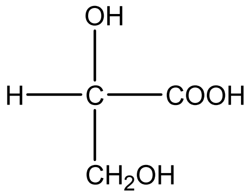
Which of the following can produce compound **S** using a similar method?



$H{-}C(COOH)(CH_2COOH){-}CH_2COOH$

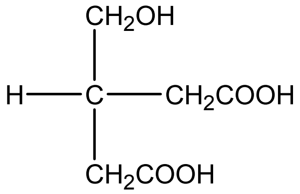
compound **S**

A



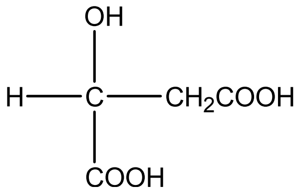
$H{-}C(OH)(CH_2OH){-}COOH$

B



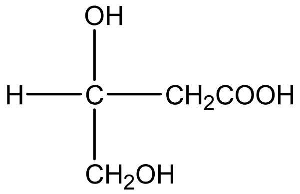
$H{-}C(CH_2OH)(CH_2COOH){-}CH_2COOH$

C



$H{-}C(OH)(COOH){-}CH_2COOH$

D



$H{-}C(OH)(CH_2OH){-}CH_2COOH$

22 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

1 It reacts with excess CH_3CH_2Cl to form the compound, $C_{13}H_{22}NCl$.

2 It reacts with CH_3COOH to form $C_6H_5CH_2NHCOCH_3$.

3 It can be distinguished from $CH_3CH_2NH_2$ by the use of aqueous bromine.

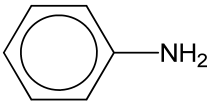
A 1, 2 and 3

B 1 and 2 only

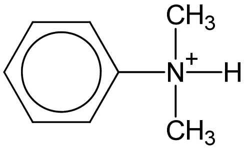
C 1 only

D 2 and 3 only

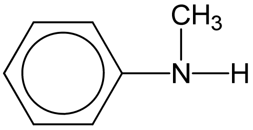
23 The structures of some nitrogen containing compounds are shown below.



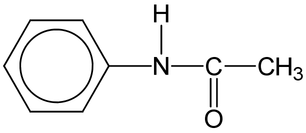
compound **H**



compound **I**



compound **J**



compound **K**

What is the order of increasing basicity of the nitrogen containing compounds?

	least basic	⟶		most basic
A	**I**	**H**	**K**	**J**
B	**I**	**K**	**H**	**J**
C	**I**	**K**	**J**	**H**
D	**K**	**I**	**J**	**H**

24 *Use of Data Booklet is relevant to this question.*

Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power decreases from chlorine to iodine.

2 The bond length of the molecule increases from chlorine to iodine.

3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 and 2 only

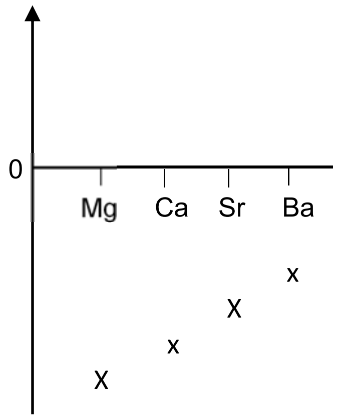
B 1 and 3 only

C 2 and 3 only

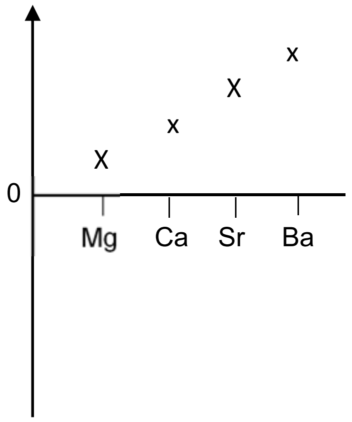
D 1, 2 and 3

25 Which diagram correctly shows the trend in a property of the Group 2 elements Mg, Ca, Sr, Ba?

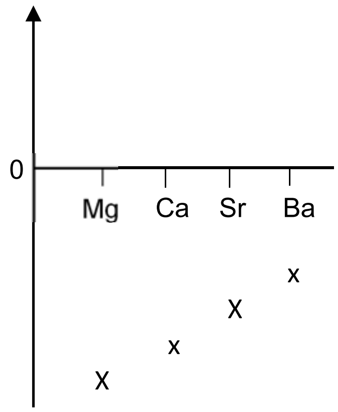
A ΔH_{hyd}, the enthalpy change of hydration of M^{2+}(g)



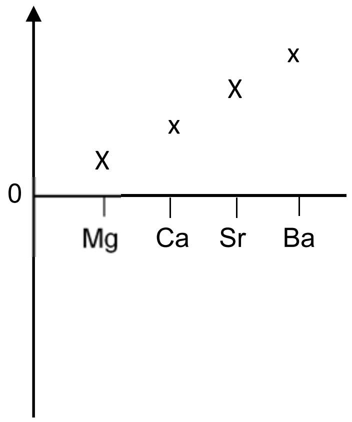
B *I*, the first ionisation energy



C $E^\ominus$, the standard electrode potential of M^{2+}(aq)I M(s) electrode



D Electronegativity value



26 Three half cells are constructed as follows.

Half cell **I**: an electrode of metal **Q** in a 1.0 M solution of **Q**$^+$(aq) ions

Half cell **II**: an electrode of metal **R** in a 1.0 M solution of **R**$^+$(aq) ions

Half cell **III**: an electrode of Cu metal in a 1.0 M solution of Cu^{2+}(aq) ions

The half cells are connected in pairs, as shown below, to form a series of galvanic cells. For each cell, the polarity of the electrodes and the voltage generated are recorded.

half cells used	positive electrode	negative electrode	voltage (V)
I and **III**	Cu	**Q**	0.57
II and **III**	Cu	**R**	1.10
I and **II**	**Q**	**R**	0.53

Which one of the following lists the metals in order of **increasing** strength as reducing agents?

A **R**, **Q**, Cu

B **Q**, Cu, **R**

C Cu, **R**, **Q**

D Cu, **Q**, **R**

27 Some standard redox potential ($E^\ominus$) values are given in the table below.

electrode reaction	$E^\ominus$/ V
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$	+1.45

Which of the following reactions would occur under standard conditions?

1 $Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

2 $Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

3 $2Ce^{4+}(aq) + Sn^{2+}(aq) \longrightarrow 2Ce^{3+}(aq) + Sn^{4+}(aq)$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

28 A current was passed through two cells connected in series. The first cell contained molten sodium chloride while the other contained a molten aluminium salt.

What would be the mass of aluminium liberated from the other cell if 4.6g of sodium was liberated from the first cell?

A 0.9 g

B 1.8 g

C 2.7 g

D 3.6 g

29 Which of the following does **not** act as a ligand in the formation of complexes?

A SCN^-

B Cl^-

C AlH_4^-

D $C_2O_4^{2-}$

30 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **X** and **Y** are copper-containing species.

$$\mathrm{CuSO_4(aq)} \xrightarrow[\text{I}]{\mathrm{NH_3(aq)}} \mathbf{X} \xrightarrow[\text{II}]{\substack{\text{excess} \\ \mathrm{NH_3(aq)}}} \mathbf{Y} \xrightarrow[\text{III}]{\mathrm{Na_4edta(aq)}} \mathrm{[Cu(edta)]^{2-}(aq)}$$

Which of the following statements is true?

1 NH_3 acts as a ligand in reaction I.

2 Reaction II is a redox reaction.

3 The entropy of the system increases when reaction III occurs.

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3 only

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/01

Paper 1 Multiple Choice

29 August 2018
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluids.
Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **18** printed pages.

1	D	**11**	C	**21**	D
2	B	**12**	B	**22**	C
3	B	**13**	D	**23**	B
4	A	**14**	D	**24**	A
5	B	**15**	D	**25**	A
6	C	**16**	B	**26**	D
7	C	**17**	A	**27**	A
8	C	**18**	D	**28**	B
9	A	**19**	A	**29**	C
10	B	**20**	D	**30**	B

1 The Basic Oxygen steel-making process is a method of preparing steel from carbon-rich molten pig iron. The process is basic because chemical bases are added to remove impurities. One such impurity is phosphorus pentoxide, P_4O_{10}. Calcium oxide, CaO, is added to remove it and the only product of the reaction is the salt, calcium phosphate, $Ca_3(PO_4)_2$.

How many moles of CaO reacted with one mole of P_4O_{10} in this reaction?

A 1

B 1.5

C 3

D 6

$P_4O_{l0} + 6CaO \rightarrow 2Ca_3(PO_4)_2$

Given that Ca_3PO_4 is the only product, write the balanced equation between P_4O_{10} and CaO to form Ca_3PO_4. Based on mole ratio, 6 moles of CaO is required to completely react with one mole of P_4O_{l0}.

Answer: **D**

2 Two moles of an oxidising agent, XO_4^- in the presence of excess acid oxidised 96 dm^3 of nitrogen dioxide gas at room temperature and pressure to NO_3^-.

What is the number of moles of electrons accepted by one mole of XO_4^-?

A 1 **B** 2 **C** 3 **D** 4

$n(NO_2) = 96/24 = 4$

$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ + e$

$XO_4^- \equiv NO_2$

2 : 4

1 : 2

2 mol of NO_2 donate 2 mol of e which is accepted by 1 mol of XO_4^-

3 *Use of the Data Booklet is relevant to this question.*

The ion $\textbf{T}^+$ contains 28 electrons and 35 neutrons.

Which of the following statements about $\textbf{T}^+$ or **T** is correct?

A **T** and Ga^{3+} are isoelectronic species.

B The elemental form of **T** can be oxidised by chlorine.

C The electronic configuration of $\textbf{T}^+$ ion is $1s^22s^22p^63s^23p^63d^94s^1$.

D The angle of deflection of $^{27}Al^{3+}$ is approximately three times that of $\textbf{T}^+$ in an electric field.

Since ion $\textbf{T}^+$ contains 28 electrons, element **T** is copper which contains 29 electrons.

Option A is wrong as Ga^{3+} has 28 electrons, hence **T** and Ga^{3+} do not have the same number of electrons.

Option B is correct as Cu can be oxidised to Cu^{2+} by chlorine.
$Cu^{2+} + 2e \rightleftharpoons Cu \quad E^\ominus = +0.34\ V$
$Cl_2 + 2e \rightleftharpoons 2Cl^- \quad E^\ominus = +1.36\ V$
$E^\ominus_{cell} = +1.36 - (+0.34) = +1.02\ V$

Option C is wrong as the electronic configuration of $\textbf{T}^+$ ion is $1s^22s^22p^63s^23p^63d^{10}$.

Option D is wrong as the angle of deflection of $^{27}Al^{3+}$ is not approximately three times that of $\textbf{T}^+$ in an electric field.

The angle of deflection depends on the charge-to-mass ratio of the particles.

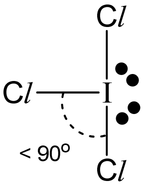
Angle of deflection of $Al^{3+} = k(\frac{3}{27}) = 0.111\ k$

Angle of deflection of $\textbf{T}^+ = k(\frac{1}{64}) = 0.0156\ k$

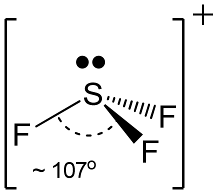
Answer: **B**

4 Which of the following species has a different bond angle from the rest?

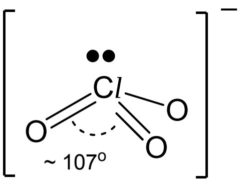
A ICl_3



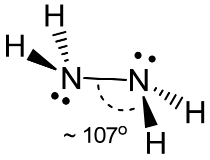
B SF_3^+



C ClO_3^-



D N_2H_4



Answer: **A**

5 What will happen to the volume of a bubble of air submerged in water under a lake at 10.0 °C and 2.00 atm if it rises to the surface where the temperature is 20.0 °C and the pressure is 1.00 atm?

A The volume will increase by a factor of 2.00.

B The volume will increase by a factor of 2.07.

C The volume will decrease by a factor of 2.00.

D The volume will decrease by a factor of 1.93.

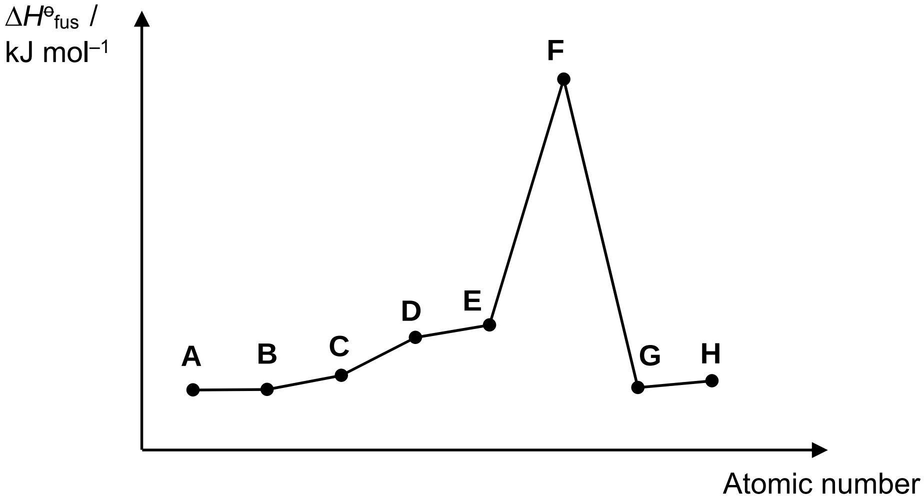
Answer : **B**

$P_1V_1/T_1 = P_2V_2/T_2$
$2(V_1)/(273+10) = 1(V_2)/(273+20)$

$V_2 = 293 \times (2) \times V_1 / 283 = 2.07\, V_1$

6 The graph below shows the variation in the standard enthalpy change of fusion, $\Delta H^\ominus_{fus}$ for 8 consecutive elements from period 2 to 3 in the periodic table.

Standard enthalpy change of fusion is the heat absorbed when one mole of a substance changes its state from solid to liquid under standard conditions.



Which of the following statements is true based on the information deduced from the above graph?

A The chlorides become more acidic from **A** to **C**.

B An oxide of **E** dissolves in water to form an alkaline solution.

C Element **G** has a higher first ionisation energy than element **F** and **H**.

D Element **D** has a lower electrical conductivity as compared to element **F**.

Since **F** is an element from period 2 to 3, and it has the largest $\Delta H^\ominus_{fus}$ (the rest of the elements have much lower $\Delta H^\ominus_{fus}$), **F** must be Si. Si has a giant covalent structure with high melting point and $\Delta H^\ominus_{fus}$.

So **A** is fluorine, **B** is neon, **C** is sodium, **D** is magnesium, **E** is aluminium, **G** is phosphorus and **H** is sulfur.

Option A is wrong as sodium chloride is a neutral chloride and there is no chloride of fluorine (fluorine reacts with chlorine to form chlorine fluoride instead). There is no reaction between neon and chlorine.

Option B is wrong as aluminium oxide is insoluble in water.

Option C is correct as phosphorus has a higher first ionisation energy than silicon and sulfur.

Option D is wrong as magnesium has a higher electrical conductivity as compared to silicon.

Answer: **C**

7 Some enthalpy changes of combustion are given below.

	ΔH_c / kJ mol^{-1}
$CO(g)$	–283
$H_2(g)$	–286
$CH_3OH(l)$	–715

What is the enthalpy change of the following reaction?

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$$

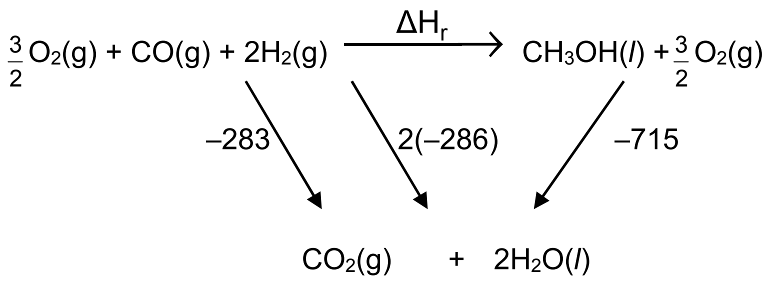
A –146

B +146

C –140

D +140

Answer: C



By Hess' law: $\Delta H_r = \Delta H_c\,(reactants) - \Delta H_c\,(products)$

= –283 + 2(–286) – (–715) = **–140** kJ mol^{-1}

8 The reaction of nitrogen monoxide and hydrogen gas

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

is thought to involve the following steps:

I $NO + NO \rightleftharpoons N_2O_2$ (fast)

II $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$ (slow)

III $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

Which of the following about the reaction is true?

A H_2 acts as the catalyst.

B The rate equation for the reaction is rate = $k[N_2O_2][H_2]$.

C The overall order of the reaction is 3.

D Increasing the concentration of NO does not change the rate of reaction.

Answer: C

A is incorrect as there is insufficient information to deduce that H_2 is the catalyst.

B is incorrect.

Based on the slow step:

Rate = k $[N_2O_2]$ $[H_2]$

However, N_2O_2 is not present in the final equation, this show that it is an intermediate and should not be present in the rate equation.

Based on step I,

$[N_2O_2]$ α k'$[NO]^2$

Rate = k'$[NO]^2[H_2]$

C is correct.

Based on the rate equation, overall order is 3.

D is incorrect. Since NO is present in the rate equation, increasing the concentration will increase the rate of reaction

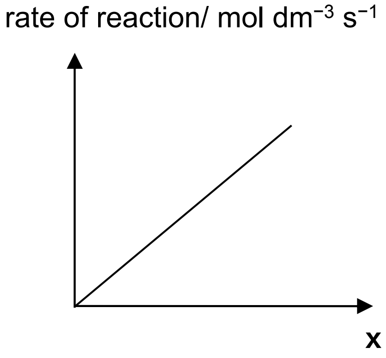
9 Hydrogen peroxide reacts with acidified iodide ions liberating iodine according to the equation below:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

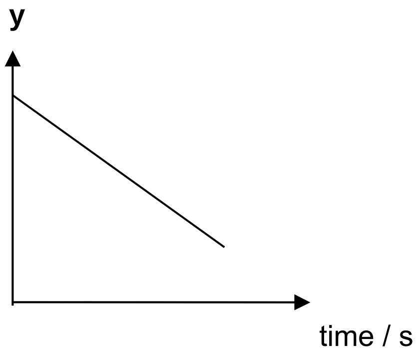
The kinetics of this reaction was investigated and it was found to have the following rate equation: rate = k $[H_2O_2]$ $[I^-]$

Two series of experiments were conducted, giving rise to **Graph A** and **Graph B**.

Graph A



Graph B



Which of the following shows the correct labelling of the x-axis for **Graph A** and y-axis for **Graph B**?

	x-axis	y-axis
A	$[H_2O_2]$ $[I^-]$ / mol^2 dm^{-6}	$[H^+]$ / mol dm^{-3}
B	$[H^+]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}
C	$[H_2O_2]$ $[I^-]$ / mol^2 dm^{-6}	$[I^-]$ / mol dm^{-3}
D	$[H^+]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}

Answer: A

Graph A:

As the rate eqn is rate = k $[H_2O_2]$ $[I^-]$

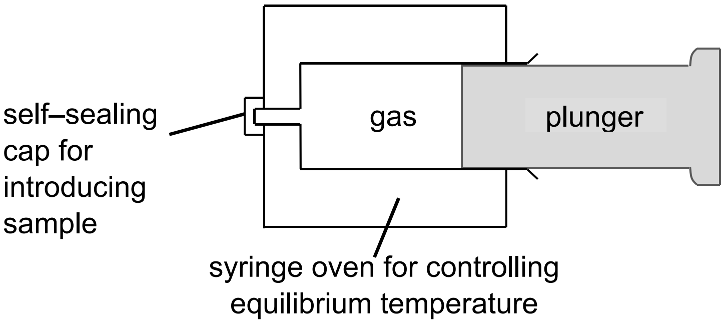
If y = mx , then y axis = rate

x-axis is $[H_2O_2]$ $[I^-]$

Graph B: It shows a zero order concentration-time graph (constant rate/grad), it is first order wrt to $[H_2O_2]$ and $[I^-]$. It is zero order wrt to $[H^+]$.

10 A gaseous dimer, **Z**, is introduced into an empty gas syringe which has a movable, tightly–fitting plunger. The gas is allowed to expand until equilibrium is reached at a controlled temperature at which 20 % of **Z** dissociates into its monomer **W**.

$$\mathbf{Z}(g) \rightleftharpoons 2\mathbf{W}(g)$$



Which of the following statements is correct?

A The forward reaction is exothermic.

B The value of the equilibrium constant, K_p is 0.167 atm.

C The pressure inside the syringe at equilibrium will be higher than the atmospheric pressure.

D The dissociation of dimer **Z** will be favoured when the plunger is pushed back into the equilibrium mixture.

Answer: **B**

Option A

The dissociation of a dimer only involves "bond breaking" and thus is an endothermic process.

Option B

Let the initial amount (mol) of **X** be 'a'

	$\mathbf{X}(g)$ $\rightleftharpoons$	$2\mathbf{W}(g)$
Initial/mol	a	0
Change/mol	–0.2a	+0.4a
Eqm/mol	0.8a	0.4a

P_W = (0.4a / 1.2a) x 1 atm = 1/3 atm

P_X = (0.8a / 1.2a) x 1 atm = 2/3 atm

$K_p = P_W^2 / P_X = (1/3)^2 / (2/3) = 1/6$ atm = 0.167 atm

Option C

The final pressure inside the syringe will have to be the same as atmospheric pressure (1 atm) to ensure that the syringe stops moving.

Option D

Pushing the plunger back will decrease volume, and thus cause the pressure of the system to increase.

Based on Le Chatelier's Principle, equilibrium position will shift to the left which has lesser gaseous particles to reduce the pressure. Thus association of **W** is favoured.

11 The acid dissociation constants for the diprotic acid, malonic acid $H_2C_3H_2O_4$ are $K_{a1} = 1.5 \times 10^{-3}$ and $K_{a2} = 2.0 \times 10^{-6}$.

What is K_b for $HC_3H_2O_4^-$?

A $K_w \times K_{a1}$

B $K_w \times K_{a2}$

C K_w / K_{a1}

D K_w / K_{a2}

Answer: **C**

$H_2C_3H_2O_4 \rightleftharpoons HC_3H_2O_4^- + H^+ \quad K_{a1} = 1.5 \times 10^{-3}$

$HC_3H_2O_4^- \rightleftharpoons C_3H_2O_4^{2-} + H^+ \quad K_{a2} = 2.0 \times 10^{-6}$

Measurement for K_b, $HC_3H_2O_4^-$ would be acting as a base accepting proton

$HC_3H_2O_4^- + H^+ \rightleftharpoons H_2C_3H_2O_4$

$K_w = K_{a1}(H_2C_3H_2O_4) \times K_b(HC_3H_2O_4^-)$ ($H_2C_3H_2O_4$ and $HC_3H_2O_4^-$ are conjugate acid-base pair)

$K_b(HC_3H_2O_4^-) = K_w / K_{a1}(H_2C_3H_2O_4)$

12 Hardness in tap water can be determined by titrating a sample against a reagent which forms complex ions with dissolved metal ions. The indicator for this titration requires the pH to be maintained at about 10.

Which of the following, in aqueous solution, could be used to do this?

A 10 cm^3 of 2.0 g dm^{-3} of sodium hydroxide neutralised by 10 cm^3 of 0.025 mol dm^{-3} of ethanoic acid

B 5 cm^3 of 1.7 g dm^{-3} of ammonia neutralised by 10 cm^3 of 0.025 mol dm^{-3} hydrochloric acid

C 20 cm^3 of 0.05 mol dm^{-3} of hydrochloric acid neutralised by 5 cm^3 of 1.7 g dm^{-3} ammonia

D 10 cm^3 of 0.05 mol dm^{-3} of ethanoic acid neutralised by 5 cm^3 of 2.0 g dm^{-3} of sodium hydroxide

Answer: **B**

To maintain solution at pH10 we need basic buffer which is made of weak base and its salt

Option (A) is made of sodium hydroxide (strong acid) and sodium ethanoate salt

Option (B) is made of ammonia and ammonium chloride (weak base and its salt)

Option (C) is made of hydrochloric acid and ammonium chloride

Option (D) is made up of ethanoic acid and sodium ethanoate

13 The solubility product of some sparingly soluble lead compounds are shown below. Which compound will have the lowest concentration of Pb^{2+} (aq) ions in a saturated solution?

	compound	numerical value of solubility product (at 25 °C)
A	lead(II) fluoride	2.7×10^{-8}
B	lead(II) bromide	4.0×10^{-5}
C	lead(II) iodide	7.1×10^{-9}
D	lead(II) sulfate	1.6×10^{-8}

For the lead halides, $K_{sp} = [Pb^{2+}][X^-]^2$ where X = F, Br or I

Let $[Pb^{2+}]$ be x mol dm^{-3}

Hence $[X^-]$ is 2x mol dm^{-3}

Ksp is hence $4x^3$

For $PbBr_2$, $[Pb^{2+}] = 0.0215$ mol dm^{-3}

For PbF_2, $[Pb^{2+}] = 1.89 \times 10^{-3}$ mol dm^{-3}

For PbI_2, $[Pb^{2+}] = 1.21 \times 10^{-3}$ mol dm^{-3}

For $PbSO_4$, $K_{sp} = [Pb^{2+}][SO_4^{2-}]$.

Hence $[Pb^{2+}] = \sqrt{K_{sp}}$

$[Pb^{2+}] = 1.26 \times 10^{-4}$ mol dm^{-3}

Answer: **D**

14 Morphine is a powerful narcotic painkiller which could be isolated from opium poppy. Though it relieves pain effectively, it can cause addiction so readily that it should only be used in the cases where other pain medications are inadequate.

morphine

Which of the following claims about morphine is true?

1 There are 5 chiral carbons present in the molecule.

2 There are 7 C–C bonds formed by $sp^3 - sp^3$ overlap.

3 The molecule cannot exhibit cis-trans isomerism at the C=C double bond.

A 1 only

B 2 only

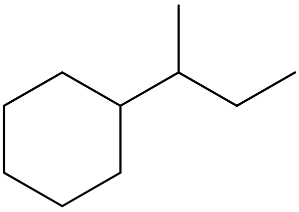
C 2 and 3 only

D 1, 2 and 3

There are 5 chiral carbons present in the molecule, indicated by the asterisks and there are 7 C–C bonds formed by $sp^3 - sp^3$ overlap, highlighted in the diagram. The molecule cannot exhibit cis-trans isomerism at the C=C double bond as the trans isomer could not exist.

Answer: **D**

15 Compound **L** reacts with limited chlorine gas in the presence of sunlight.



compound **L**, $C_{10}H_{20}$

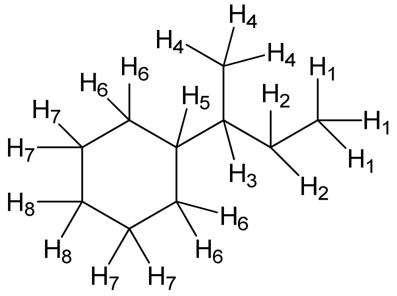
Assuming that only mono-chlorination takes place and ignoring the relative rates of abstraction of the different type of hydrogen atom, which of the following statements is **incorrect**?

A The maximum number of chlorinated products formed is 8.

B $C_{20}H_{38}$ is present in small quantities in the products.

C Homolytic fission occurs in both initiation and propagation step.

D The ratio of primary to secondary to tertiary chloroalkanes formed is 3:6:2.

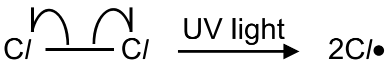


Option A is correct. The maximum number of chlorinated products formed is 8.

Option B is correct. Since compound **L** has the molecular formulae of $C_{10}H_{20}$, it can form a radical with the molecular formula of $C_{10}H_{19}$ in the first step of propagation. Hence two radicals of $C_{10}H_{19}$ can react in the termination step to form $C_{20}H_{38}$ as one of the side products.

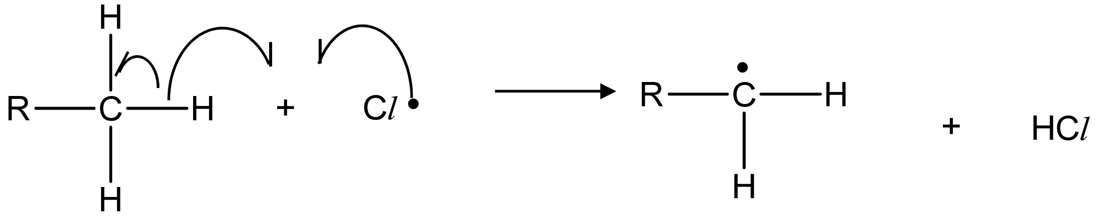
Option C is correct. Homolytic fission occurs in both initiation and propagation step.

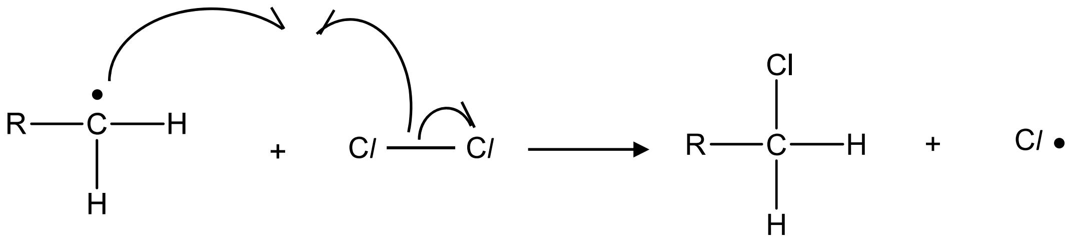
Initiation step:



Propagation step:

Let R be the rest of the molecule.





Option D is incorrect.

When H_1 and H_4 atoms are substituted (total of 6 hydrogen atoms), primary chloroalkanes will be formed.

When H_2, H_6, H_7 and H_8 atoms are substituted (total of 12 hydrogen atoms), secondary chloroalkanes will be formed.

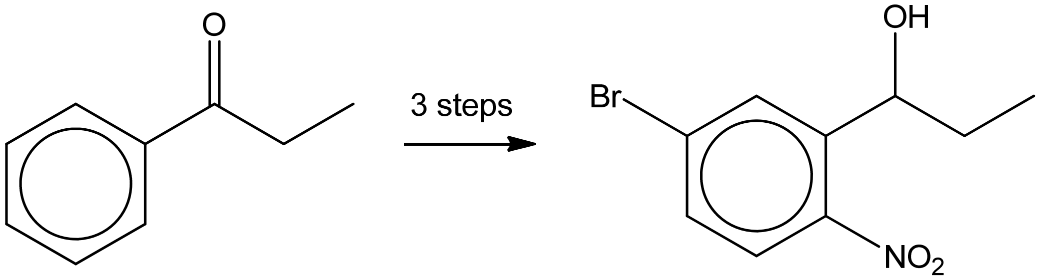
When H_3 and H_5 atoms are substituted (total of 2 hydrogen atoms), tertiary chloroalkanes will be formed.

Hence the ratio of primary to secondary to tertiary chloroalkanes formed is 6:12:2 => 3:6:1 instead of 3:6:2.

Answer: **D**

16 *Use of the Data Booklet is relevant to this question.*

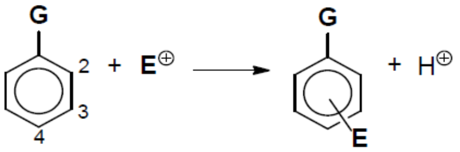
The following transformation takes place in three steps.



Which of the following shows the best choice of reagents and conditions to carry out the transformation?

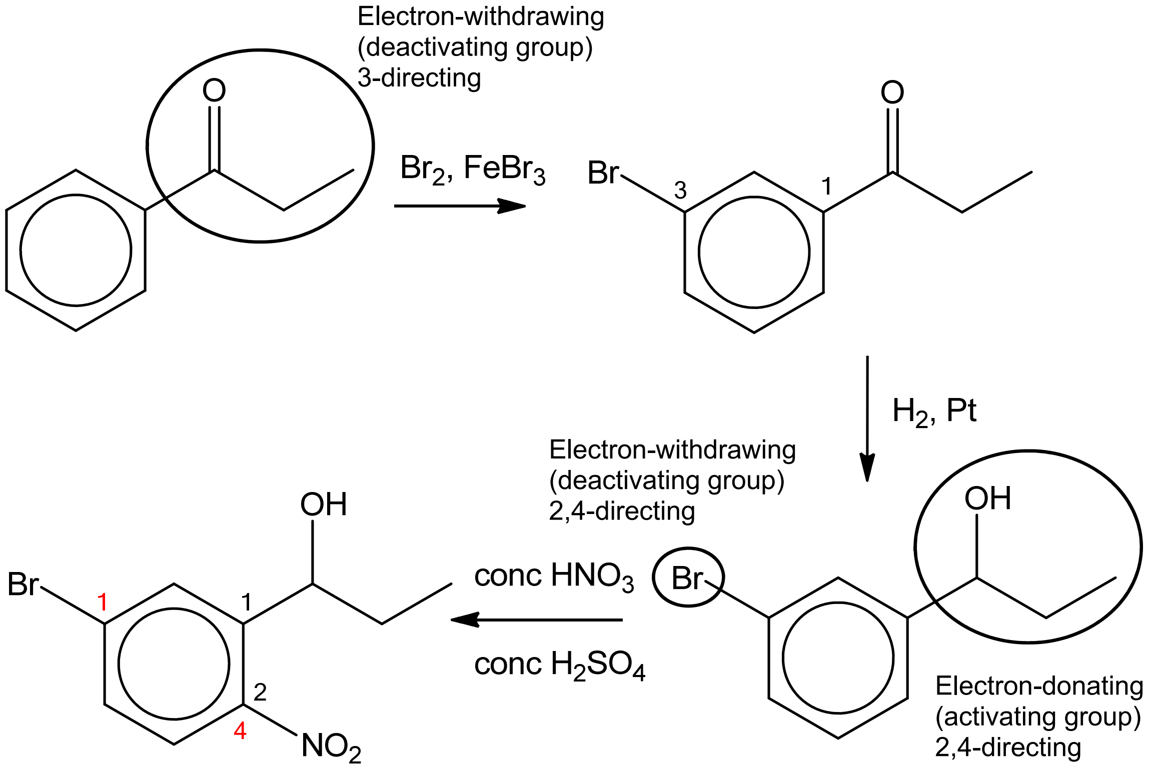
	step 1	step 2	step 3
A	H_2, Pt	conc HNO_3, conc H_2SO_4	Br_2, $FeBr_3$
B	Br_2, $FeBr_3$	H_2, Pt	conc HNO_3, conc H_2SO_4
C	H_2, Pt	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4
D	Br_2, $FeBr_3$	conc HNO_3, conc H_2SO_4	H_2, Pt

The position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.



G	–alkyl –OH or –OR –NH$_2$, –NHR or –NR$_2$ –NHCOR	–Cl, –Br, –I	–CHO, –COR –CO$_2$H, –CO$_2$R –NH$_3^+$ –NO$_2$, –CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

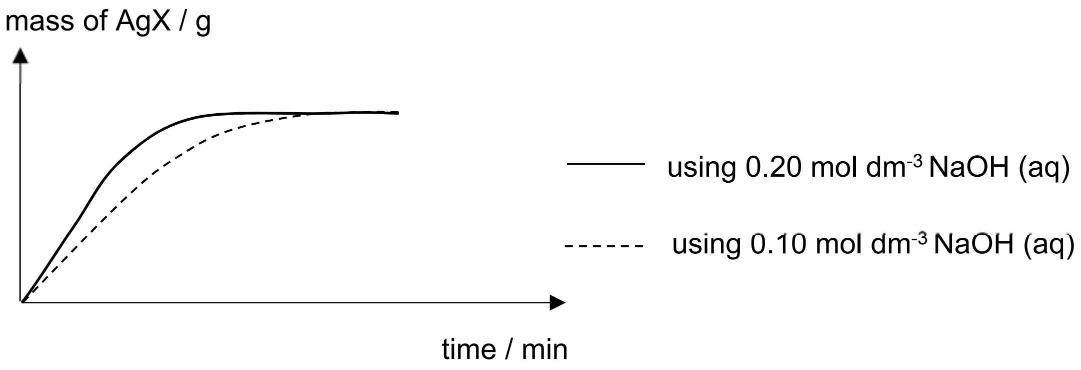
The circled groups will be needed to decide the correct way of transformation in this question.



Note that -NO$_2$ group is an electron-withdrawing group and strong deactivating, it will direct incoming electrophile to the 3rd position relative to itself.

Answer: **B**

17 A halogen-containing compound, **U**, is heated with 2 different concentrations of aqueous sodium hydroxide. After acidifying the mixture and adding excess aqueous silver nitrate, the mass of silver halide formed is analysed over a period of time. The following graph for the mass of silver halide precipitate against time was obtained.



Which of the following is the likely structure of **U**?

A

B

C

D

The gradient of the graph gives the rates of reaction.

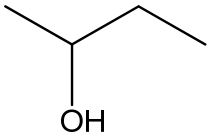
The graph shows that the rate of formation of the ppt increases when [OH^-] increases from 0.10 M to 0.20 M. Hence the nucleophilic substitution of the alkyl halide involves OH^- in the slow step. (i.e. Compound U can undergo SN2 mechanism, so it must be primary or secondary alkyl halide)

A is a secondary alkyl halide, so its rate of reaction is affected by [OH^-].
B is a tertiary alkyl halide, so its rate of reaction is not affected by [OH^-].
C is a vinyl halide (halogen atom bonded to alkene functional group), so it is resistant to nucleophilic substitution.
D is a chloride salt, so it form silver halide ppt immediately.

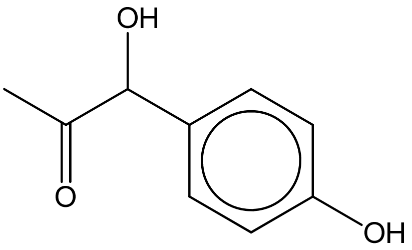
Answer: **A**

18 The following two compounds react with alkaline aqueous iodine to form yellow precipitate of tri-iodomethane as one of the products.

What is the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively?

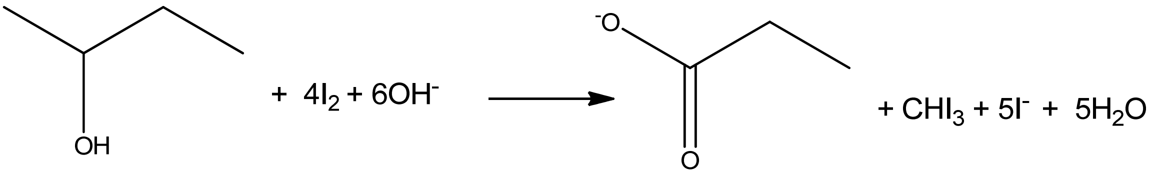


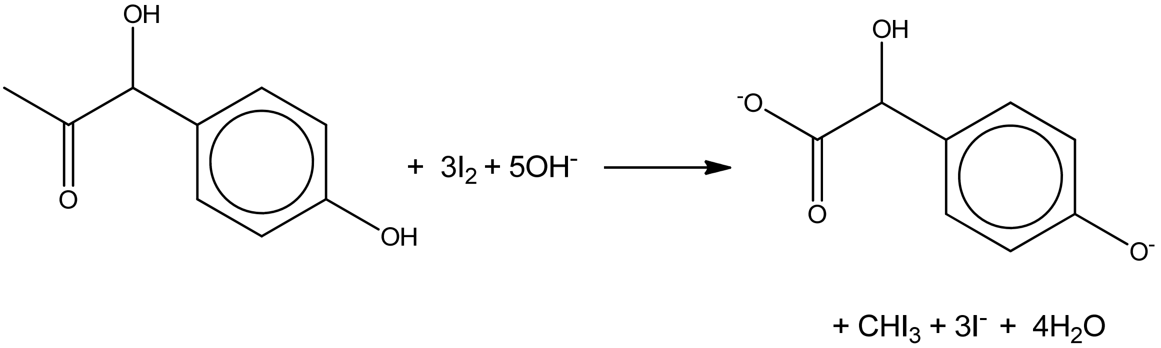
compound **V**



compound **W**

	compound **V**	compound **W**
A	4	4
B	4	6
C	6	4
D	6	5





Hence the ratio of sodium hydroxide used to react with 1 mol of compound **V** and 1 mol of compound **W** respectively is 6: 5.

Note that phenol is acidic enough to react with sodium hydroxide, but not alcohol.

Answer: **D**

19 A fresh salad with tomatoes may contain compound $CH_3CH_2CH_2CH{=}CHCHO$ which provides an aroma for tomatoes. What will be the final product, **P** in this sequence of reactions?

$$CH_3CH_2CH_2CH{=}CHCHO \xrightarrow[\text{then } H_2O]{NaBH_4 \text{ in } CH_3OH} \mathbf{O} \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} \mathbf{P}$$

A $CH_3CH_2CH_2CH{=}CHCOOH$

B $CH_3CH_2CH_2CH_2CH_2COOH$

C $CH_3CH_2CH_2CH{=}CHCH_2OH$

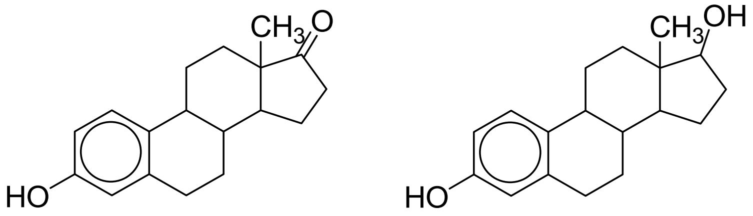
D $CH_3CH_2CH_2COOH$

In $CH_3CH_2CH_2CH{=}CHCHO$ the aldehyde group undergoes reduction by $NaBH_4$ to form primary alcohol group in P, $CH_3CH_2CH_2CH{=}CHCH_2OH$. The primary alcohol group in P is then oxidized to acid group in **Q** $CH_3CH_2CH_2CH{=}CHCOOH$ by $K_2Cr_2O_7/H^+$, heat

C=C is not reduced by $NaBH_4$ and not oxidized by $K_2Cr_2O_7/H^+$, heat

Answer: <u>**A**</u>

20 Two female sex hormones are oestrone and oestradiol.



oestrone oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

1 $SOCl_2$

2 $KMnO_4/H^+$

3 $LiAlH_4$ in dry ether

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Answer: **D** (1 only is correct)

Option 1 (Correct)

$SOCl_2$ reacts with the secondary alcohol group in oestradiol to give white fumes of HCl. Oestrone does not have the secondary alcohol group.

Option 2 (Wrong)

Both can react with $KMnO_4$ due to the alkyl side chain of benzene, in addition to the secondary alcohol group in oestradiol.

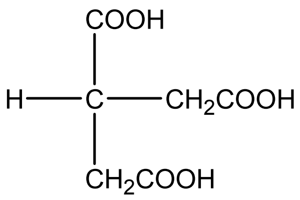
Option 3 (Wrong)

While $LiAlH_4$ reacts with the ketone group in oestrone and not with oestradiol, there is no way to distinguish based on absence of visible change.

21 Ethanoic acid can be made by direct carbonylation of methanol, in presence of a rhodium catalyst.

$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

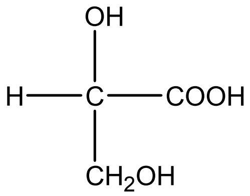
Which of the following can produce compound **S** using a similar method?



$H-C(COOH)(CH_2COOH)-CH_2COOH$

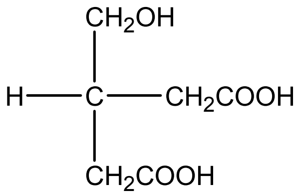
compound **S**

A



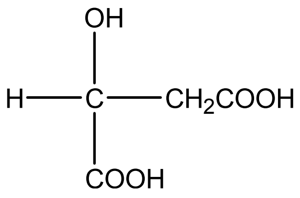
$H-C(OH)(CH_2OH)-COOH$

B

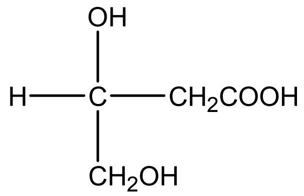


$H-C(CH_2OH)(CH_2COOH)-CH_2COOH$

C



$H-C(OH)(COOH)-CH_2COOH$

D 

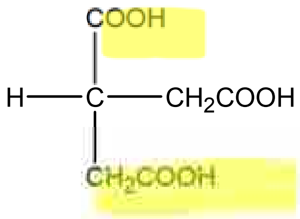
$$H-\overset{\displaystyle OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2COOH$$

Answer: D

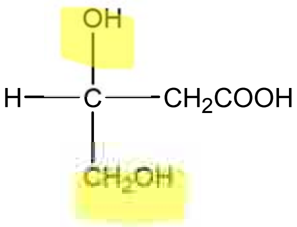
Pattern recognition of adding a CO between the C and O atom.

$$CH_3OH + CO \xrightarrow{\text{rhodium catalyst}} CH_3COOH$$

To form compound S,



$$H-\overset{\displaystyle COOH}{\underset{\displaystyle CH_2COOH}{C}}-CH_2COOH$$



$$H-\overset{\displaystyle OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2COOH$$

22 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which of the following statements about benzylamine is correct?

1 It reacts with excess CH_3CH_2Cl to form the compound, $C_{13}H_{22}NCl$.

2 It reacts with CH_3COOH to form $C_6H_5CH_2NHCOCH_3$.

3 It can be distinguished from $CH_3CH_2NH_2$ by the use of aqueous bromine.

A 1, 2 and 3

B 1 and 2 only

C 1 only

D 2 and 3 only

1 is correct

Benzylamine undergoes nucleophilic substitution with CH_3CH_2Cl to form a quarternary ammonium salt.

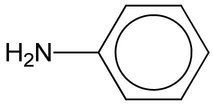
2 is incorrect

Benzylamine reacts with CH_3COOH to form an ionic salt.

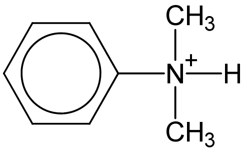
3 is incorrect

Both cannot decolourise bromine. Phenylamine will decolourise bromine but not benzylamine.

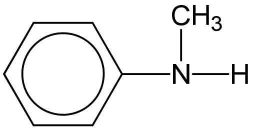
23 The structures of some nitrogen containing compounds are shown below.



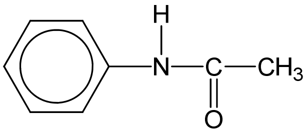
compound **H**



compound **I**



compound **J**



compound **K**

What is the order of increasing basicity of the nitrogen containing compounds?

	least basic	⟶		most basic
A	**I**	**H**	**K**	**J**
B	**I**	**K**	**H**	**J**
C	**I**	**K**	**J**	**H**
D	**K**	**I**	**J**	**H**

Methyl group is electron donating and it increases the electron density on nitrogen in J

Lone pair of electrons on nitrogen in H is delocalised into the benzene ring , hence it is less available for accepting a proton.

K is a neutral compound as the lone pair of electrons on nitrogen is delocalised into C=O group.

I is an acidic compound due to salt hydrolysis, hence it is least basic.

24 *Use of Data Booklet is relevant to this question.*

Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power decreases from chlorine to iodine.

2 The bond length of the molecule increases from chlorine to iodine.

3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

Option 1 (Correct)

Down the group from chlorine to iodine, increasing shielding effect results in lower effective nuclear charge, hence less ability to attract electrons resulting in decreasing oxidizing power down the group

Option 2 (Correct)

Down the group, size of atoms increases resulting in less effective orbital overlap between two halogen atoms in a covalent bond and hence longer bond length of the molecule

Option 3 (Incorrect)

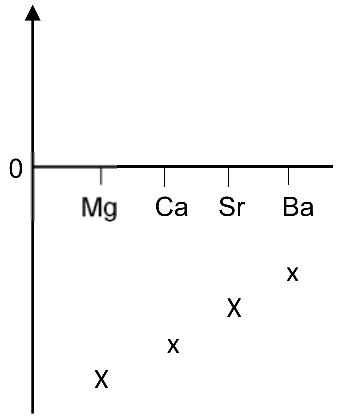
$X(g) + e^- \longrightarrow X^-(g)$

The magnitude of first electron depends on the effective nuclear charge which decreases as the shielding effect increases down the group from chlorine to iodine

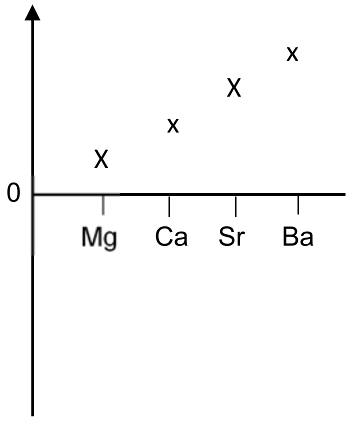
Answer: **A**

25 Which diagram correctly shows the trend in a property of the Group 2 elements Mg, Ca, Sr, Ba?

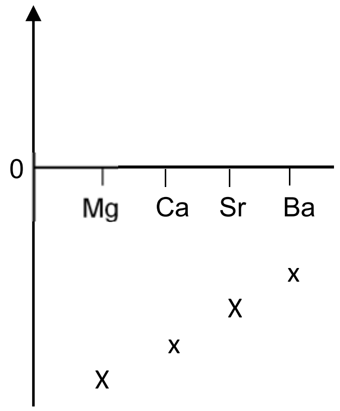
A ΔH_{hyd}, the enthalpy change of hydration of M^{2+}(g)



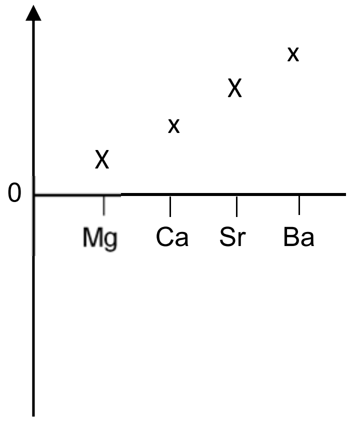
B *I*, the first ionisation energy



C $E^{\ominus}$, the standard electrode potential of M^{2+}(aq)I M(s) electrode



D Electronegativity value



Enthalpy change of hydration is proportional to charge/radius of cation and it is an attraction force hence exothermic

As cation radii, increases from Mg^{2+} to Ba^{2+}, the enthalpy change of hydration becomes less exothermic.

Answer: **A**

26 Three half cells are constructed as follows.

Half cell **I**: an electrode of metal **Q** in a 1.0 M solution of $\mathbf{Q}^{+}$(aq) ions

Half cell **II**: an electrode of metal **R** in a 1.0 M solution of $\mathbf{R}^{+}$(aq) ions

Half cell **III**: an electrode of Cu metal in a 1.0 M solution of Cu^{2+}(aq) ions

The half cells are connected in pairs, as shown below, to form a series of galvanic cells. For each cell, the polarity of the electrodes and the voltage generated are recorded.

half cells used	positive electrode	negative electrode	voltage (V)
I and **III**	Cu	**Q**	0.57
II and **III**	Cu	**R**	1.10
I and **II**	**Q**	**R**	0.53

Which one of the following lists the metals in order of **increasing** strength as reducing agents?

A **R**, **Q**, Cu

B **Q**, Cu, **R**

C Cu, **R**, **Q**

D Cu, **Q**, **R**

Answer: D

In a galvanic cell the reducing agent is oxidised; oxidation occurs at the anode; the anode is the negative electrode. In each cell the stronger reducing agent is at the negative electrode.

According to the data relative strength of the reducing agents are:

For half cells:

II and IV **Q** > Cu;

III and IV **R** > Cu;

II and III **R** > **Q**

Hence, the order of increasing strength of the reducing agents is Cu < **Q** < **R**

27 Some standard redox potential ($E^{\ominus}$) values are given in the table below.

electrode reaction	$E^{\ominus}$/ V
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$	+1.45

Which of the following reactions would occur under standard conditions?

1 $Ce^{4+}(aq) + Fe^{2+}(aq) \longrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

2 $Sn^{2+}(aq) + 2Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

3 $2Ce^{4+}(aq) + Sn^{2+}(aq) \longrightarrow 2Ce^{3+}(aq) + Sn^{4+}(aq)$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

Answer: A

Checking for reactions 1,2 and 3:

Reaction 1: $E^{\ominus}_{cell}$= +1.45 – 0.77 = +0.68V

Reaction 2: $E^{\ominus}_{cell}$= +0.77 – 0.15 = +0.62 V

Reaction 3: $E^{\ominus}_{cell}$= +1.45 – 0.15 = +1.3V

All the values are >0, hence the reactions are all spontaneous.

28 A current was passed through two cells connected in series. The first cell contained molten sodium chloride while the other contained a molten aluminium salt.

What would be the mass of aluminium liberated from the other cell if 4.6g of sodium was liberated from the first cell?

A 0.9 g

B 1.8 g

C 2.7 g

D 3.6 g

Answer: B

Amt of electrons transferred in the two electrolytic cells is the same.

[R]: $Na^+ + e \rightarrow Na\ (s)$

Amt of sodium = 4.6/23 = 0.2 mol

Amt of electrons = 0.2 mol

[R]: $Al^{3+} + 3e \rightarrow Al\ (s)$

Amt of electrons transferred = 0.2 mol

Amt of Al = 0.2/3 = 0.06667 mol

Mass of Al = 0.06667 x 27 = 1.8g

29 Which of the following does **not** act as a ligand in the formation of complexes?

A SCN^-

B Cl^-

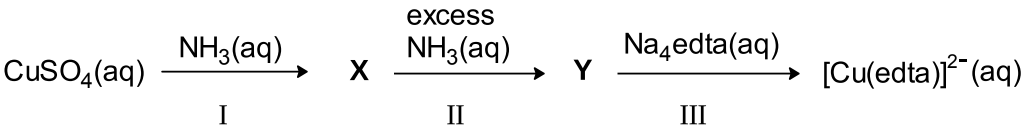
C AlH_4^-

D $C_2O_4^{2-}$

Out of all the species present, AlH_4^- has no available lone pairs of electrons for donation to form a dative covalent bond as all the electrons are used for bonding.

Answer: **<u>C</u>**

30 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **X** and **Y** are copper-containing species.



$$CuSO_4(aq) \xrightarrow[\text{I}]{NH_3(aq)} \textbf{X} \xrightarrow[\text{II}]{\text{excess } NH_3(aq)} \textbf{Y} \xrightarrow[\text{III}]{Na_4edta(aq)} [Cu(edta)]^{2-}(aq)$$

Which of the following statements is true?

1 NH_3 acts as a ligand in reaction I.

2 Reaction II is a redox reaction.

3 The entropy of the system increases when reaction III occurs.

A 1 only

B 3 only

C 1 and 3 only

D 1, 2 and 3 only

In reaction I, NH_3 is acting as a weak base to generate OH^- a to form the ppt **X.** NH3 only acts as a ligand in reaction II.

In reaction II, it is a ligand exchange reaction, hence there is no change in the oxidation state of the metal centre.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

Oxidation state of the Cu centre is still +2.

In reaction III, edta displaces the NH_3 and H_2O ligands.

$[Cu(NH_3)_4(H_2O)_2]^{2+} + edta^{4-} \rightleftharpoons [Cu(edta)]^{2-} + 4NH_3 + 2H_2O$

There is an increase in the number of particles from 2 to 7 after the reaction and hence the entropy of the system increases in reaction III.

Answer: **B**

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/02

Paper 2 Structured Questions

16 August 2018
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

For Examiner's Use	
Question no.	**Marks**
1	**/ 14**
2	**/ 6**
3	**/ 9**
4	**/ 13**
5	**/ 12**
6	**/ 9**
7	**/ 12**
TOTAL	**/ 75**

This document consists of 21 printed pages, including this cover page.

9729/02/Prelim/18

ANGLO-CHINESE JUNIOR COLLEGE
Department of Chemistry

[Turn over

Answer **all** the questions in the spaces provided.

1 A mixture contains two white solids **X**CO_3 and **Y**SO_4 where **X** and **Y** could be either magnesium, zinc or barium. The following investigations were carried out to determine the identity of **X** and **Y**.

(a) When the mixture of solids was treated with excess dilute hydrochloric acid, a colourless gas was evolved and some, but not all, of the mixture dissolved.

The resulting mixture was filtered. To the filtrate, dilute aqueous ammonia was added dropwise till in excess. The white precipitate formed was insoluble in excess aqueous ammonia.

Deduce the identity of elements **X** and **Y**, showing your reasoning clearly. [3]

- **X- Mg Y- Ba**
- **$BaSO_4$ insoluble in dil HCl ,**
- **filtrate contains Mg^{2+} which ppt to form $Mg(OH)_2$ white ppt insol in excess aq ammonia**
  OR
- **White ppt contains Mg^{2+} as Zn^{2+} forms ppt but it is soluble in excess NH_3**

(b) Group 2 carbonates decompose according to the following equation:

$$ZCO_3\ (s) \longrightarrow ZO\ (s) + CO_2\ (g)$$

element	magnesium	calcium	barium
enthalpy change for the reaction, ΔH_r/ kJ mol^{-1}	+101	+178	+269

(i) Use the data above to state and explain the trend in the thermal stability of the Group 2 carbonates. [3]

- **ΔH_r become more endo, thermal stability increases**
- **increasing ionic radii leading to decreasing charge density/ polarising power and**
- **less distortion of electron cloud of large anion**

(ii) Lithium carbonate, a Group 1 carbonate, decomposes on heating.

Use relevant data from the Data booklet to calculate relative charge densities of the above cations and hence deduce which of the above **ΔH_r** values in the table is likely to be the nearest to that of lithium carbonate. [2]

	Mg^{2+}	Ca^{2+}	Ba^{2+}	Li^{+}
Relative charge density	**2/0.065 =30.8**	**2/0.099 =20.2**	**2/0.135 =14.8**	**1/0.06 =16.7**

ΔH_r of Li_2CO_3 resembles that of $BaCO_3$

(c) Patients with digestive tract problems are sometimes asked to take an x-ray after they have swallowed a "barium meal", consisting of a suspension of $BaSO_4$ in water.

(i) Write an expression for the solubility product, K_{sp}, for $BaSO_4$, including its units.

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$ units: $mol^2\ dm^{-6}$

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

In saturated solution, IP = K_{sp}
$[Ba^{2+}] = \sqrt{1.30 \times 10^{-10}} = 1.14 \times 10^{-5}$ mol dm^{-3}

(iii) Although Ba^{2+} ions are toxic, the $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause any problems of toxicity.

The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that of $BaSO_4$, but $BaCO_3$ is **very** poisonous if ingested. Suggest a reason why this might be so.

$BaCO_3$ reacts with the acid in the stomach to release Ba^{2+} ions.

(iv) $BaSO_4$ is commonly prepared in the laboratory by combining solutions containing Ba^{2+} and SO_4^{2-}.

Determine if $BaSO_4$ will form when equal volumes of 2.00×10^{-2} mol dm^{-3} $Ba(NO_3)_2$ and 4.00×10^{-2} mol dm^{-3} Na_2SO_4 are mixed.

$[Ba^{2+}]$ after mixing = 1.00×10^{-2} mol dm^{-3}
$[SO_4^{2-}]$ after mixing = 2.00×10^{-2} mol dm^{-3}

IP on mixing = $2.00 \times 10^{-4} > K_{sp}$ (1.14×10^{-10})
Hence precipitation will take place.

[2]

[Total: 14]

2 A student conducted two separate electrolysis using inert electrodes under room temperature and pressure.

electrolysis reaction	electrolyte	volume of gas collected at anode / cm^3	duration
1	concentrated hydrochloric acid	150	10 minutes
2	aqueous sodium sulfate	37.5	

(a) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **1**. [1]

$2Cl^-$ (aq) → Cl_2 (g)+ $2e^-$

(ii) Calculate the current that was used in electrolysis reaction **1**. [2]

Amt of Cl_2 collected = 150/24000 = 6.25×10^{-3} mol

Amt of electrons passed through = $6.25 \times 10^{-3} \times 2$ = 0.0125 mol

Quantity of charge passed through = 0.0125 x 96500 = 1206.25 C

Current used = 1206.25 / (10 x 60) = 2.01 A

(b) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **2**. [1]

$2H_2O$ (l) → O_2 (g) + $4H^+$ (aq) + $4e^-$

(ii) Determine the current used in electrolysis reaction **2**. [2]

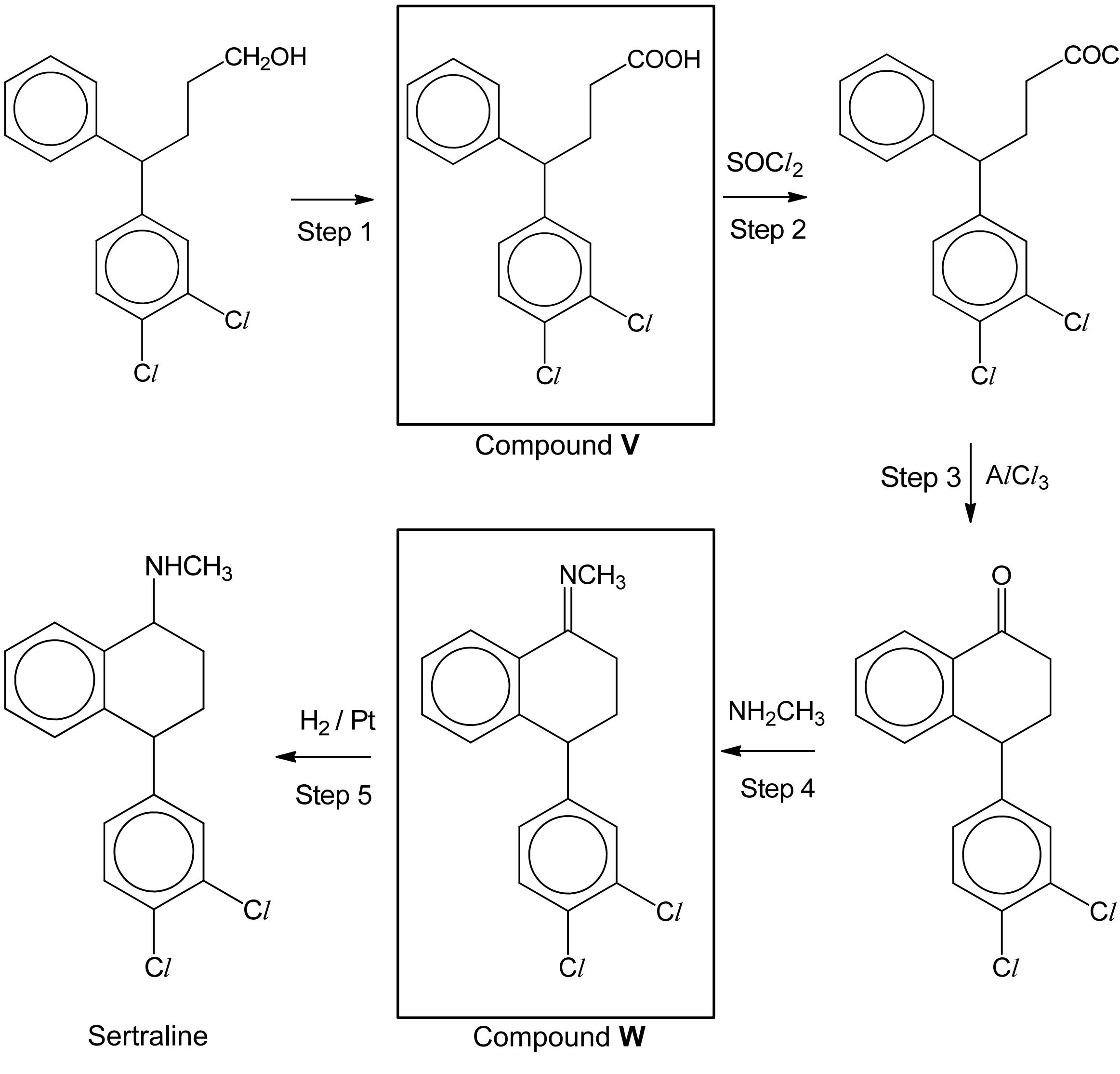
If the current used was the same, the volume of gas obtained in reaction should be halved based on the number of e- required. Since the volume of gas is four times less than that in reaction 1, the current used must be halved.

Current used = ½ x 2.01 =1.005 = 1.01A

[Total: 6]

3 Sertraline is an antidepressant used to treat depression, obsessive compulsive disorder, post-traumatic stress disorder and related conditions. This medication can help to improve mood, mental alertness, energy level and sleep pattern for the patients. Sertraline works by helping to restore the balance of serotonin, a neurotransmitter in the brain which regulates anxiety, mood and happiness.

A proposed synthesis route of sertraline is shown below.

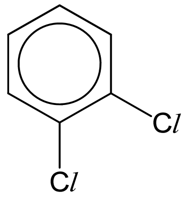


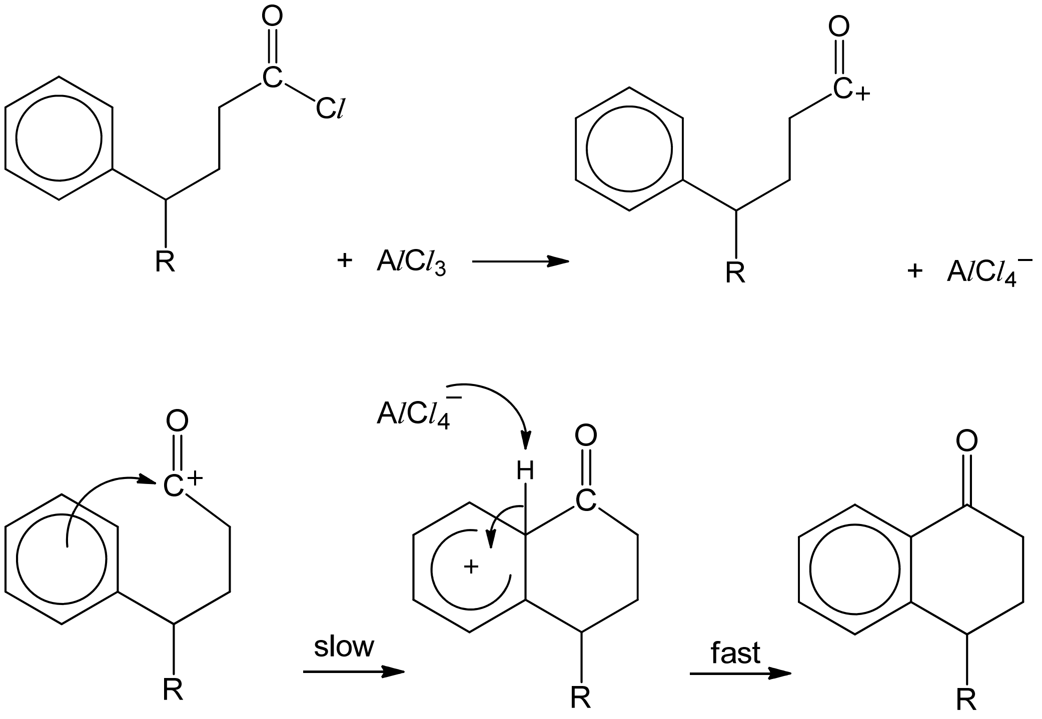
(a) State the reagents and conditions needed for step 1 and draw the structure of compound **V** in the box above.

$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux

(b) Electrophilic substitution takes place in step 3 where $AlCl_3$ acts as a Lewis acid catalyst and reacts with the acyl chloride functional group to generate the electrophile.

Write an equation to show the generation of the electrophile and hence draw the mechanism for the reaction that occurs in step 3.

You may use R to represent  in Sertraline for part **(b)** and part **(d)**.

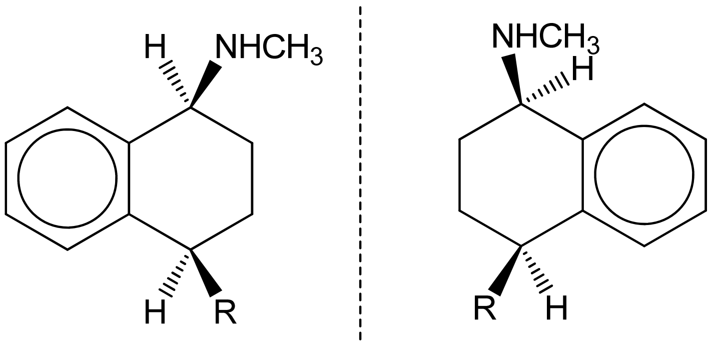


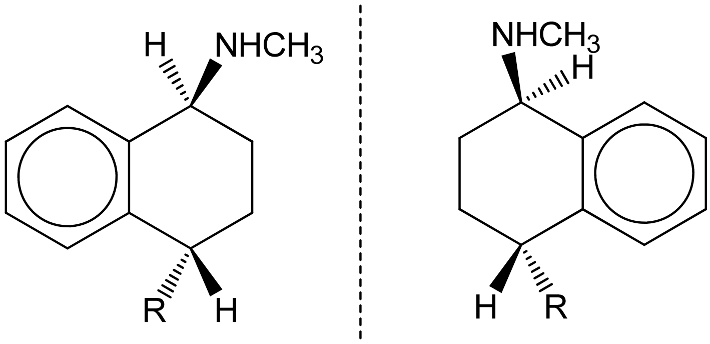
+ $AlCl_3$ + HCl

(c) State the type of reaction taking place in step 4 and draw the structure of compound **W** in the box above.

Condensation

(d) Sertraline exists as a mixture of stereoisomers. Draw the structures of the stereoisomers of Sertraline.





[Total: 9]

4 **(a)** The change in colour from blue to pink of the cobalt complexes has been the basis of cobalt chloride indicator papers for the detection of the presence of water.

The two differently coloured cobalt(II) complex ions, $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$, exist together in equilibrium in solution in the presence of chloride ions. This is represented by the equation below.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

An experiment is conducted to investigate the effects on the equilibrium position by imposing a series of changes on the system. The shift in equilibrium position can be indicated by any colour change of the solution.

species	**colour**
$Co(H_2O)_6^{2+}$ (aq)	pink
$CoCl_4^{2-}$ (aq)	blue
initial equilibrium mixture containing $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$	purple

After a 3.00 cm^3 sample of an initial equilibrium mixture was placed in three separate boiling tubes, a different substance was added to each tube, as indicated in Table 4.1.

(i) Complete Table 4.1 by predicting:

- the change in concentration, if any, of each ions in solution compared to the initial solution, after a new equilibrium position is reached.
- the colour change, if any, that takes place from the initial purple-coloured solution.

Table 4.1

Substance added	Change in concentration from initial solution to new equilibrium (increase, decrease, unchanged)			Colour change (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$				
Concentrated HCl				

$AgNO_3$(aq)				

[3]

Substance added	**Change in concentration from initial equilibrium to final equilibrium (increase, decrease, unchanged)**			**Colour favoured (pink, blue or unchanged)**
	$[Co(H_2O)_6]^{2+}$	**Cl^-**	**$[CoCl_4]^{2-}$**	
$H_2O(l)$	**decrease**	**decrease**	**decrease**	**pink**
Concentrated HC*l*	**decrease**	**increase**	**increase**	**blue**
$AgNO_3$(aq)	**increase**	**decrease**	**decrease**	**pink**

[3]

(ii) Another experiment was conducted to investigate the effect of temperature on the same equilibrium mixture. When 3.00 cm^3 of the original equilibrium mixture in a test tube was placed in an ice bath, the solution became pink.

Determine whether the forward reaction, as illustrated by the equation above, is exothermic or endothermic. Use Le Châtelier's Principle to justify your answer.

A decrease in temperature shifts position of equilibrium to the left (pink colour) and a decrease in temperature favours exothermic reaction to release heat.

Hence the reverse reaction is exothermic and the forward reaction is endothermic.

(b) At room temperature, a solution of sodium tartrate, $Na_2C_4H_4O_6$, does not react with hydrogen peroxide. When heated in a water bath, the reaction mixture reacts giving a very slow stream of carbon dioxide.

When a few drops of an aqueous pink cobalt(II) salt are added, the colour of the solution soon turns green and a vigorous effervescence of carbon dioxide takes place.

When the reaction stops, the pink colour is restored.

The half equation for the oxidation of tartrate ions is given as shown:

$$C_4H_4O_6^{2-}(aq) + 8OH^-(aq) \longrightarrow 4CO_2(g) + 6H_2O(l) + 10e^-$$

(i) In alkaline medium, H_2O_2 exists as hydroperoxide ions, HO_2^-. Construct a balanced half equation for the reduction of HO_2^- to OH^-.

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

(ii) Write a balanced ionic equation for the reaction between tartrate ions and hydroperoxide ions.

Oxidation half-equation
$C_4H_4O_6^{2-} + 8OH^- \rightarrow 4CO_2 + 6H_2O + 10e^-$

Reduction half-equation

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$

Balanced eqn:
$C_4H_4O_6^{2-} + 5\,HO_2^- \rightarrow 4CO_2 + H_2O + 7OH^-$

(iii) Suggest why there is no reaction observed when tartrate ions and hydroperoxide ions are mixed at room temperature even though the reaction is energetically feasible.

The activation energy is high due to electrostatic repulsion between the two negatively charged ions.

(iv) Explain why a slow stream of carbon dioxide is observed when reaction mixture is heated in a water bath.

As temperature increases, more particles have energy more than or equal to the activation energy and
hence frequency of effective collision increases and rate increases.

(v) State the identity of the aqueous ions responsible for the green colour.

Aqueous cobalt (III) ions

(vi) Use your answer in **(b)(v)** to describe the catalysed two-step reactions involving aqueous cobalt ions with the tartrate ions and hydroperoxide ions.

New mechanism:

Step 1- pink cobalt(II) ions is oxidised by hydroperoxide ions to green cobalt(III) ions

Step 2-green cobalt(III) ions are reduced by tartrate ions back to pink cobalt(II) ions, thus regenerating the catalyst.

Or
Step 1
$2Co^{2+} + HO_2^- + H_2O \rightarrow 2Co^{3+} + 3OH^-$

Step 2
$C_4H_4O_6^{2-} + 8OH^- + 10Co^{3+} \rightarrow 4CO_2 + 6H_2O + 10Co^{2+}$

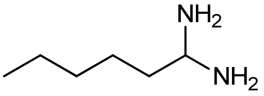
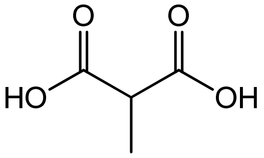
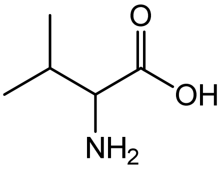
[Total: 13]

5 **(a)** Amino acids are biologically-important organic compounds containing both amine ($-NH_2$) and carboxylic acid (-COOH) functional groups.

To consider the effect of having both an amine and a carboxylic acid functional group on the same molecule, amino acids can be compared with other organic compounds such as diamines and dicarboxylic acids.

Amino acids have significantly higher melting points than diamines and dicarboxylic acids of similar mass and structure as shown in Table 5.1 below.

Table 5.1

compound type	example	molar mass / g mol^{-1}	melting point / ^{o}C
diamine	 hexane-1,1-diamine	116.2	39
dicarboxylic acid	 methylpropanedioic acid	118.1	184
amino acid	 2-amino-3-methylbutanoic acid (valine)	117.2	298

Explain why the melting points show an increasing trend from diamine to amino acid in terms of structure and bonding.

Diamine and dicarboxylic acid have simple molecular structures with hydrogen bonds between polar molecules.

Dicarboxylic acid has stronger hydrogen bonds than diamine as O-H bond is more polarised and has more extensive hydrogen bonds than diamines.

Hence more energy is needed to break hydrogen bonds in dicarboxylic acid than in diamine, hence it has higher m.p.

Valine has a giant ionic lattice with strong electrostatic forces of attraction(or ionic-bonds) between the zwitterions.

More energy is needed to break stronger ionic bonds compared to hydrogen bonds, hence it has the highest m.p.

(b) When 50.0 cm^3 of hexane was shaken with 20.0 cm^3 of an aqueous solution containing 1.10 g of 2-amino-3-methylbutanoic acid (valine), it was found that 0.050 g of valine was extracted into the hexane. At equilibrium, the ratio of the concentration of valine in the two immiscible solvents is a constant called partition coefficient where

$$K_{\text{partition}} = \frac{[\text{valine}]_{\text{hexane}}}{[\text{valine}]_{\text{aq}}}$$

(i) Calculate the partition coefficient, $K_{\text{partition}}$, of valine between hexane and water.

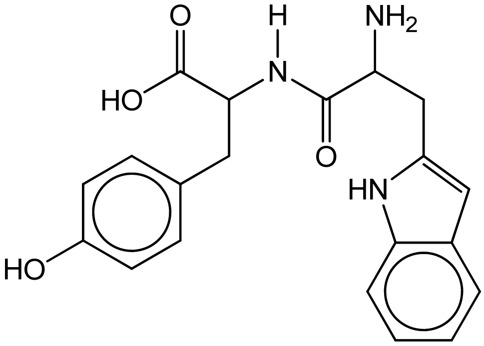
$\mathbf{K_{partition} = [valine]_{hexane}/[valine]_{aq}}$

$\mathbf{= (0.05/50)/(1.05/20) = 0.0190}$

(ii) State which is a better solvent for valine and explain the reason for its solubility in that solvent.

Water is a better solvent as valine exists as zwitterion and forms ion-dipole interactions with water.

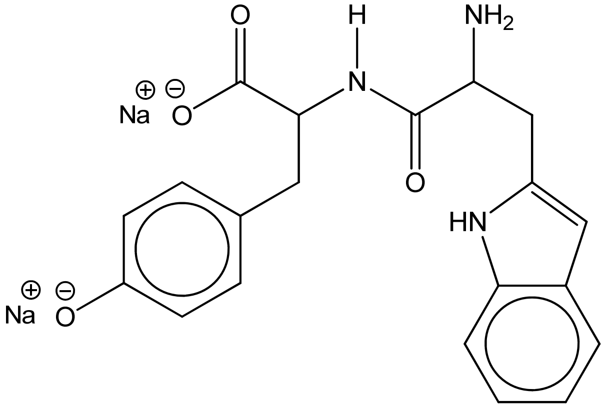
(c) Tryptophan is an essential amino acid found in foods such as chicken, eggs, cheese and milk. It is needed to create the neurotransmitter serotonin which promotes sleep. Two amino acids, tyrosine (tyr) and tryptophan (trp), form a dipeptide, tyr-trp, as shown by the following structure.



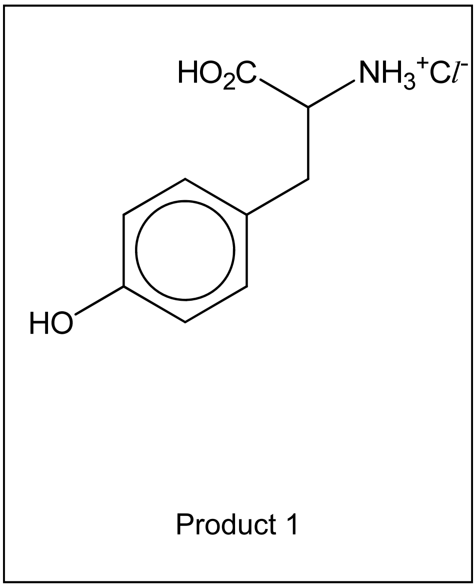
tyr–trp

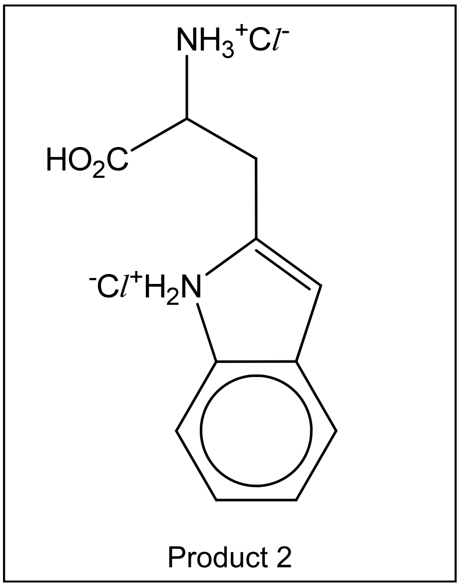
Draw the structures of the products of the reactions of tyr-trp with an excess of each of the following reagents.

(i) NaOH(aq) at room temperature

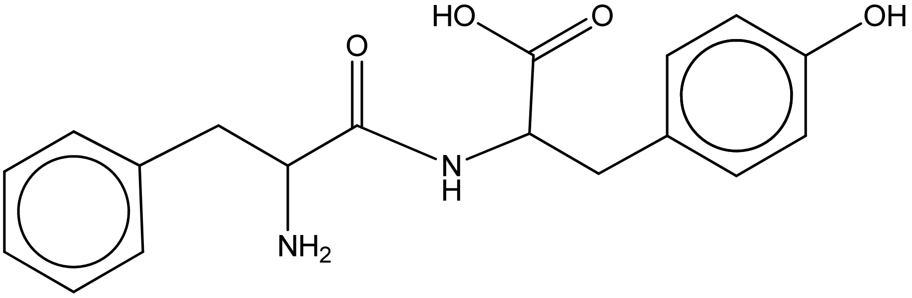


(ii) HC*l*(aq) and heat under reflux

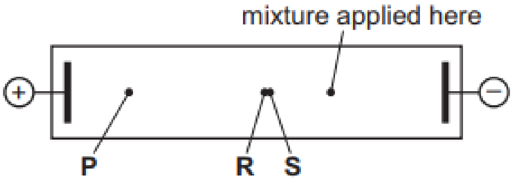

Product 1


Product 2

(d) Phenylalanine and tyrosine form another dipeptide (phe-tyr) as shown below.


phe-tyr

A mixture of the dipeptide (phe-tyr) and its two constituent amino acids (phenylalanine and tyrosine) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phenylalanine, tyrosine and the dipeptide, phe-tyr.

(i) Draw the structural formula of the species responsible for spot **P.**

[1]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

dipeptide / phe-tyr) has 2– and its M_r is about double that of phe with 1

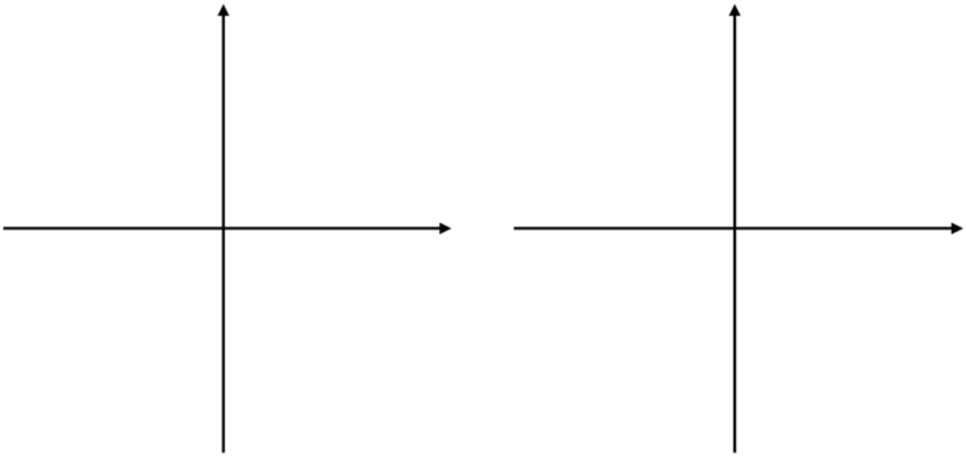
OR

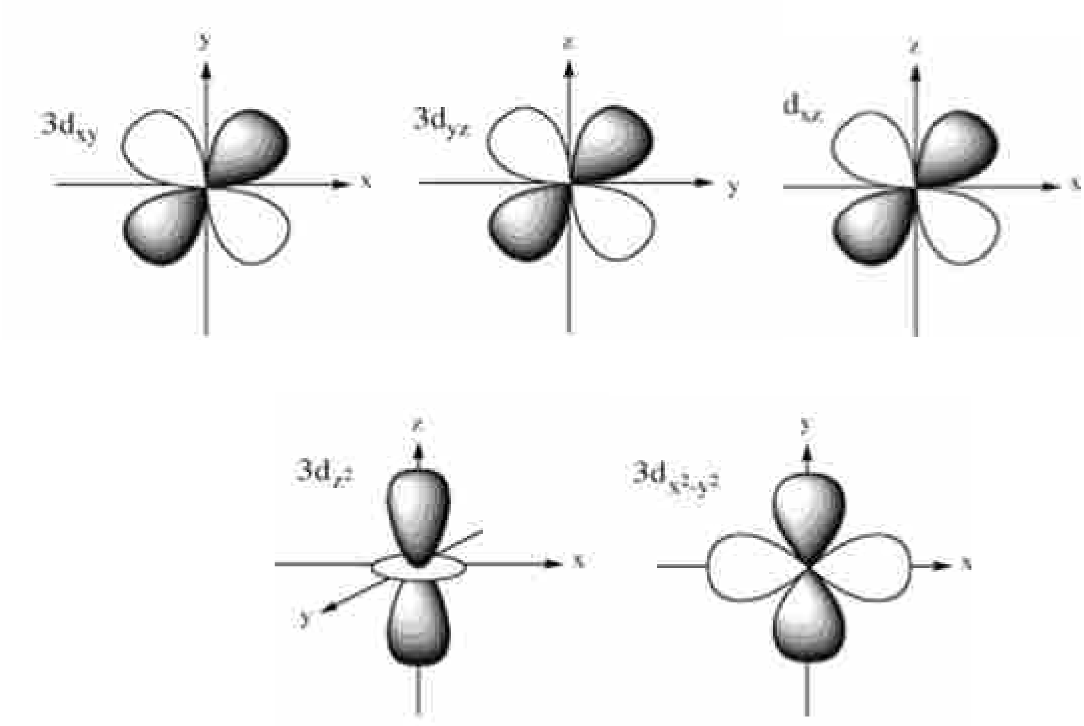
charge / mass ratios are about the same for the dipeptide (phe-tyr) and phe

[Total: 12]

6 In an isolated transition metal atom, the five 3d-orbitals are degenerate. However, in an octahedral complex ion, the presence of ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.

(a) Using the axes provided below, draw and label the shape of **one** d-orbital in **each** of the two groups mentioned above.





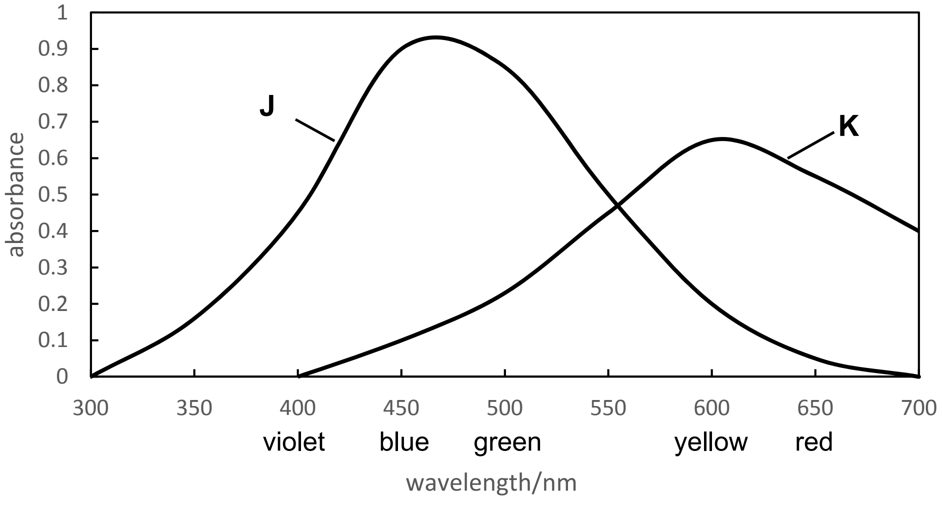
(b) Explain how the presence of the six ligands, L, in $[NiL_6]^{2+}$ splits the five 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

Ligands have lone pairs of electrons and they approach the metal ion along the primary axes.

The d electrons in the orbitals pointing towards the ligands experience repulsion and hence of a higher energy level.

Since the $d(x^2-y^2)$ and dz^2 orbitals point towards the ligands, the two-orbital group is higher in energy.

(c) The absorbance spectra of solutions of two transition metal complexes **J** and **K** are shown in the diagram below.



A list of possible colours for these complexes is as follows.

yellow red green blue

Choose one of the colours above to describe the observed colour of each solution.

Solution **J** ……………………….. Solution **K** ………………………..

Solution J red **Solution K blue**

(d) Ligands are classified based on their ability to split the five 3d orbitals into two groups with an energy difference (ΔE). Strong field ligands produce a large ΔE while weak field ligands produce a small ΔE.

The energy of a photon can be obtained by Planck's equation:

$$E = \frac{hc}{\lambda}$$

where:

E is the energy of the photon
λ is the wavelength of the photon
h is Planck's constant
c is the speed of light in vacuum

Use the data below as well as data from the *Data Booklet*, complete the table and arrange the ligands in order of increasing field strength.

species	$[M(CN)_6]^{2-}$	$[M(F)_6]^{4-}$	$[M(H_2O)_6]^{2+}$
λ / nm	430	650	600
ΔE / J			

Increasing field strength: …………………<…………………<………………… [2]

species	**$[M(CN)_6]^{2-}$**	**$[M(F)_6]^{4-}$**	**$[M(H_2O)_6]^{2+}$**
λ/nm	**430**	**650**	**600**
ΔE/ J	**4.63×10^{-19}**	**3.06×10^{-19}**	**3.32×10^{-19}**

Increasing field strength: $F^- < H_2O < CN^-$

[Total: 9]

7 The oxidising power of our atmosphere has been well-studied and is of importance as many environmental trace gases, such as methane, are removed.

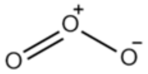
The most abundant oxidants in the atmosphere are oxygen and ozone molecules. These molecules have strong bonds and are hence relatively unreactive except towards radicals. Research in the 1950s suggested that the hydroxyl radical, •OH, is a strong oxidant.

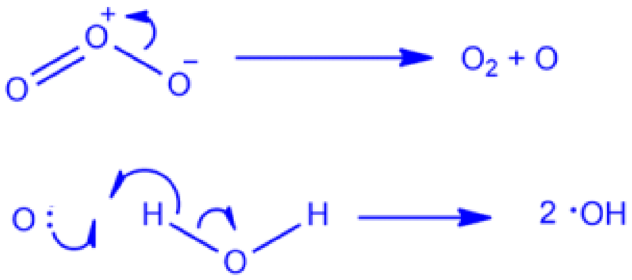
In the stratosphere, UV light from the sun heterolytically breaks ozone molecules into oxygen molecules and oxygen atoms. The oxygen atoms react homolytically with water vapour to produce hydroxyl radicals, •OH.

$$O_3 \xrightarrow{UV} O_2 + O \qquad \text{--------------------(1)}$$

$$O + H_2O \longrightarrow 2{\bullet}OH \qquad \text{--------------------(2)}$$

(a) Use equations (1) and (2) to draw the mechanism for the formation of the hydroxyl radical, •OH. Include in your mechanism the necessary curly arrows and electrons. [2]

Use  as the structure of ozone.



(b) Hydroxyl radicals are particularly reactive towards H-containing molecules due to H-abstraction converting •OH back to H_2O.

$${\bullet}OH + CH_4 \longrightarrow H_2O + {\bullet}CH_3 \quad \text{--------------------(3)}$$

Some information about an elementary reaction (3) was obtained.

[•OH] / molecules cm^{-3}	1.0×10^6
[CH_4] / molecules cm^{-3}	4.4×10^{13}
rate constant, k / cm^3 molecule^{-1} s^{-1}	1.4×10^{-5}

Source: Jacob, D. J. Introduction to Atmospheric Chemistry; Princeton University Press: 1999

(i) Use information in the table to write an equation to represent the rate equation for the pseudo-first-order reaction with respect to the concentration of the hydroxyl radical, •OH.

rate = k' [•OH]

(ii) Calculate the half-life of the hydroxyl radical, •OH to the nearest **2 significant figures**.

rate = k' [•OH], k' = k [CH_4]

$k' = 1.4 \times 10^{-5} \times 4.4 \times 10^{13} = 6.16 \times 10^{8}\ s^{-1}$

$t_{1/2} = \frac{ln2}{k'} = \frac{ln2}{6.16\times10^8} = 1.1 \times 10^{-9}$ s

(c) The relative rates of disappearance in air at 305 K for a series of hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. Absolute rate constants obtained from the reaction are as follows.

hydrocarbon	k / × 10^9 mol^{-1} dm^3 s^{-1}
butane	1.8
hexane	3.8
cis-but-2-ene	39.2

Source: *J. Phys. Chem.* 80, 8, 789-794

(i) Use the information given in **(b)** and refer to the bonding within butane and hexane to suggest a reason for the difference in their reactivity.

There are more C–H bonds in hexane than butane, leading to a faster rate of H-abstraction.

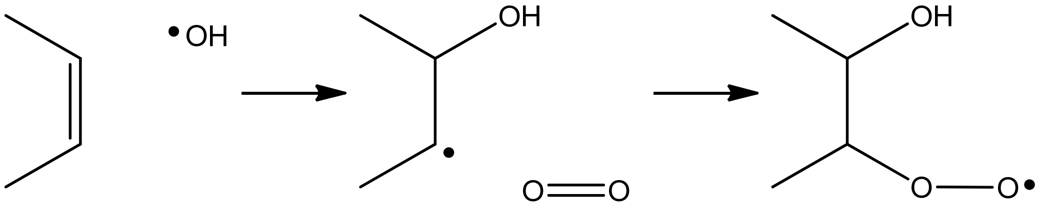
(ii) The reaction between hydroxyl radicals and alkenes proceed via a different mechanism and this increases the rate of reaction.

Account for this difference referring to the terms 'sigma' and 'pi'.

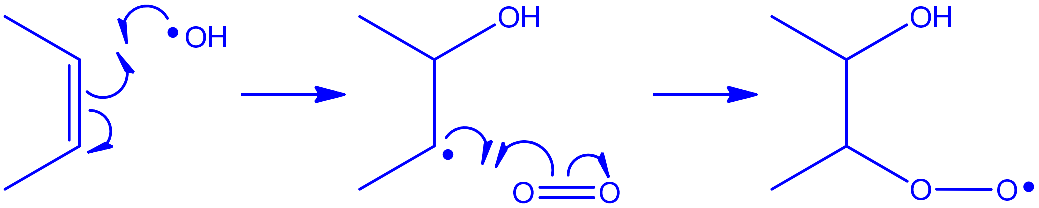
The pi electrons in the alkene C=C bond are less tightly bound to the nucleus
OR
weaker as compared to the sigma electrons in the C–H bond and hence reaction with alkenes proceed faster.

After the attack of the hydroxyl radical on cis-but-2-ene, the intermediate is now reactive enough to react with molecular oxygen.

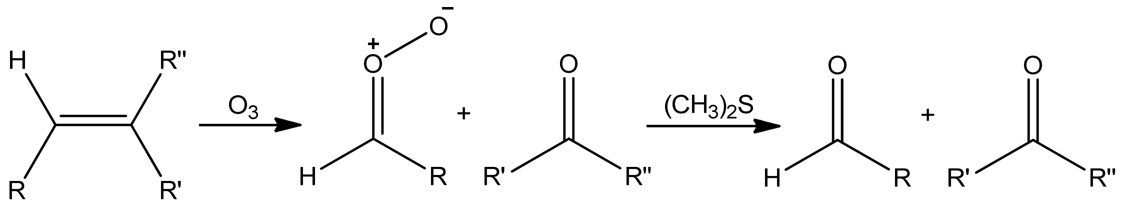
(iii) Complete the diagram to suggest a mechanism to show how the hydroxyperoxyl radical is formed. Show the movement of electrons by using curly arrows.



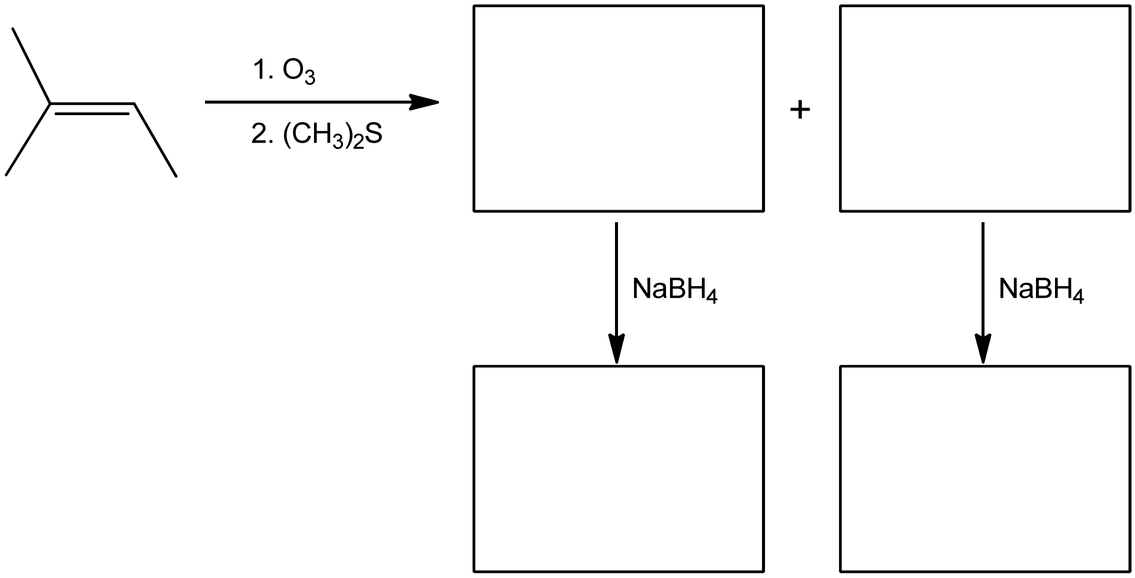
[2]



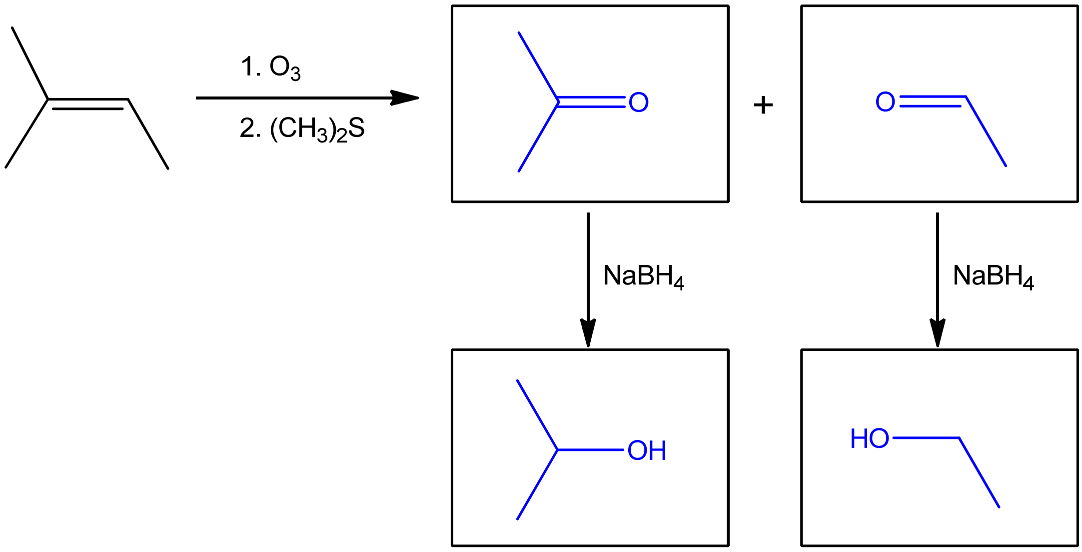
(d) Alkenes can also react with ozone directly via a process known as ozonolysis and the first step produces a carbonyl oxide and a carbonyl compound. Quenching with dimethyl sulfide produces two carbonyl compounds.



Complete the reaction scheme below.



[3]



[Total: 12]

~ End of Paper~

Name	Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/02

Paper 2 Structured Questions

16 August 2018
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS CAREFULLY

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Question no.	**Marks**
1	**/ 14**
2	**/ 6**
3	**/ 9**
4	**/ 13**
5	**/ 12**
6	**/ 9**
7	**/ 12**
Presentation of answers	
TOTAL	**/ 75**

This document consists of **21** printed pages and **1** blank page.

BLANK PAGE

Answer **all** the questions in the spaces provided.

1 A mixture contains two white solids **X**CO_3 and **Y**SO_4 where **X** and **Y** could be either magnesium, zinc or barium. The following investigations were carried out to determine the identity of **X** and **Y**.

(a) When the mixture of solids was treated with excess dilute hydrochloric acid, a colourless gas was evolved and some, but not all, of the mixture dissolved.

The resulting mixture was filtered. To the filtrate, dilute aqueous ammonia was added dropwise till in excess. The white precipitate formed was insoluble in excess aqueous ammonia.

Deduce the identity of elements **X** and **Y**, showing your reasoning clearly.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

…………………………………………………………………………………………… [3]

(b) Group 2 carbonates decompose according to the following equation:

$$ZCO_3(s) \longrightarrow ZO(s) + CO_2(g)$$

element	magnesium	calcium	barium
enthalpy change for the reaction, ΔH_r / kJ mol^{-1}	+101	+178	+269

(i) Use the data above to state and explain the trend in the thermal stability of the Group 2 carbonates.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [3]

(ii) Lithium carbonate, a Group 1 carbonate, decomposes on heating.

Use relevant data from the Data booklet to calculate relative charge densities of the above cations and hence deduce which of the above ΔH_r values in the table is likely to be the nearest to that of lithium carbonate.

[2]

(c) Patients with digestive tract problems are sometimes asked to take an x-ray after they have swallowed a "barium meal", consisting of a suspension of $BaSO_4$ in water.

(i) Write an expression for the solubility product, K_{sp} for $BaSO_4$, including its units.

………………………………………………………………………………………… [2]

(ii) The numerical value of K_{sp} is 1.30×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.

[1]

(iii) Although Ba^{2+} ions are toxic, the $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause any problems of toxicity.

The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that of $BaSO_4$, but $BaCO_3$ is **very** poisonous if ingested. Suggest a reason why this might be so.

…………………………………………………………………………………………

………………………………………………………………………………………… [1]

(iv) $BaSO_4$ is commonly prepared in the laboratory by combining aqueous solutions containing Ba^{2+} and SO_4^{2-}.

Determine if $BaSO_4$ will form when equal volumes of 2.00×10^{-2} mol dm^{-3} aqueous $Ba(NO_3)_2$ and 4.00×10^{-2} mol dm^{-3} aqueous Na_2SO_4 are mixed.

[2]

[Total: 14]

2 A student conducted two separate electrolysis using inert electrodes under room temperature and pressure.

electrolysis reaction	electrolyte	volume of gas collected at anode / cm^3	duration
1	concentrated hydrochloric acid	150	10 minutes
2	aqueous sodium sulfate	37.5	

(a) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **1**.

…………………………………………………………………………………………. [1]

(ii) Calculate the current that was used in electrolysis reaction **1**.

[2]

(b) **(i)** Write the half-equation with state symbols for the reaction occurring at the anode for electrolysis reaction **2**.

…………………………………………………………………………………………. [1]

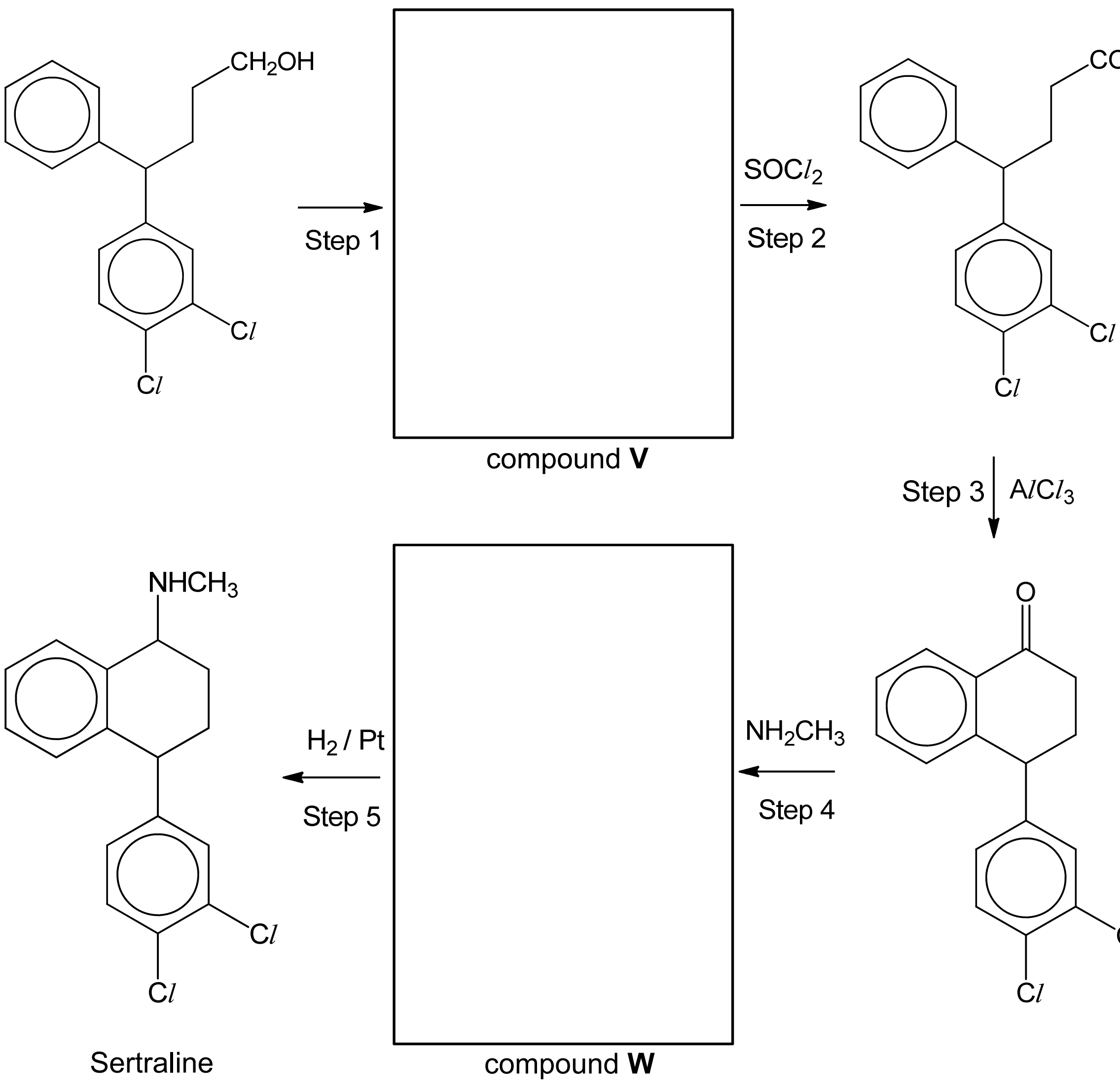
(ii) Determine the current used in electrolysis reaction **2**.

[2]

[Total: 6]

3 Sertraline is an antidepressant used to treat depression, obsessive compulsive disorder, post-traumatic stress disorder and related conditions. This medication can help to improve mood, mental alertness, energy level and sleep pattern for the patients. Sertraline works by helping to restore the balance of serotonin, a neurotransmitter in the brain which regulates anxiety, mood and happiness.

A proposed synthesis route of sertraline is shown below.

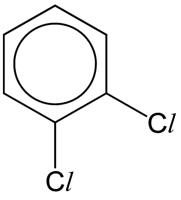


(a) State the reagents and conditions needed for step 1 and draw the structure of compound **V** in the box above.

.... [2]

(b) Electrophilic substitution takes place in step 3 where $AlCl_3$ acts as a Lewis acid catalyst and reacts with the acyl chloride functional group to generate the electrophile.

Write an equation to show the generation of the electrophile and hence draw the mechanism for the reaction that occurs in step 3.

You may use R to represent  in Sertraline for part **(b)** and part **(d)**.

[3]

(c) State the type of reaction taking place in step 4 and draw the structure of compound **W** in the box above.

.... [2]

(d) Sertraline exists as a mixture of stereoisomers. Draw the structures of the stereoisomers of Sertraline.

[2]

[Total: 9]

4 **(a)** The change in colour from blue to pink of the cobalt complexes has been the basis of cobalt chloride indicator papers for the detection of the presence of water.

The two differently coloured cobalt(II) complex ions, $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$, exist together in equilibrium in solution in the presence of chloride ions. This is represented by the equation below.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$

An experiment is conducted to investigate the effects on the equilibrium position by imposing a series of changes on the system. The shift in equilibrium position can be indicated by any colour change of the solution.

species	**colour**
$Co(H_2O)_6^{2+}$ (aq)	pink
$CoCl_4^{2-}$ (aq)	blue
initial equilibrium mixture containing $Co(H_2O)_6^{2+}$ and $CoCl_4^{2-}$	purple

After a 3.00 cm^3 sample of an initial equilibrium mixture was placed in three separate boiling tubes, a different substance was added to each tube, as indicated in Table 4.1.

(i) Complete Table 4.1 by predicting:

- the change in concentration, if any, of each ions in solution compared to the initial solution, after a new equilibrium position is reached.
- the colour change, if any, that takes place from the initial purple-coloured solution.

Table 4.1

Substance added	Change in concentration from initial solution to new equilibrium (increase, decrease, unchanged)			Colour change (pink, blue or unchanged)
	$[Co(H_2O)_6]^{2+}$	Cl^-	$[CoCl_4]^{2-}$	
$H_2O(l)$				
Concentrated HCl				
$AgNO_3$(aq)				

[3]

(ii) Another experiment was conducted to investigate the effect of temperature on the same equilibrium mixture. When 3.00 cm^3 of the original equilibrium mixture in a test tube was placed in an ice bath, the solution became pink.

Determine whether the forward reaction, as illustrated by the equation above, is exothermic or endothermic. Use Le Châtelier's Principle to justify your answer.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………. [2]

(b) At room temperature, a solution of sodium tartrate, $Na_2C_4H_4O_6$, does not react with hydrogen peroxide. When heated in a water bath, the reaction mixture reacts giving a very slow stream of carbon dioxide.

When a few drops of an aqueous pink cobalt(II) salt are added, the colour of the solution soon turns green and a vigorous effervescence of carbon dioxide takes place.

When the reaction stops, the pink colour is restored.

The half equation for the oxidation of tartrate ions is given as shown:

$$C_4H_4O_6^{2-}(aq) + 8OH^-(aq) \longrightarrow 4CO_2(g) + 6H_2O(l) + 10e^-$$

(i) In alkaline medium, H_2O_2 exists as hydroperoxide ions, HO_2^-. Construct a balanced half equation for the reduction of HO_2^- to OH^-.

………………………………………………………………………………………. [1]

(ii) Write a balanced ionic equation for the reaction between tartrate ions and hydroperoxide ions.

………………………………………………………………………………………. [1]

(iii) Suggest why there is no reaction observed when tartrate ions and hydroperoxide ions are mixed at room temperature even though the reaction is energetically feasible.

…………………………………………………………………………………………

……………………………………………………………………………………….[1]

(iv) Explain why a slow stream of carbon dioxide is observed when reaction mixture is heated in a water bath.

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………….. [2]

(v) State the identity of the aqueous ions responsible for the green colour.

……………………………………………………………………………………….. [1]

(vi) Use your answer in **(b)(v)** to describe the catalysed two-step reactions involving aqueous cobalt ions with the tartrate ions and hydroperoxide ions.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………….. [2]

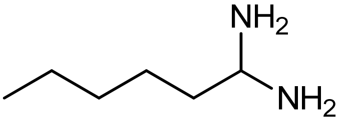
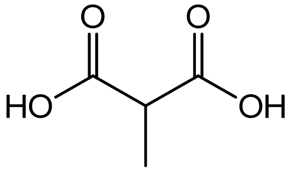
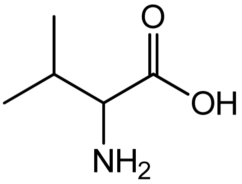
[Total: 13]

5 **(a)** Amino acids are biologically-important organic compounds containing both amine (-NH_2) and carboxylic acid (-COOH) functional groups.

To consider the effect of having both an amine and a carboxylic acid functional group on the same molecule, amino acids can be compared with other organic compounds such as diamines and dicarboxylic acids.

Amino acids have significantly higher melting points than diamines and dicarboxylic acids of similar mass and structure as shown in Table 5.1 below.

Table 5.1

compound type	example	molar mass /g mol^{-1}	melting point /^{o}C
diamine	 hexane-1,1-diamine	116.2	39
dicarboxylic acid	 methylpropanedioic acid	118.1	184
amino acid	 2-amino-3-methylbutanoic acid (valine)	117.2	298

Explain why the melting points show an increasing trend from diamine to amino acid in terms of structure and bonding.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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……………………………………………………………………………………………

……………………………………………………………………………………………[4]

(b) When 50.0 cm^3 of hexane was shaken with 20.0 cm^3 of an aqueous solution containing 1.10 g of 2-amino-3-methylbutanoic acid (valine), it was found that 0.050 g of valine was extracted into the hexane. At equilibrium, the ratio of the concentration of valine in the two immiscible solvents is a constant called partition coefficient where

$$K_{\text{partition}} = \frac{[\text{valine}]_{\text{hexane}}}{[\text{valine}]_{\text{aq}}}$$

(i) Calculate the partition coefficient, $K_{\text{partition}}$, of valine between hexane and water.

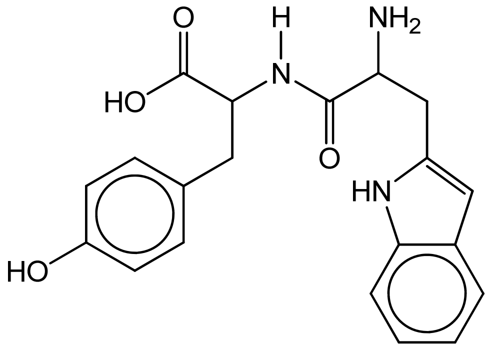
[1]

(ii) State which is a better solvent for valine and explain the reason for its solubility in that solvent.

…………………………………………………………………………………………………

…………………………………………………………………………………………….. [2]

(c) Tryptophan is an essential amino acid found in foods such as chicken, eggs, cheese and milk. It is needed to create the neurotransmitter serotonin which promotes sleep. Two amino acids, tyrosine (tyr) and tryptophan (trp), form a dipeptide, tyr-trp, as shown by the following structure.



tyr–trp

Draw the structures of the products of the reactions of tyr-trp with an excess of each of the following reagents.

(i) NaOH(aq) at room temperature

[1]

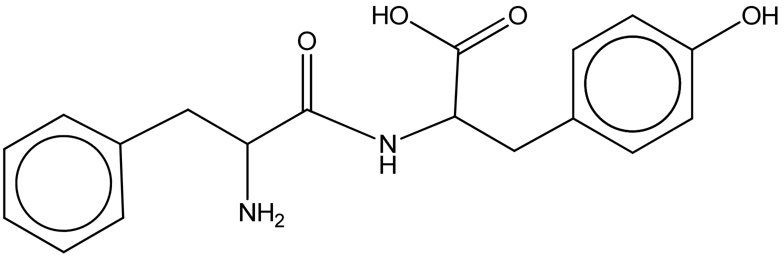
(ii) HC*l*(aq) and heat under reflux

product 1

product 2

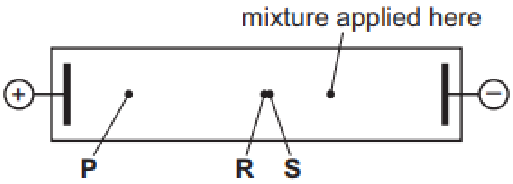
[2]

(d) Phenylalanine and tyrosine form another dipeptide (phe-tyr) as shown below



phe-tyr

A mixture of the dipeptide (phe-tyr) and its two constituent amino acids (phenylalanine and tyrosine) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phenylalanine, tyrosine and the dipeptide, phe-tyr.

(i) Draw the structural formula of the species responsible for spot **P.**

[1]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

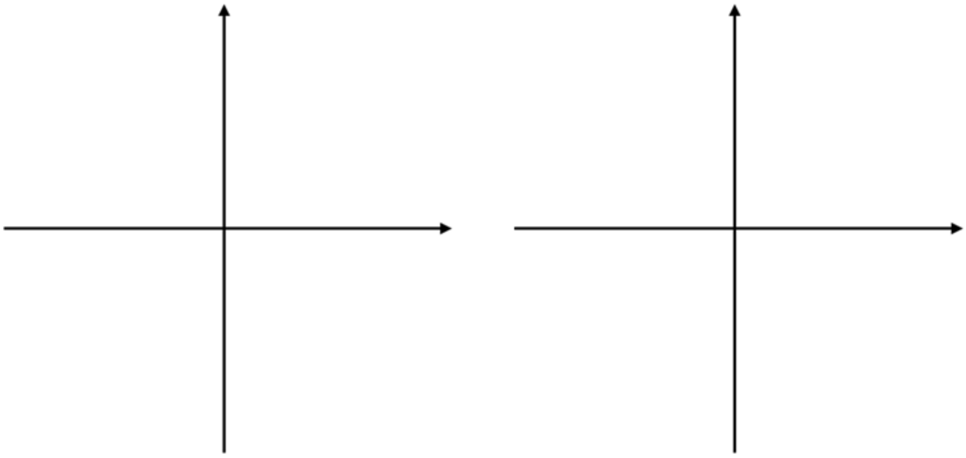
....

.... [1]

[Total: 12]

6 In an isolated transition metal atom, the five 3d-orbitals are degenerate. However, in an octahedral complex ion, the presence of ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies.

(a) Using the axes provided below, draw and label the shape of **one** d-orbital in **each** of the two groups mentioned above.



[2]

(b) Explain how the presence of the six ligands, **L**, in $[\mathrm{Ni}\mathbf{L}_6]^{2+}$ splits the five 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

…………………………………………………………………………………………………......

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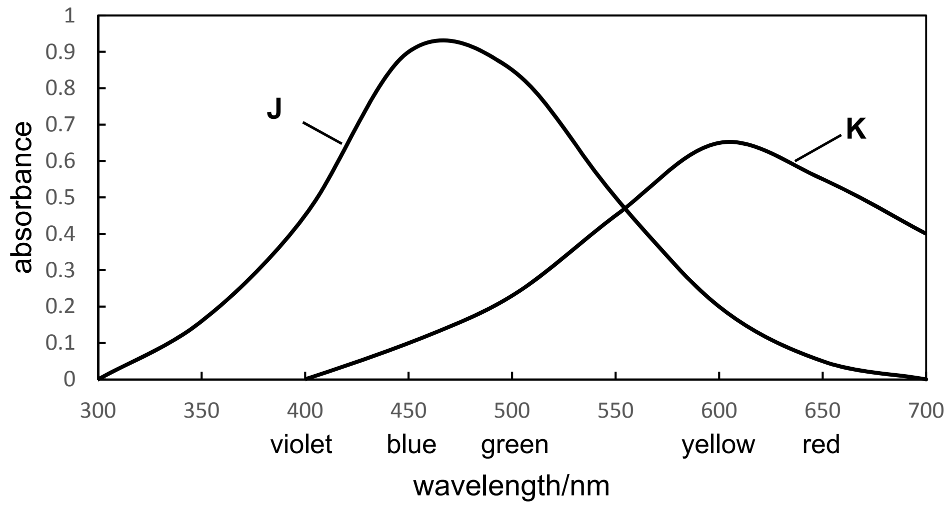
………………………………………………………………………………………………….

………………………………………………………………………………………… [3]

(c) The absorbance spectra of solutions of two transition metal complexes **J** and **K** are shown in the diagram below.



A list of possible colours for these complexes is as follows.

yellow	red	green	blue

Choose one of the colours above to describe the observed colour of each solution.

Solution **J** ……………………….. Solution **K** ………………………..

[2]

(d) Ligands are classified based on their ability to split the five 3d orbitals into two groups with an energy difference (ΔE). Strong field ligands produce a large ΔE while weak field ligands produce a small ΔE.

The energy of a photon can be obtained by Planck's equation:

$$E = \frac{hc}{\lambda}$$

where: E is the energy of the photon (in J)
λ is the wavelength of the photon (in m)
h is Planck's constant
c is the speed of light in vacuum

Use the data below as well as data from the *Data Booklet*, complete the table and arrange the ligands in order of increasing field strength.

species	$[M(CN)_6]^{2-}$	$[M(F)_6]^{4-}$	$[M(H_2O)_6]^{2+}$
λ / nm	430	650	600
ΔE / J			

Increasing field strength: …………………<…………………<………………… [2]

[Total: 9]

7 The oxidising power of our atmosphere has been well-studied and is of importance as many environmental trace gases, such as methane, are removed.

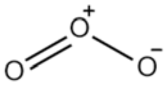
The most abundant oxidants in the atmosphere are oxygen and ozone molecules. These molecules have strong bonds and are hence relatively unreactive except towards radicals. Research in the 1950s suggested that the hydroxyl radical, •OH, is a strong oxidant.

In the stratosphere, UV light from the sun heterolytically breaks ozone molecules into oxygen molecules and oxygen atoms. The oxygen atoms react homolytically with water vapour to produce hydroxyl radicals, •OH.

$$O_3 \xrightarrow{UV} O_2 + O \qquad \text{--------------------(1)}$$

$$O + H_2O \longrightarrow 2{\bullet}OH \qquad \text{--------------------(2)}$$

(a) Use equations (1) and (2) to draw the mechanism for the formation of the hydroxyl radical, •OH. Include in your mechanism the necessary curly arrows and electrons.

Use  as the structure of ozone.

[2]

(b) Hydroxyl radicals are particularly reactive towards H-containing molecules due to H-abstraction converting •OH back to H_2O.

$${\bullet}OH + CH_4 \longrightarrow H_2O + {\bullet}CH_3 \quad \text{--------------------(3)}$$

Some information about an elementary reaction (3) was obtained.

[•OH] / molecules cm^{-3}	1.0×10^{6}
[CH_4] / molecules cm^{-3}	4.4×10^{13}
rate constant, k / cm^{3} molecule^{-1} s^{-1}	1.4×10^{-5}

Source: Jacob, D. J. Introduction to Atmospheric Chemistry; Princeton University Press: 1999

(i) Use information in the table to write an equation to represent the rate equation for the pseudo-first-order reaction with respect to the concentration of the hydroxyl radical, •OH.

…………………………………………………………………………………………….. [1]

(ii) Calculate the half-life of the hydroxyl radical, •OH to the nearest **2 significant figures**.

[2]

(c) The relative rates of disappearance in air at 305 K for a series of hydrocarbons were measured in an environmental chamber under simulated atmospheric conditions. Absolute rate constants obtained from the reaction are as follows.

hydrocarbon	k / × 10^9 mol^{-1} dm^3 s^{-1}
butane	1.8
hexane	3.8
cis-but-2-ene	39.2

Source: J. Phys. Chem. 80, 8, 789-794

(i) Use the information given in **(b)** and refer to the bonding within butane and hexane to suggest a reason for the difference in their reactivity.

…………………………………………………………………………………………..

…………………………………………………………………………………………. [1]

(ii) The reaction between hydroxyl radicals and alkenes proceed via a different mechanism and this increases the rate of reaction.

Account for this difference referring to the terms 'sigma' and 'pi'.

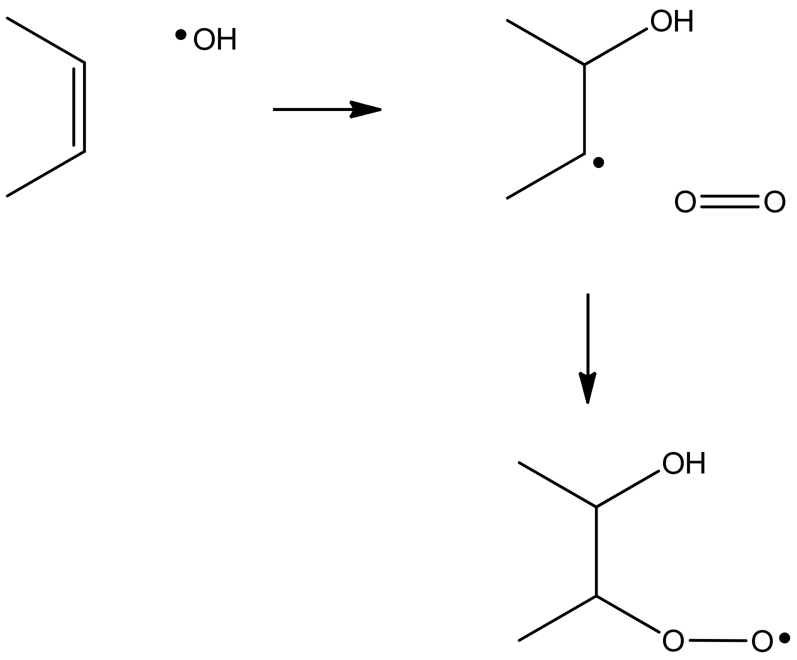
…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………. [1]

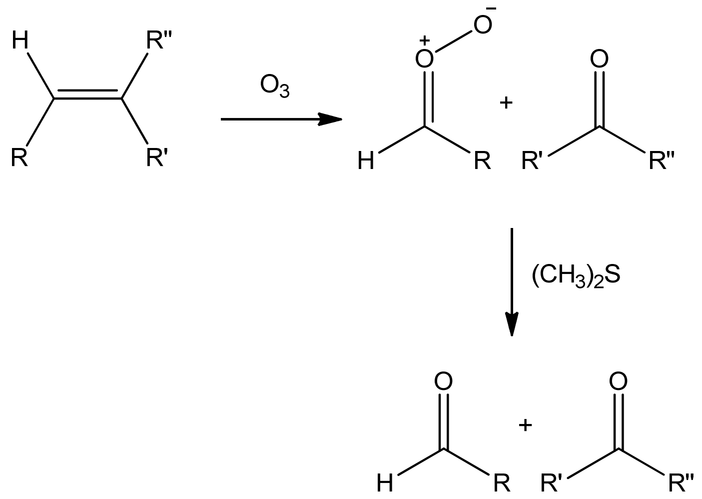
After the attack of the hydroxyl radical on cis-but-2-ene, the intermediate is now reactive enough to react with molecular oxygen.

(iii) Complete the diagram to suggest a mechanism to show how the hydroxyperoxyl radical is formed. Show the movement of electrons by using curly arrows.

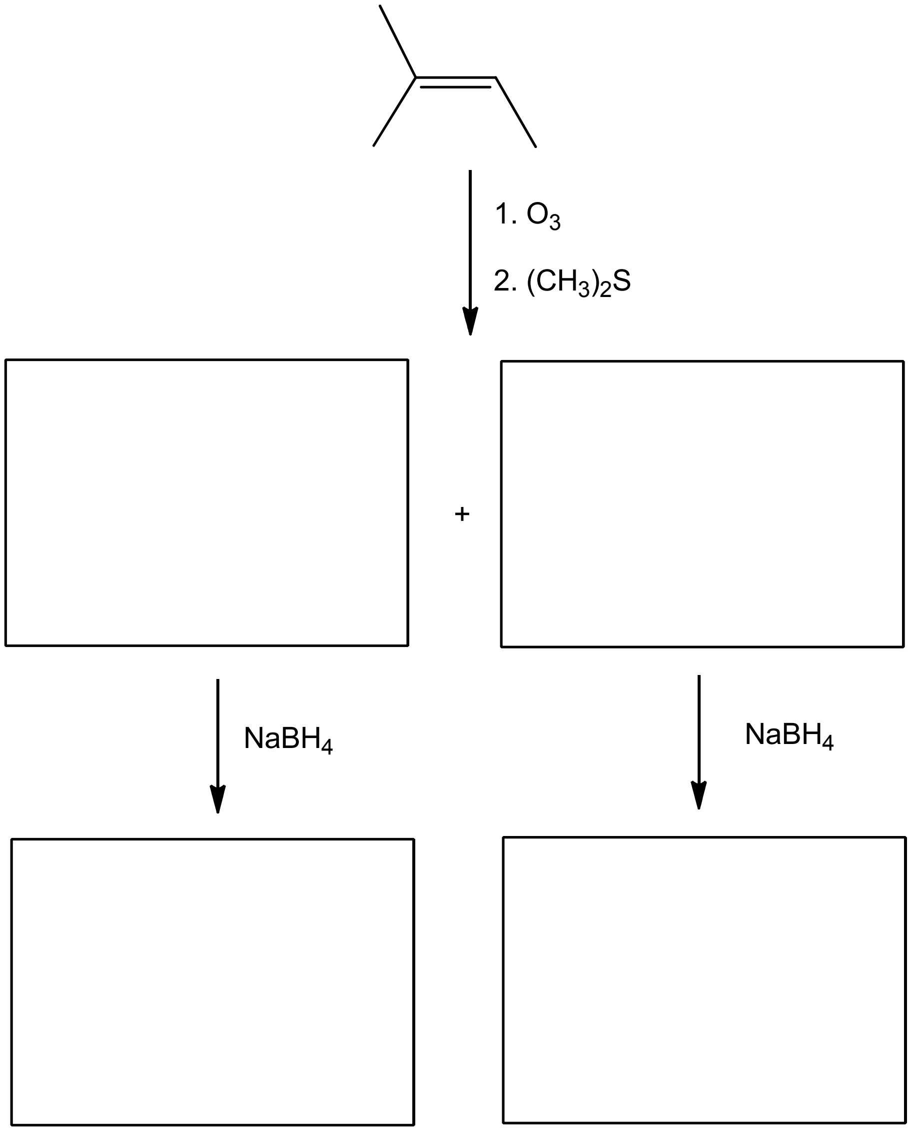


[2]

(d) Alkenes can also react with ozone directly via a process known as ozonolysis and the first step produces a carbonyl oxide and a carbonyl compound. Quenching with dimethyl sulfide produces two carbonyl compounds.



Complete the reaction scheme below.

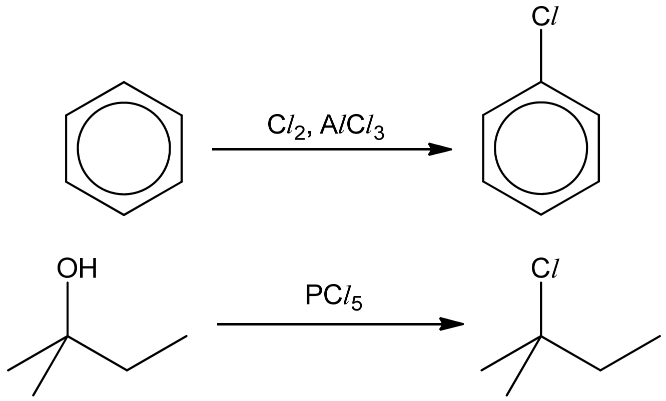


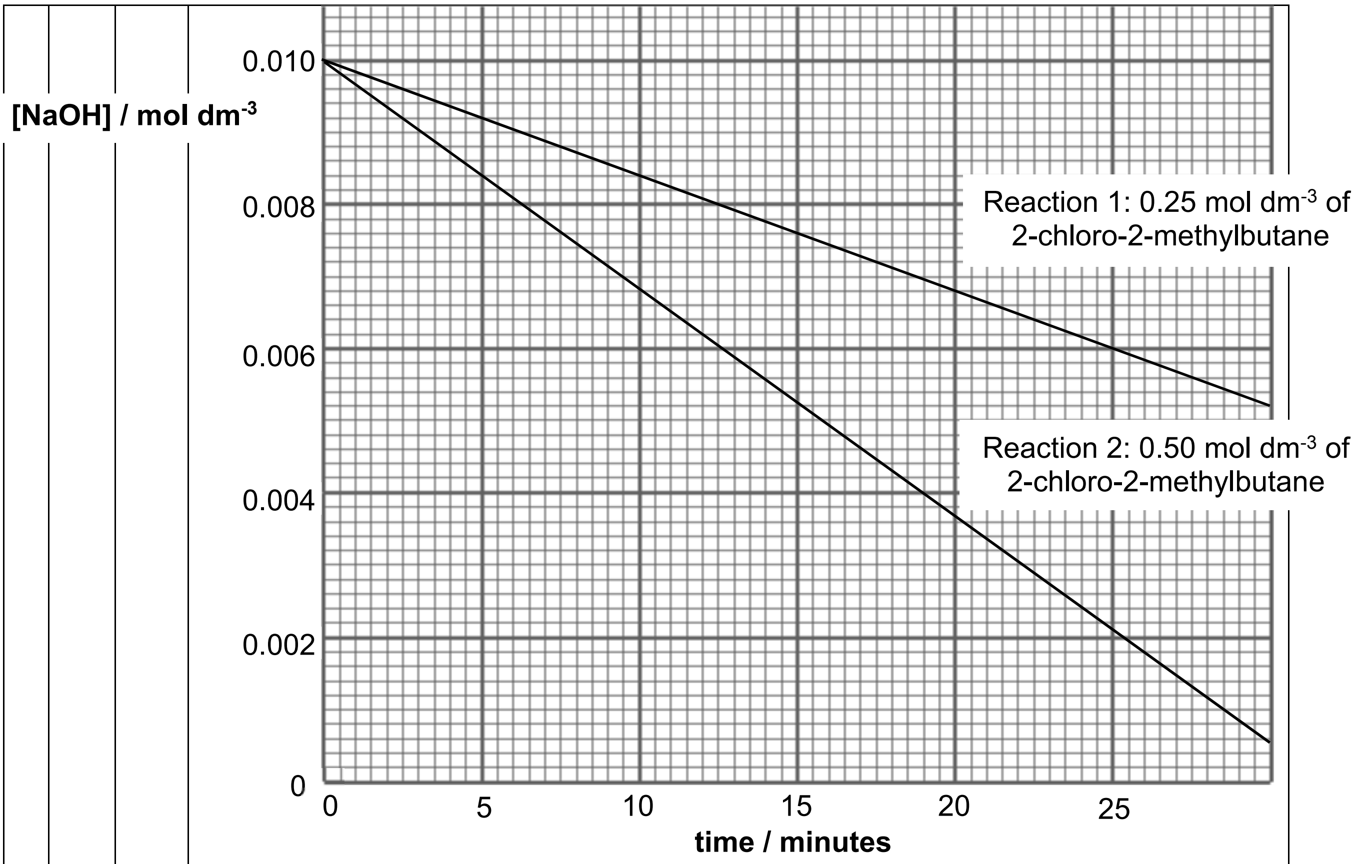
[3]

[Total: 12]

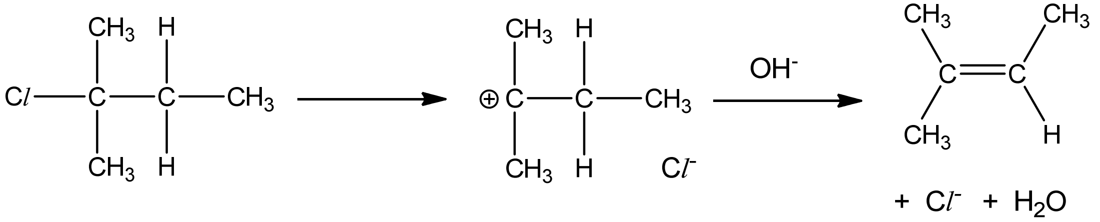
Section A

Answer **all** questions in this section.

1	**(a)**	**(i)**	Due to reactivity of $AlCl_3$ and PCl_5 in water, the following reactions are carried out under anhydrous conditions.  Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]
			$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$ $[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$ **pH 3** $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$ **OR** $PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$ **pH 2**
		(ii)	Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added. State and explain the difference in observations. Write equations for the reactions that occur. [3]
			2-chloro-2-methylbutane forms a white ppt while chlorobenzene does not. **The C–C*l* bond in chlorobenzene is strengthened by partial double bond character due to the overlap of p-orbital on C*l* atom and π-orbital of benzene. Hence chlorobenzene is resistant to hydrolysis.** $CH_3C(CH_3)ClCH_2CH_3 + OH^- \longrightarrow CH_3C(CH_3)OHCH_2CH_3 + Cl^-$ $Ag^+ + Cl^- \longrightarrow AgCl$
	(b)	**(i)**	To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature. A [NaOH]–time graph was plotted using the results obtained from the experiments.

			
		(i)	Deduce the order of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]
			Using Reaction 1 (or 2), when [NaOH] decreases, gradient remains constant, hence rate of reaction is constant. Rate of reaction is independent of [NaOH], hence the reaction is zero order wrt [NaOH]. **Comparing reactions 1 and 2, when [2-chloro-2-methylbutane] doubles from 0.25 to 0.50 mol dm^{-3}, the gradient doubles, showing that the rate of reaction doubles from 1.60×10^{-4} to 3.15×10^{-4} mol dm^{-3} min^{-1}. Rate of reaction $\propto$ [2-chloro-2-methylbutane], hence the reaction is first order wrt [2-chloro-2-methylbutane].**
		(ii)	Hence, state the rate equation of this reaction. [1]
			Rate = k[2-chloro-2-methylbutane]

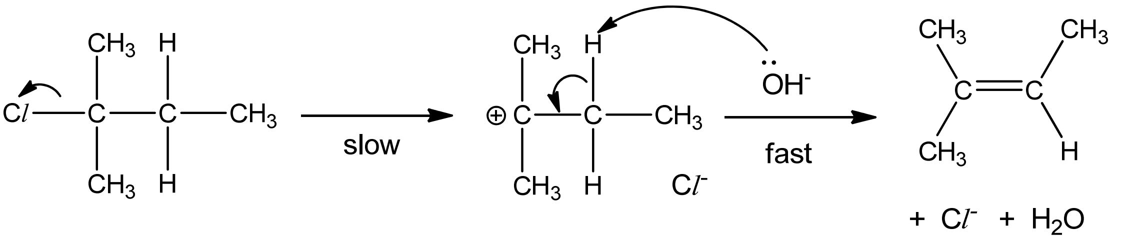
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



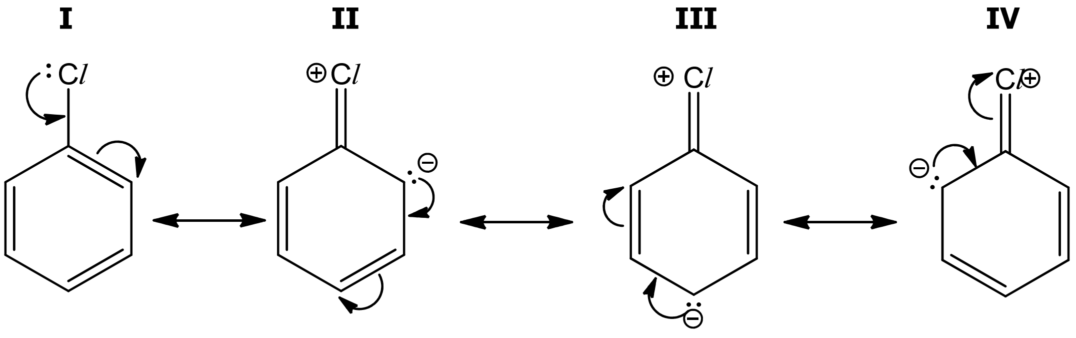
Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step.

[3]



(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



The negative charges are located on positions 2 and 4 with respect to the chloro-group, hence the electrophilic attack is more likely to occur at these positions OR electrophile is more likely to react at these positions.

(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

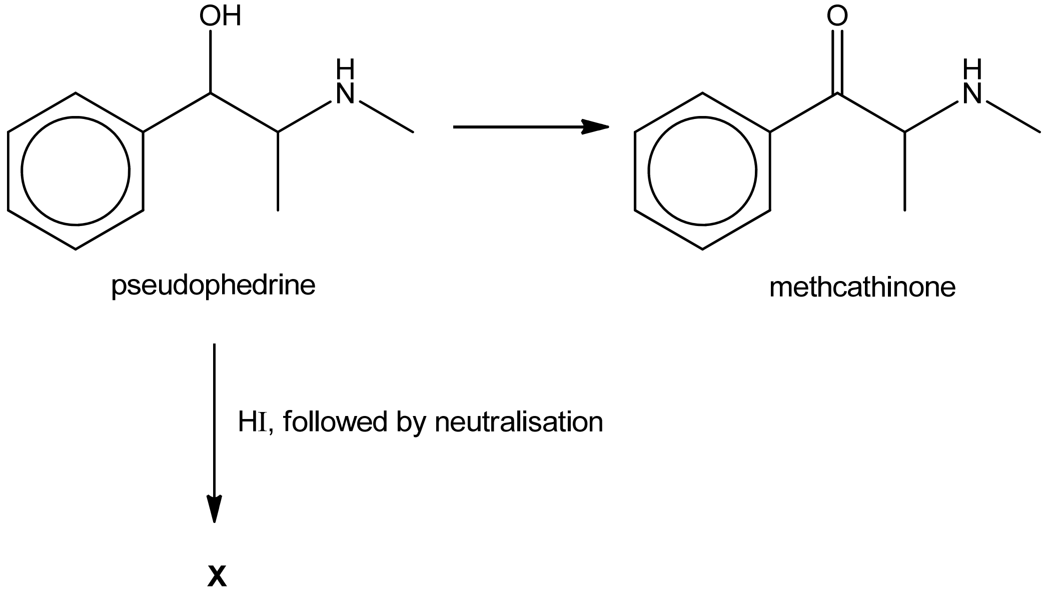
(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

$CH_3CH_2CH_2\dot{C}H_2$ and $CH_3CH_2\dot{C}HCH_3$

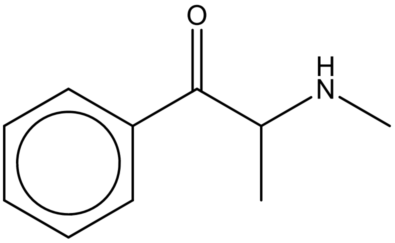
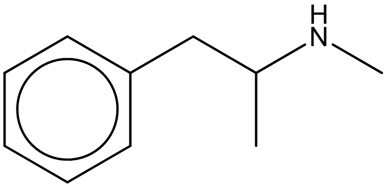
3 : 2

		(ii)	During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]
			• **$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ 3/5 x 3/5 = 9/25** • **$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$ 2/5 x 2/5 = 4/25** • **$CH_3CH_2CH_2CH_2CH(CH_3)CH_2CH_3$ 2 (3/5 x 2/5) = 12/25** • **Ratio = 9 : 4 : 12**
	(e)	Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.	
		(i)	Suggest one reason why CFCs were originally used for this purpose. [1]
			CFCs have high heat capacity OR They are not easily flammable.
		(ii)	Suggest one potential hazard of using alkanes instead of CFCs. [1]
			Alkanes are flammable.
			[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.



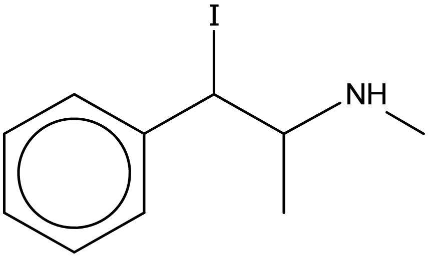
(a) **(i)** The structure of methcathinone and methamphetamine with pK_b values at 298 K, are shown in the table below.

compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

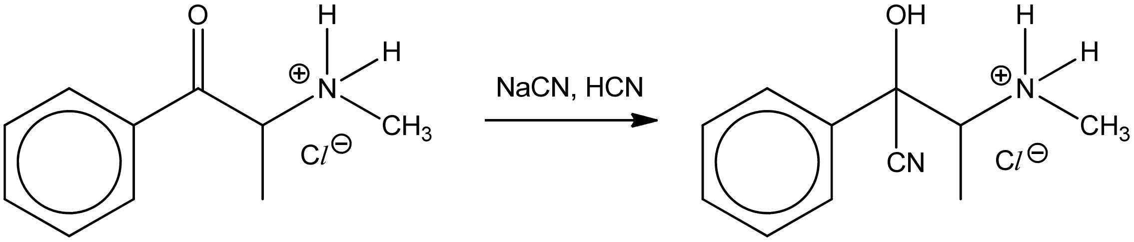
Methcathinone is a weaker base (higher pK_b) as it has a carbonyl (C=O) functional group two carbons away from secondary amine functional group, which is electron withdrawing. Hence the lone pair of electrons on N for methcathinone is less available for coordination with H^+ ion. (dative bonding with H^+ ion)

(ii) Suggest the structure of intermediate **X**. [1]



(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.

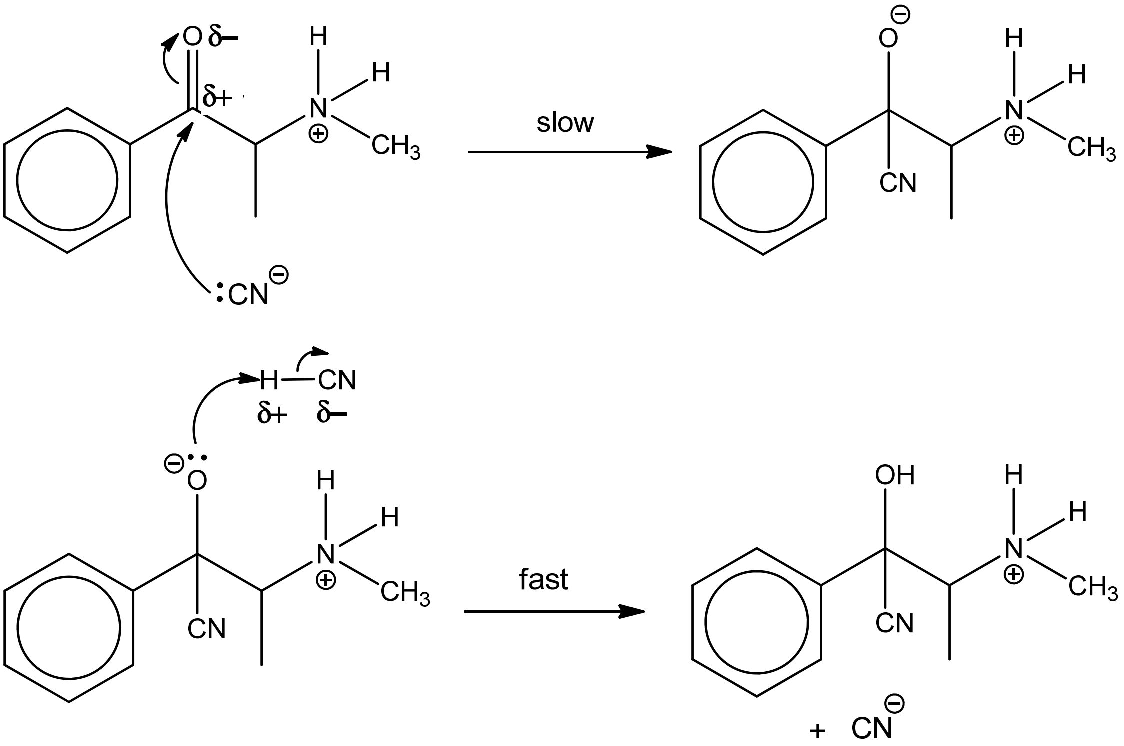


methcathinone hydrochloride

Y

Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

Nucleophilic addition



(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

		The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties. $N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$	
		(i)	During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]
			Hydrazine N_2H_4 is basic and it can react with HI (acidic) to form a salt $N_2H_5^+I^-$
		(ii)	Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]
			$\mathbf{2HI \longrightarrow H_2 + I_2}$
		(iii)	Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]
			At is below I in Group 17 so it forms weaker covalent bond with hydrogen. As a result, HAt has lower thermal stability than HI.
	(d)	A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation : $(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$ The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C. In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given : $K_p = K_c(RT)^4$ Assume that the gases are under ideal conditions.	
		(i)	Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]
			$\mathbf{K_p = (P_{NH3})^2(P_{H2O})(P_{CO2})}$ **Using pV = nRT** **P = (n/V)RT = CRT** $\mathbf{K_p = ([NH_3]RT)^2\ ([H_2O]RT)\ ([CO_2]RT)}$ $\mathbf{= [NH_3]^2\ [H_2O][CO_2]\ (RT)^4}$ $\mathbf{= K_c(RT)^4}$
		(ii)	Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

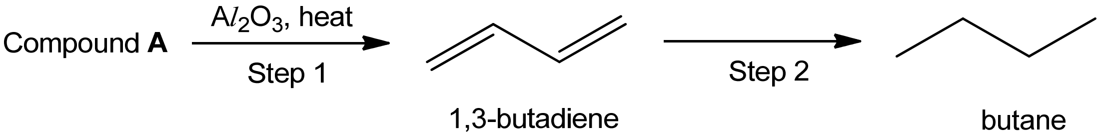
			$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$ I / atm 0 0 0 C / atm +2x +x +x E / atm 2x x x $K_p = (P_{NH_3})^2(P_{H_2O})(P_{CO_2})$ $0.295 = (2x)^2(x)\,x$ $x = 0.521$ $P_{NH_3} = 2x = 1.04$ atm
		(iii)	Calculate the total pressure inside the flask at equilibrium. [1]
			$P_{total} = (P_{NH_3}) + (P_{H_2O}) + (P_{CO_2})$ $= 2(0.521) + (0.521) + (0.521)$ $= 2.08$ atm
		(iv)	Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]
			PV = nRT $(0.521 \times 101325\ Pa)(0.003\ m^3) = n\ (8.31)(673\ K)$ n = 0.02832 mol Mass of $(NH_4)_2CO_3 = (40.0 – 0.02832) \times (2(14.0) + 8(1.0) + 12.0 + 3(16.0))$ $= 37.3$ g
			[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

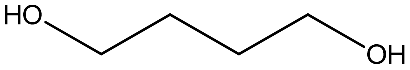
1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.

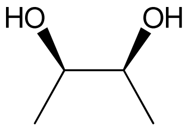


(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

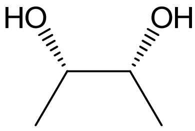


Elimination

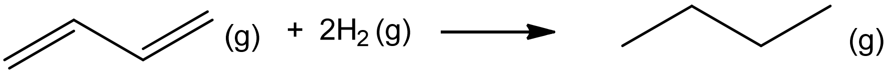
Alternative answer:



or



(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2. [1]

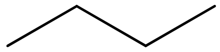


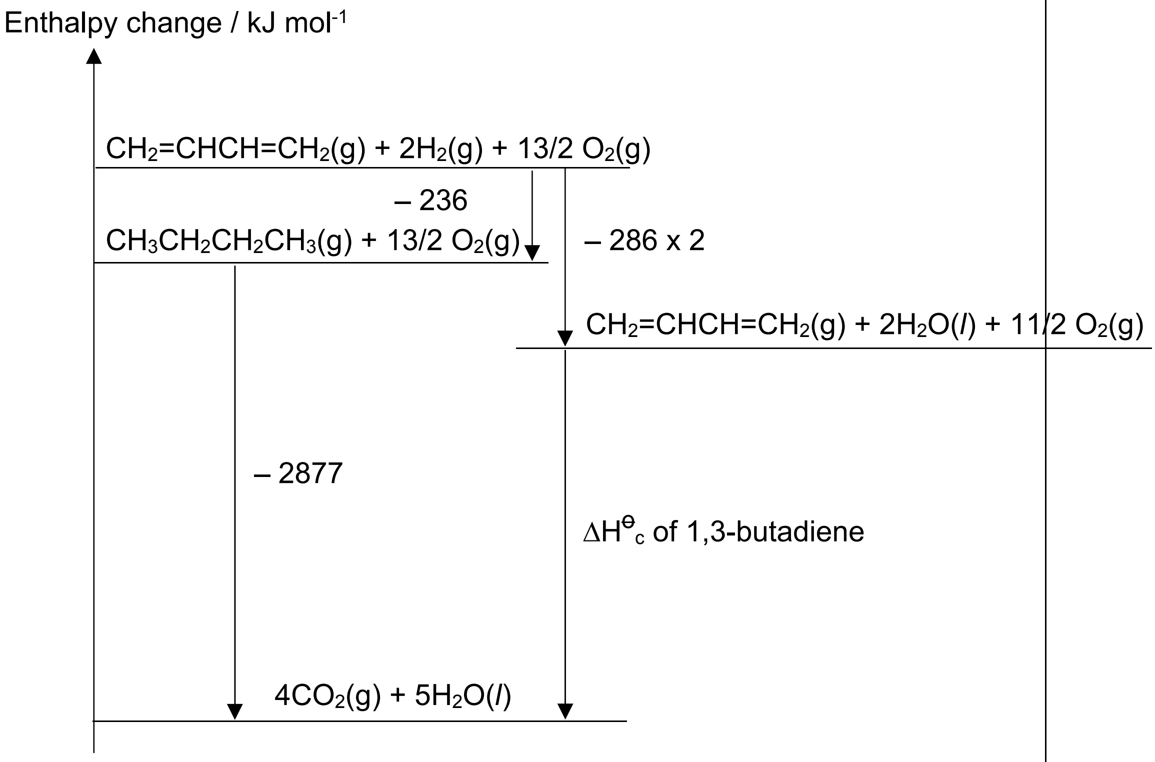
(iii) A student calculated the expected $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2 to be –252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene. [1]

Actual $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene = – 252 + 16 = –236 kJ mol^{-1}

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_c$ of 1,3-butadiene. [3]

substance	$\Delta H^{\ominus}_c$ / kJ mol^{-1}
	**–2877**
H_2	**–286**



$\Delta H^{\ominus}_c$ of 1,3-butadiene = – 2(–286) – 236 – 2877 = –2540 kJ mol^{-1}

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

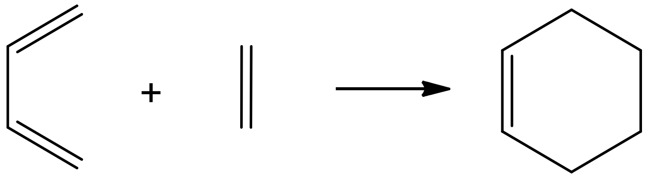
By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

The C–C single bond in 1,3-butadiene are formed from the sigma overlap of sp^2 orbitals while the C–C single bond in butane are formed from the sigma overlap of sp^3 orbitals.

Since sp^2 orbital has more s character than sp^3 orbital, the electrons are sp^2 orbitals are closer to the nucleus, resulting in a stronger bond formed. Hence the extra stability of 1,3-butadiene results from the greater amount of s character in the orbital forming the stronger C–C single bond.

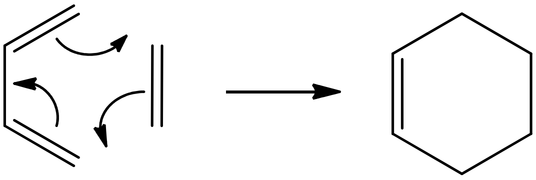
(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

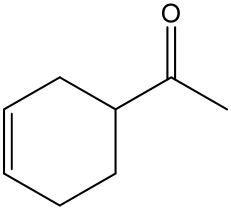
(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]



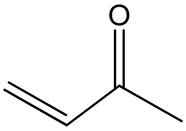
(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

Compound **B**:

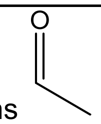


Compound **C**:



[

	Deductions
Compound **B** can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction.	• Compound **B** is a <u>cyclic</u> compound which contains an <u>alkene</u> functional group. • Compound **C** contains an <u>alkene</u> functional group which allows it to react with 1,3-butadiene.
Compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2.	• Compound **C** undergoes <u>reduction</u> with 2 moles of hydrogen gas as it has <u>two unsaturated bonds / alkene and ketone functional group.</u>

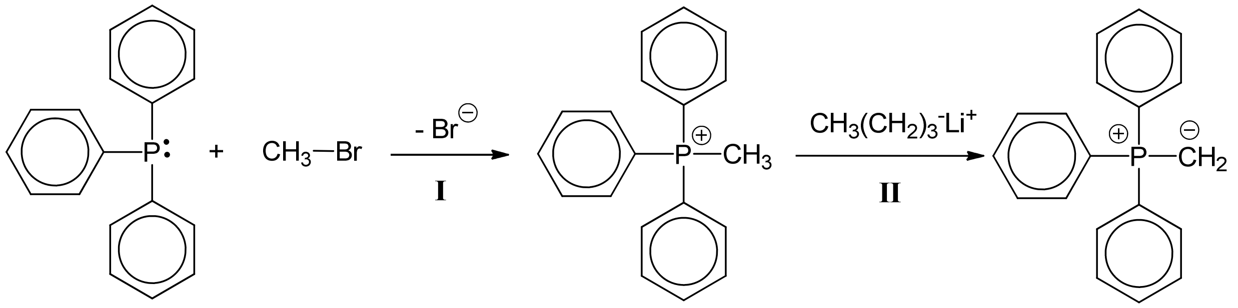
				• Compound **C** contains  group.
			Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test for Tollens' reagent.	• Compound **C** undergoes condensation with 2,4-DNPH and it contains a ketone functional group.
	(c)	Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.		
		(i)	Aluminium oxide has unique chemical properties as it is able to react with both acid and base. Write balanced chemical equations for the reactions between aluminium oxide and the following respectively. • HBr • KOH [2] **$Al_2O_3(s) + 6HBr(aq) \longrightarrow 2AlBr_3(aq) + 3H_2O(l)$** **$Al_2O_3(s) + 2KOH(aq) + 3H_2O(l) \longrightarrow 2K[Al(OH)_4](aq)$**	
		(ii)	Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3] **Aluminium oxide has a giant ionic lattice structure with strong electrostatic forces of attraction between Al^{3+} and O^{2-} ions. However, due to the high charge density of the Al^{3+} ion, there is considerable covalent character in the compound, hence resulting it being an amphoteric oxide which can react with both acids and alkalis.**	

Section B

Answer **one** question from this section.

4 **(a)** The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium. During the reaction, the number of carbon atoms also increases.

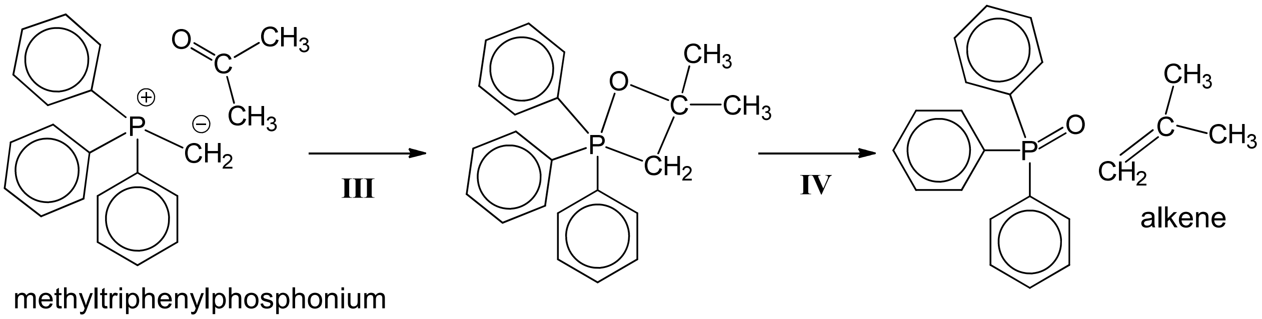
Stage 1 – Preparation of methyltriphenylphosphonium



triphenylphosphine

methyltriphenylphosphonium

Stage 2 – Formation of alkene



methyltriphenylphosphonium

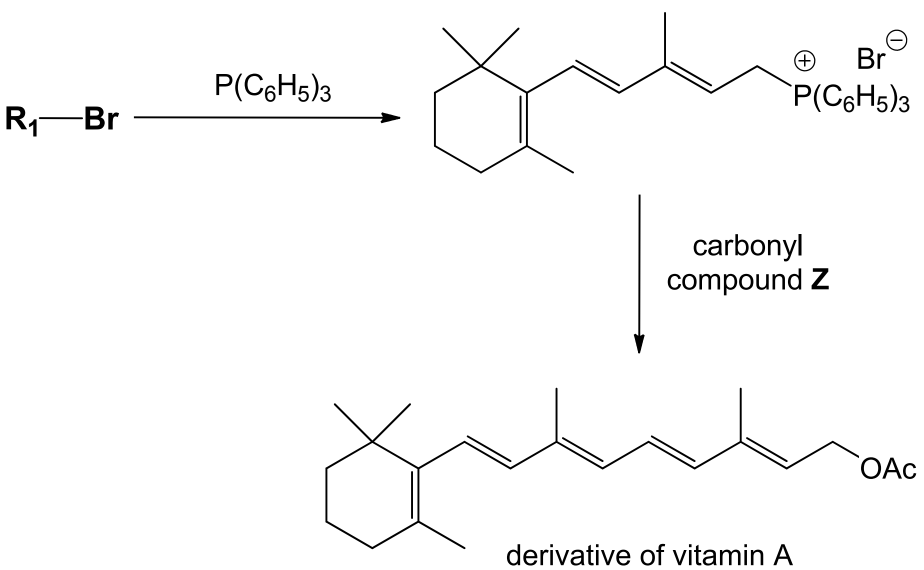
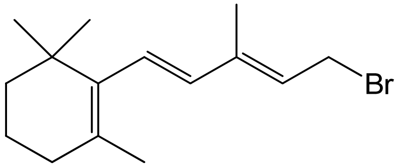
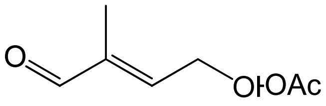
Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

(i) The melting points of four compounds are given below.

compound	*formula*	*melting point / °C*
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2{}^+Br^-$	232
sodium chloride	$NaCl$	801

With reference to their structure and bonding, suggest why the melting point of

1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride [4]

			1. Both compounds have simple molecular structures with weak intermolecular forces of attraction between their molecules. Triphenylphosphine has larger and more polarizable electron cloud than water. Thus is has stronger instantaneous dipole-induced dipole interaction than (the hydrogen bonding of) water. **2. Both compounds have giant ionic lattice structures. Methyltriphenylphosphonium bromide has ions with larger radii than NaC*l*, hence lattice energy is less exothermic and melting point is lower.**
		(ii)	State the type of reaction in step **I**. [1]
			Nucleophilic substitution or S_N2
		(iii)	State the role of $CH_3(CH_2)_3^-Li^+$ in Step **II**. [1]
			Base
		(iv)	The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.  Suggest the structures of alkylbromide **R_1–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]
			 
	(b)	Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.	
		(i)	Write the balanced equation for the preparation of triphenylphosphine. [1]
			$\mathbf{PCl_3 + 3C_6H_5Cl + 6Na \longrightarrow P(C_6H_5)_3 + 6NaCl}$

(ii) Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to the equation

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$

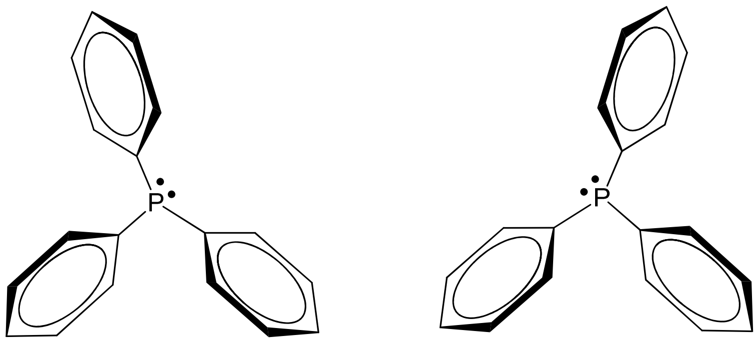
describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]

Using the mole ratio of PCl_3 and Na in the previous equation in (b)(i),
$6Na + 6H_2O \longrightarrow 6NaOH + 3H_2$

$H_3PO_3 + 2NaOH \longrightarrow Na_2HPO_4 + H_2O$
$HCl + NaOH \longrightarrow NaCl + H_2O$
OR
3 mol of NaOH is needed to completely react with 1 mol of H_3PO_3 and 1 mol of HC*l*.

Due to the excess of NaOH, universal indicator shows a blue / violet colour.

(iii) It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.



State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]

The two structures are enantiomers.
Triphenylphosphine has non-superimposable mirror images / no internal plane of symmetry.

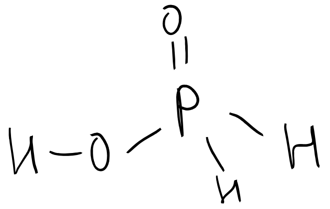
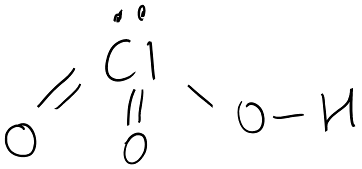
(c) (i) The aqueous solutions of two acids were prepared and their pH measured.

acid	*concentration / mol dm^{-3}*	*pH*
M	0.75	1.11
N	0.25	0.60

Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]

To determine if acid M dissociates fully:
$-\log(0.75) = 0.125$
Since pH is higher than 0.125, M did not dissociate fully. M is a weak acid.

To determine if acid N dissociates fully:
$-\log(0.25) = 0.60$

			Since pH is 0.60, N dissociated fully. N is a strong acid.
		(ii)	It is known that the electronegativity of the central atom in the acid affects its acidity. With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]
			M is H_3PO_2 and N is $HClO_3$.   **Cl atom is more electronegative than P , so it polarizes the O–H bond in $HClO_3$ to a greater extent, causing H^+ ion to be given off more readily, hence $HClO_3$ is a stronger acid, and must be N.** **OR** **Cl atom is more electronegative than P , so it disperses the negative charge on the conjugate base, ClO_3^-, to a greater extent. As the conjugate base is more stabilized, the acid is a stronger one.**
			[Total: 20]

5 *Use of the Data Booklet is relevant to this question*.

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) **(i)** Define the term *ligand*. [1]

A ligand is a neutral molecule or anion with at least one atom bearing a lone pair of electrons capable of dative bonding/coordinating to the central metal atom or ion.

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

$$\mathbf{Pt + 8HNO_3 \longrightarrow Pt^{4+} + 4NO_2 + 4NO_3^- + 4H_2O}$$

(iii) Suggest the identity of the yellow crystals obtained. [1]

$\mathbf{(NH_4)_2PtCl_6}$

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

$$\mathbf{(NH_4)_2PtCl_6\,(s) \rightleftharpoons 2NH_4^+\,(aq) + PtCl_6^{2-}\,(aq)}$$

The solubility of the yellow crystals will be reduced as the position of equilibrium in the solubility equilibria is pushed back to the left due to the common ion effect brought about by NH_4^+.

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When chloride ligands approach the Pt^{4+} central cation, the degenerate d-orbitals/d-subshell split into two groups of different energy levels. An electron in the lower level can absorb energy equivalent to the energy gap which corresponds to a certain wavelength of light from the visible region of the electromagnetic spectrum and be promoted to the higher energy level. The colour seen is complementary to the colour absorbed.

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

(b) **(i)** Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^\ominus_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^\ominus = +0.84\ V$$

Choose $\mathbf{O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^\ominus = +1.23\ V}$

$$\mathbf{E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}}$$
$$\mathbf{= +1.23 - (+0.84)}$$
$$\mathbf{= +0.39\ V}$$

(ii) Hence calculate $\Delta G^\ominus_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

$$\mathbf{\Delta G^\ominus_{cell} = -nFE^\ominus_{cell}}$$
$$\mathbf{= -(8)(96500)(+0.39)}$$
$$\mathbf{= -301\ 080\ J\ mol^{-1}}$$
$$\mathbf{= -301\ kJ\ mol^{-1}}$$

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

Since the standard entropy change is negative due to the decrease in number of moles of gaseous oxygen/loss of oxygen, the standard enthalpy change of reaction must be negative too for $\Delta G^\ominus_{cell}$ to be overall negative.

The figure below shows part of a label on a bottle of osmium tetroxide.

Osmium Tetroxide, OsO_4

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 μg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 μg = 1 x 10^{-6} g

(c) **(i)** Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2]

Gas volume = $250 - \frac{1000}{4.9} = 45.9\ cm^3$

$n(OsO_4\ vapour) = \frac{pV}{RT} = \frac{933 \times \frac{45.9}{1\ 000\ 000}}{8.31 \times 293} = 1.76 \times 10^{-5}$ mol

(ii) Hence determine the concentration of OsO_4, in μg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed.

[2]

$m(OsO_4\ vapour) = 1.76 \times 10^{-5} \times 254.2 = 4.47 \times 10^{-3}$ g

$[OsO_4] = \frac{4.47 \times 10^{-3}}{100} = 4.47 \times 10^{-5}\ g\ m^{-3} = 44.7\ \mu g\ m^{-3}$

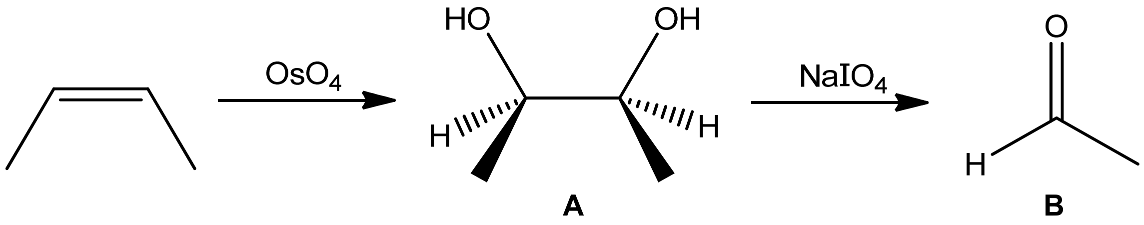
(iii) Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1]

Yes, since the effective concentration of 44.7 μg m^{-3} is less than the maximum permissible exposure limit of 200 μg m^{-3}.

OR

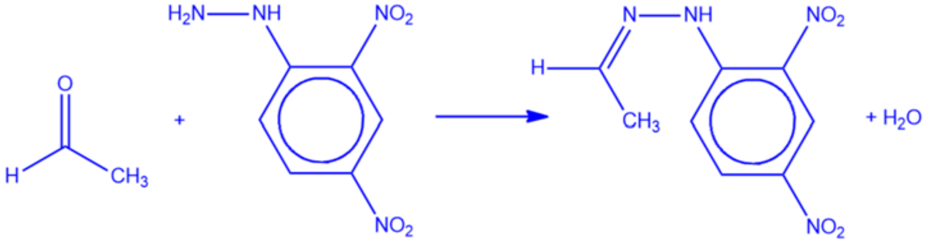
No, it is not safe as the vapour takes time to diffuse evenly throughout the room. The immediate air around the researchers will have a concentration of OsO_4 exceeding the maximum permissible limit.

Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.



(d) Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3]

2,4-DNPH, room conditions
Yellow crystals formed with **B** but no yellow crystals formed with **A**.



OR

Tollens' reagent, warm
Silver mirror formed with **B** but no silver mirror formed with **A**.
$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow 2Ag + 4NH_3 + CH_3CO_2^- + 2H_2O$

OR

Fehling's reagent, warm
Red-brown ppt formed with **B** but no red-brown ppt formed with **A**.
$CH_3CHO + 2Cu^{2+} + 5OH^- \longrightarrow CH_3CO_2^- + Cu_2O + 3H_2O$

OR

Sodium, room conditions
Effervescence observed with **A**. Gas evolved extinguishes lighted splint with a pop sound. No effervescence observed with **B**.

OR

PCl_5, room conditions
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2PCl_5 \longrightarrow CH_2ClCH_2Cl + 2POCl_3 + 2HCl$

OR

$SOCl_2$ (pyridine), heat
Steamy/White fumes observed with **A** but no white fumes observed with **B**.
$CH_2(OH)CH_2OH + 2SOCl_2 \longrightarrow CH_2ClCH_2Cl + 2HCl + 2SO_2$

[Total: 20]

– End of Paper –

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY
Higher 2

9729/03

Paper 3 Free Response

24 August 2018

Candidates answer on separate paper.

2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Start each question on a new sheet of writing paper.

A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind a cover sheet.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **15** printed pages and **1** blank page.

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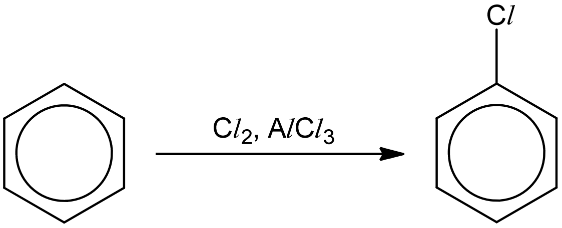
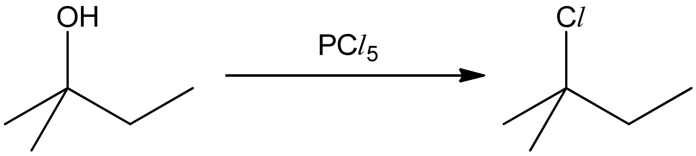
Section A

Answer **all** questions in this section.

1 (a) (i) Due to reactivity of $AlCl_3$ and PCl_5 in water, the following reactions are carried out under anhydrous conditions.





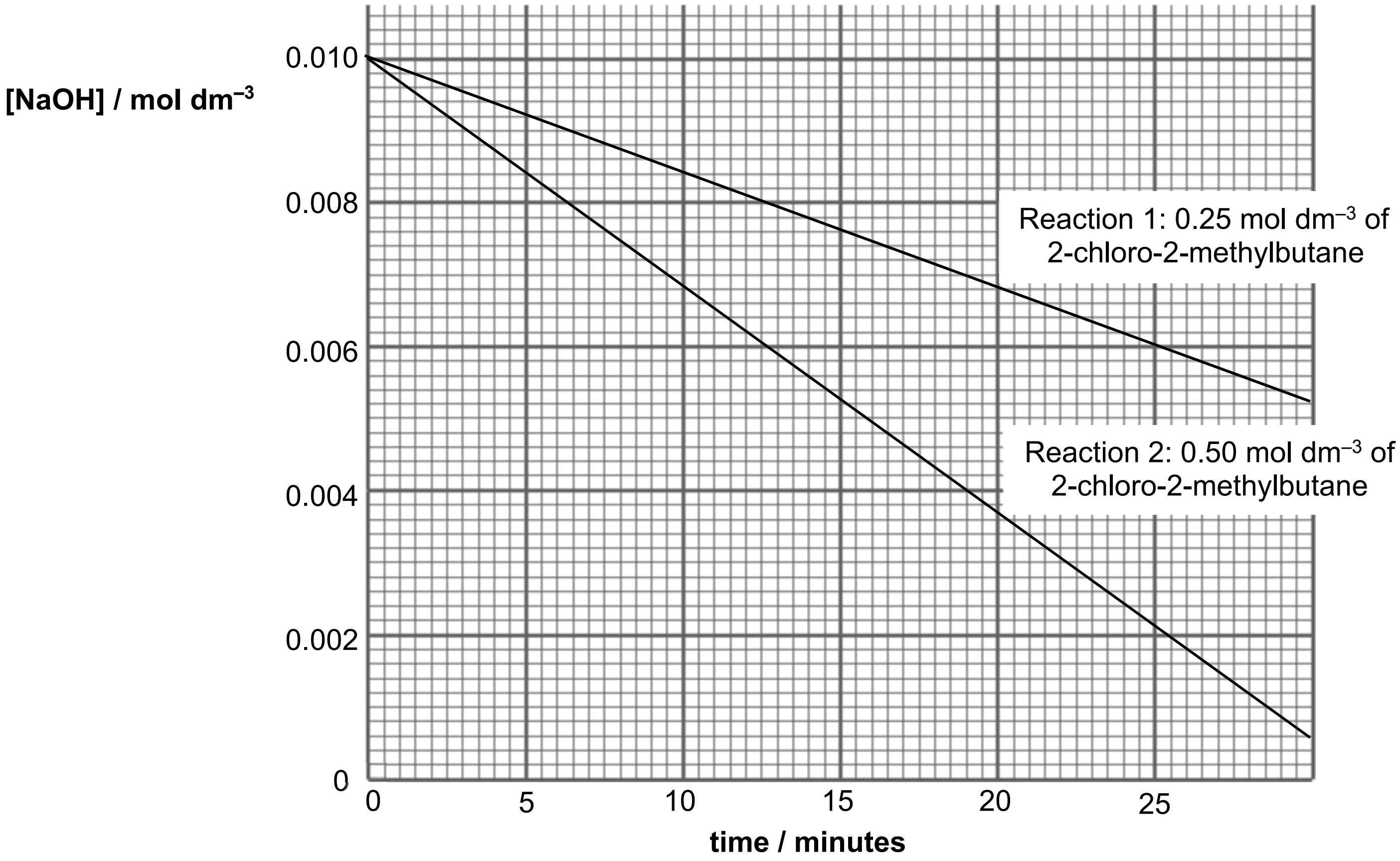
Write equations showing the reactions of aluminium chloride and phosphorus pentachloride in water. State the pH of resulting solutions. [3]

(ii) Chlorobenzene and 2-chloro-2-methylbutane are separately boiled with aqueous sodium hydroxide and acidified with nitric acid before aqueous silver nitrate is added.

State and explain the difference in observations. Write equations for the reactions that occur. [3]

(b) To study the kinetics of the reaction between 2-chloro-2-methylbutane and sodium hydroxide in alcoholic medium, two experiments with different initial concentrations of 2-chloro-2-methylbutane were carried out at constant temperature.

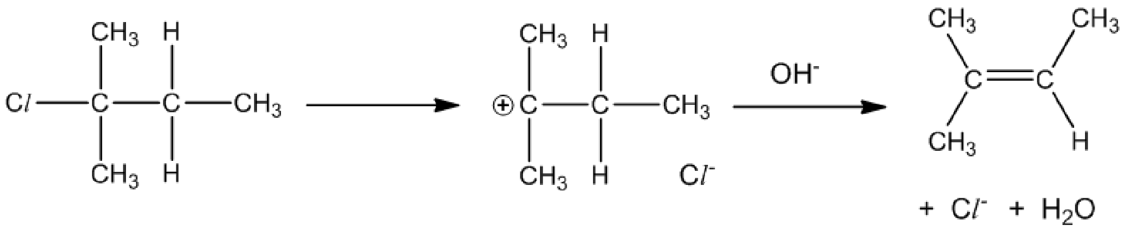
A [NaOH]–time graph was plotted using the results obtained from the experiments.



(i) Deduce the orders of reaction with respect to 2-chloro-2-methylbutane and NaOH. [2]

(ii) Hence state the rate equation of this reaction. [1]

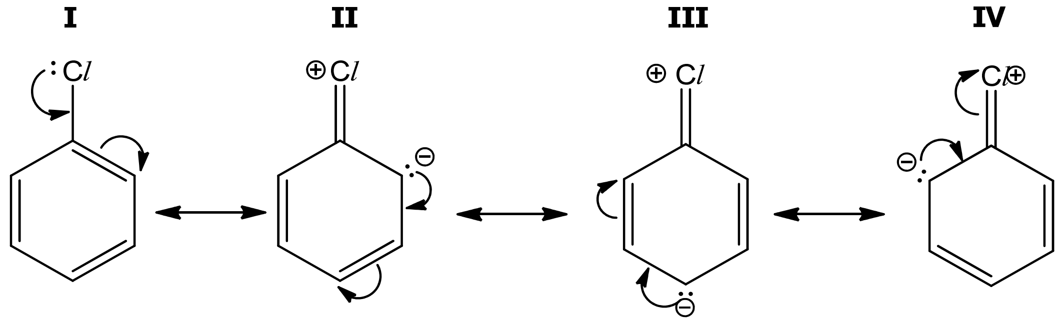
(iii) The proposed mechanism of 2-chloro-2-methylbutane with alcoholic sodium hydroxide is given below.



Using your answer in **(b)(ii)** and the above steps, suggest the complete mechanism by

- drawing curly arrows,
- showing lone pair(s) of electrons and
- identifying the slow step. [3]

(c) Chlorobenzene has the following resonance structures which represent the alternative distribution of electrons on the molecule. Using these structures, suggest why the electrophilic substitution of chlorobenzene is 2,4-directing. [2]



(d) When butane is reacted with chlorine gas under strong UV rays, a mixture of compounds is formed.

(i) Assuming that primary and secondary hydrogen atoms have similar reactivity, draw the structures of alkyl radicals formed during the reaction and state their likely ratio of formation. [2]

(ii) During the termination stage, the alkyl radicals in **(d)(i)** form three structures with the molecular formula C_8H_{18}. Suggest their structures and the ratio of these structures. [4]

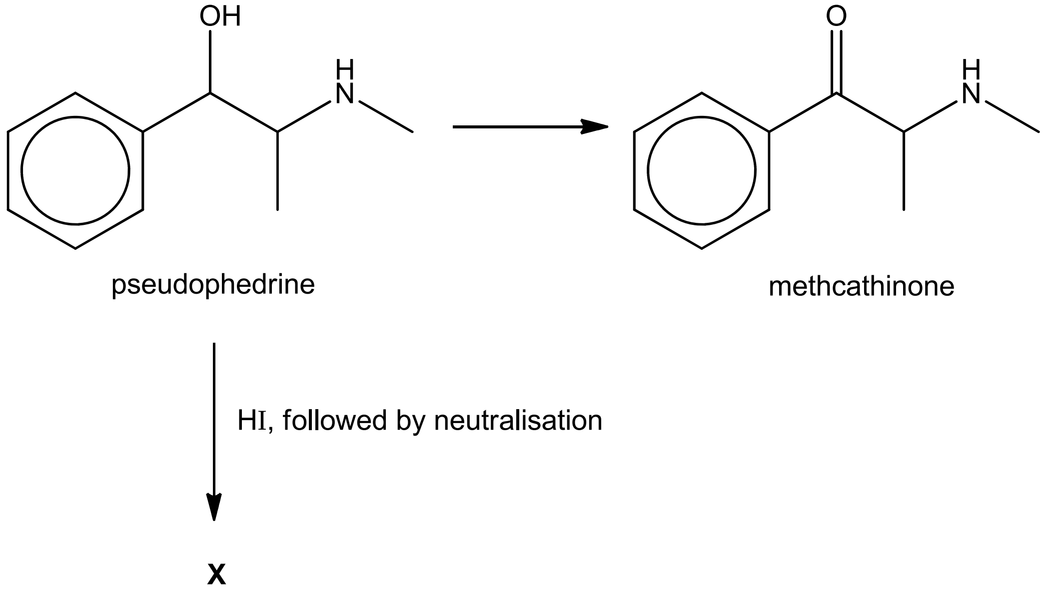
(e) Chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer.

(i) Suggest one reason why CFCs were originally used for this purpose. [1]

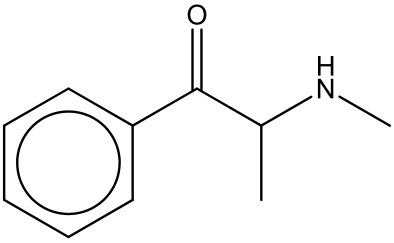
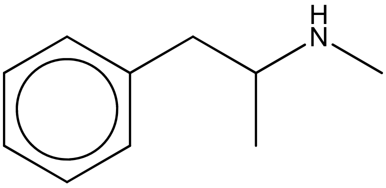
(ii) Suggest one potential hazard of using alkanes instead of CFCs. [1]

[Total: 22]

2 Recreational drugs like methamphetamine and methcathinone can be synthesised easily from pseudoephedrine, a common nasal decongestant found in cough medicine.



(a) **(i)** The structures of methcathinone and methamphetamine, with pK_b values at 298 K, are shown in the table below.

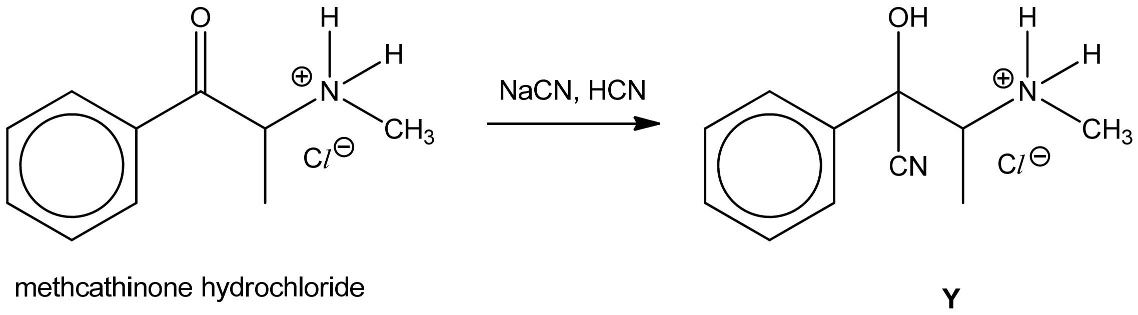
compound	pK_b
 methcathinone	5.98
 methamphetamine	3.79

Explain why methcathinone has a higher pK_b value than methamphetamine. [2]

(ii) Suggest the structure of intermediate **X**. [1]

(b) Commercially, methcathinone is sold in its salt form as solid methcathinone hydrochloride.

Methcathinone hydrochloride undergoes the following reaction to form a possible analogue, **Y**, with hallucinogenic properties.



Name the type of reaction and describe its mechanism, showing curly arrows, charges and any relevant lone pairs. [3]

(c) Hydrogen iodide, HI, is listed as a controlled substance as it is often used illegally to produce popular recreational drugs like methamphetamine.

The commercial preparation of hydrogen iodide, HI, involves the reaction of iodine I_2, with hydrazine, N_2H_4, which has ammonia-like properties.

$$N_2H_4(l) + 2I_2(aq) \longrightarrow N_2(g) + 4HI(g)$$

(i) During the preparation, gaseous hydrogen iodide produced must be removed immediately. Suggest a reason why this is done. [1]

(ii) Hydrogen halides can be unstable to heat. Write an equation for the reaction undergone on heating hydrogen iodide, HI. [1]

(iii) Using your knowledge of the chemistry of Group 17, deduce with reason how the thermal stability of hydrogen astatide, HAt, differ from that of hydrogen iodide, HI. [2]

(d) A 40.0 g sample of solid ammonium carbonate is placed in a closed evacuated 3.0 dm^3 flask and heated to 400°C. It decomposes to produce ammonia, water and carbon dioxide according to the equation :

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + H_2O(g) + CO_2(g)$$

The value of the equilibrium constant, K_p, for the reaction is 0.295 at 400 °C.

In a gaseous reaction, the reactants and products can be expressed in partial pressures in atmospheres (atm). The relationship between K_c and K_p is given :

$$K_p = K_c(RT)^4$$

Assume that the gases are under ideal conditions.

(i) Write down the expression of K_p for the above equilibrium system. Hence show that $K_p = K_c(RT)^4$. [2]

(ii) Calculate the partial pressure of $NH_3(g)$ at equilibrium at 400°C. [2]

(iii) Calculate the total pressure inside the flask at equilibrium. [1]

(iv) Calculate the mass of solid ammonium carbonate in the flask at equilibrium. [3]

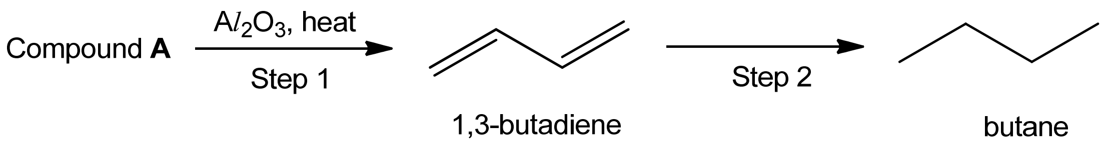
[Total: 18]

3 In chemistry, a conjugated system refers to a system of overlapping p orbitals which allows the delocalisation of π electrons in a molecule. It is represented by having alternating single and multiple bonds in the molecule.

1,3-butadiene is the simplest conjugated diene which has double bonds that is separated by a single bond. It is a colourless gas which is industrially important as a monomer in the production of synthetic rubber.

In general, conjugated dienes have similar chemical properties as the usual alkenes. However, they are associated with extra stability as the delocalisation of π electrons lowers the overall energy of the molecule.

(a) The 2-step synthesis of butane shown in the figure below makes use of 1,3-butadiene as the intermediate.



(i) Given that compound **A** does not rotate plane polarised light, suggest a structure for it and state the type of reaction that takes place in step 1. [2]

(ii) Write an equation to show the standard enthalpy change of hydrogenation, $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2. [1]

(iii) A student calculated the expected $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene in step 2 to be -252 kJ mol^{-1}. However, 1,3-butadiene is 16 kJ mol^{-1} more stable than expected.

Calculate the actual $\Delta H^{\ominus}_{\text{hydrogenation}}$ of 1,3-butadiene. [1]

(iv) Hence, using the value calculated in **(iii)** and the information given below, construct a fully labelled energy level diagram to determine the standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$ of 1,3-butadiene. [3]

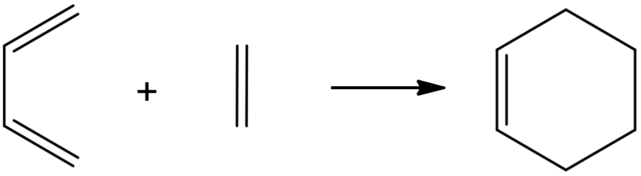
substance	$\Delta H^{\ominus}_{c}$ / kJ mol^{-1}
	-2877
H_2	-286

(v) According to valence bond theory, the stability of conjugated diene could also be explained by orbital hybridisation.

By making reference to the C–C single bond formed in 1,3-butadiene and butane, and the hybridisation of the orbitals in the two molecules, explain the extra stability of 1,3-butadiene. [2]

(b) Conjugate dienes can undergo addition with alkenes in a process called Diels-Alder reaction to form cyclic products. It is an important synthetic method which is widely used in organic chemistry to form unsaturated cyclic products.

An example of the Diels-Alder reaction is shown below where 1,3-butadiene reacts with ethene to form cyclohexene.:



In the process, the two reactants react in a single step through a cyclic redistribution of bonding electrons and two new carbon-carbon bonds are formed at the same time.

(i) By using full-headed curly arrows, suggest the mechanism that takes place in the above reaction to form cyclohexene. [1]

(ii) Compound **B** has the molecular formula of $C_8H_{12}O$ and it can be synthesised when 1,3-butadiene reacts with compound **C**, C_4H_6O, in the **Diels-Alder** reaction. It is known that compound **C** is able to react with 2 moles of hydrogen gas in the presence of Pt and produce a yellow precipitate with alkaline aqueous I_2. Compound **C** also gives a positive test with 2,4-dinitrophenylhydrazine and negative test with Tollens' reagent.

Suggest structures for compounds **B** and **C**, and explain the reactions described. [5]

(c) Compounds of aluminium such as aluminium oxide, Al_2O_3 and aluminium chloride, $AlCl_3$ are often used in organic reactions as catalysts.

(i) Aluminium oxide has unique chemical properties as it is able to react with both acid and base.

Write balanced chemical equations for the reactions between aluminium oxide and the following respectively.

- HBr
- KOH [2]

(ii) Account for the acid-base behaviour of aluminium oxide by making reference to its structure and bonding and state the nature of the oxide. [3]

[Total: 20]

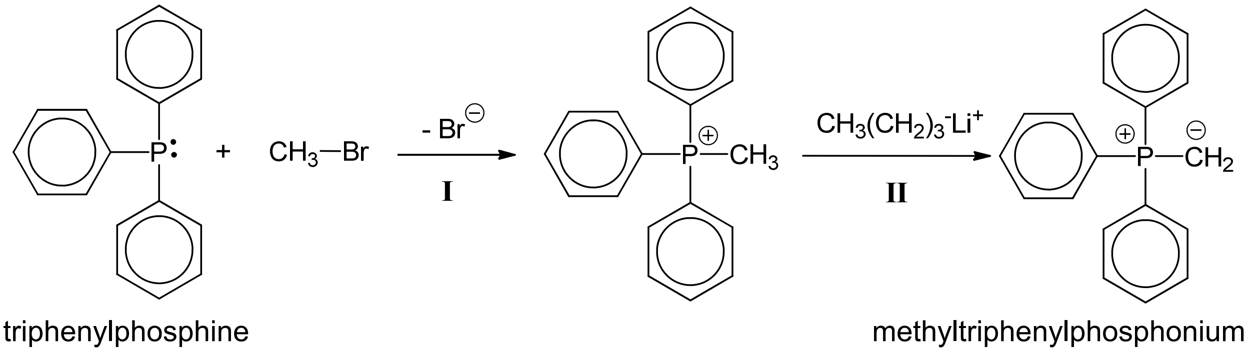
TURN OVER FOR SECTION B

Section B

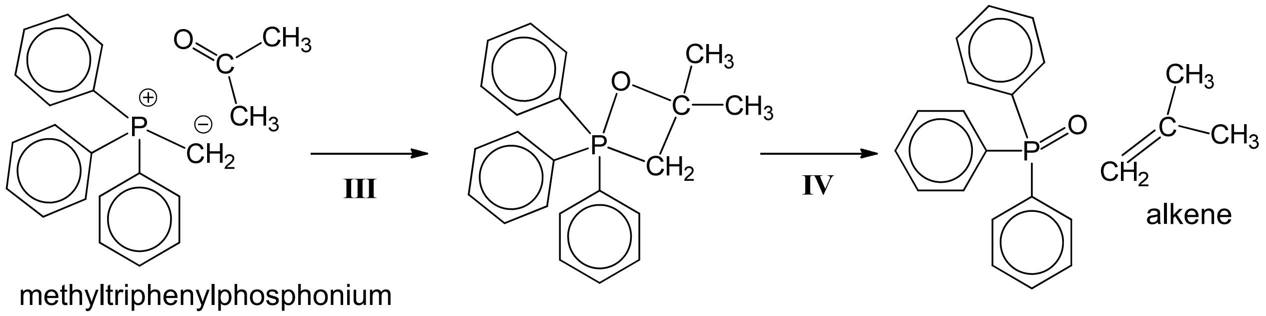
Answer **one** question from this section.

4 **(a)** The Wittig reaction converts carbonyl compounds into alkenes by reacting aldehydes or ketones with alkyltriphenylphosphonium, such as methyltriphenylphosphonium.

Stage 1 – Preparation of methyltriphenylphosphonium



Stage 2 – Formation of alkene



Different alkenes can be formed by using different carbonyl compounds and R-groups on the alkyltriphenylphosphonium.

(i) The melting points of four compounds, including triphenylphosphine and methyltriphenylphosphonium bromide are given below.

compound	formula	melting point / °C
triphenylphosphine	$P(C_6H_5)_3$	80
water	H_2O	0
methyltriphenylphosphonium bromide	$(C_6H_5)_3P{=}CH_2{}^+Br^-$	232
sodium chloride	Na*Cl*	801

With reference to their structure and bonding, suggest why the melting point of

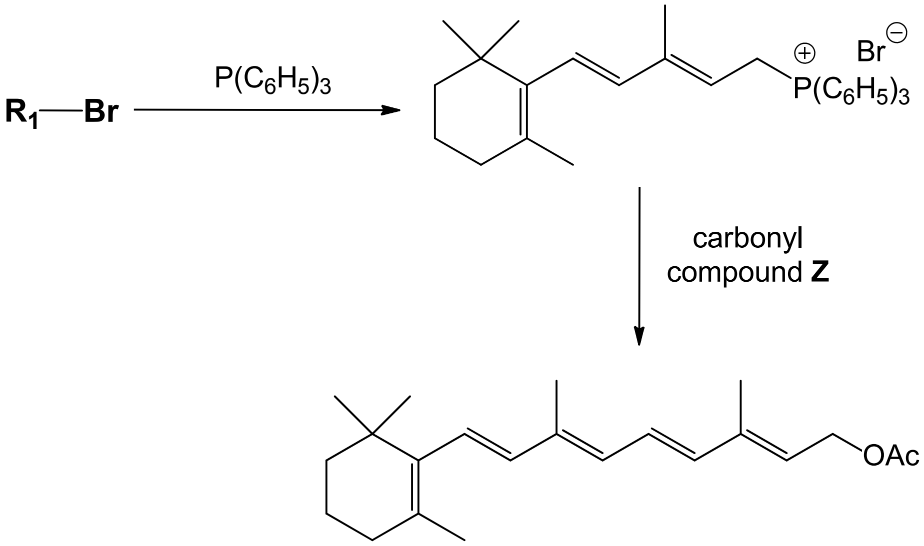
1. triphenylphosphine is higher than water; and
2. methyltriphenylphosphonium bromide is lower than sodium chloride

[4]

(ii) State the type of reaction in step **I**. [1]

(iii) State the role of $CH_3(CH_2)_3^-Li^+$ in step **II**. [1]

(iv) The advantage of Wittig reaction is the predictability of its alkene product. It is used in industrial processes such as the formation on vitamin A.



derivative of vitamin A

Suggest the structures of alkylbromide **R₁–Br** and carbonyl compound **Z** for forming the derivative of vitamin A. You may assume that the OAc group remains unchanged during the reaction. [2]

(b) Triphenylphosphine, $P(C_6H_5)_3$, is prepared by reacting phosphorus trichloride, chlorobenzene and sodium. Sodium chloride is precipitated during the reaction due to its insolubility in the organic mixture.

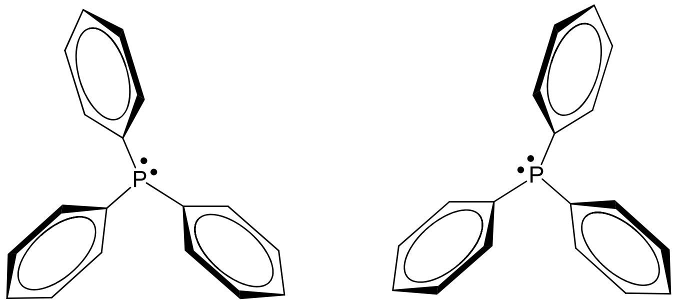
(i) Write the balanced equation for the preparation of triphenylphosphine. [1]

(ii) Triphenylphosphine does not form in the above reaction when water is present. Given that phosphorus trichloride reacts with water according to this equation

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$

describe, with the aid of equation(s), any other reactions that will take place when water is used as a solvent. Hence or otherwise, suggest the colour of universal indicator in the resulting mixture. [3]

(iii) It has been suggested that triphenylphosphine is a chiral compound. Two structures of triphenylphosphine are shown below.



State the relationship of the two structures and suggest why triphenylphosphine is a chiral compound. [2]

(c) **(i)** The aqueous solutions of two acids were prepared and their pH measured.

acid	concentration / mol dm^{-3}	pH
M	0.75	1.11
N	0.25	0.60

Given that **M** and **N** are monobasic acids, show calculations to explain whether each acid is a strong or weak acid. [3]

(ii) It is known that the electronegativity of the central atom in the acid affects its acidity.

With reference to the increasing trend of electronegativity across the period, suggest the correct identities of the acids **M** and **N**, given that they could be H_3PO_2 or $HClO_3$. [3]

[Total: 20]

5 *Use of the Data Booklet is relevant to this question*.

Osmium is a bluish-white metal found as a trace element in alloys, mostly in platinum ores. Not surprisingly, osmium was discovered in 1803 by Smithson Tennant when he noticed a residue remaining after dissolving crude platinum in aqua regia – a mixture of concentrated nitric acid and concentrated hydrochloric acid.

Platinum reacts with concentrated nitric acid to produce aqueous platinum(IV) cations, nitrogen dioxide and water. The platinum(IV) cations are then complexed with chloride *ligands* to produce hexachloroplatinate(IV) anions which are recovered through the reaction with ammonium chloride to produce yellow crystals.

(a) **(i)** Define the term *ligand*. [1]

(ii) Write a balanced ionic equation to represent the reaction of platinum with concentrated nitric acid. [1]

(iii) Suggest the identity of the yellow crystals obtained. [1]

(iv) The solubility of the yellow crystals in water at room temperature is 5.0 g dm^{-3} but decreases to 0.028 g dm^{-3} in 1 mol dm^{-3} ammonium chloride at the same temperature.

Write an equation to represent the dissolution of the yellow crystals in **(a)(iii)** and use the equation to account for the decreased solubility in 1 mol dm^{-3} ammonium chloride. [2]

(v) Explain why hexachloroplatinate(IV) is coloured. [3]

When powdered osmium is exposed to air, it forms the toxic compound osmium tetroxide, OsO_4 with a strong odour like that of chlorine.

$$Os + 2O_2 \longrightarrow OsO_4$$

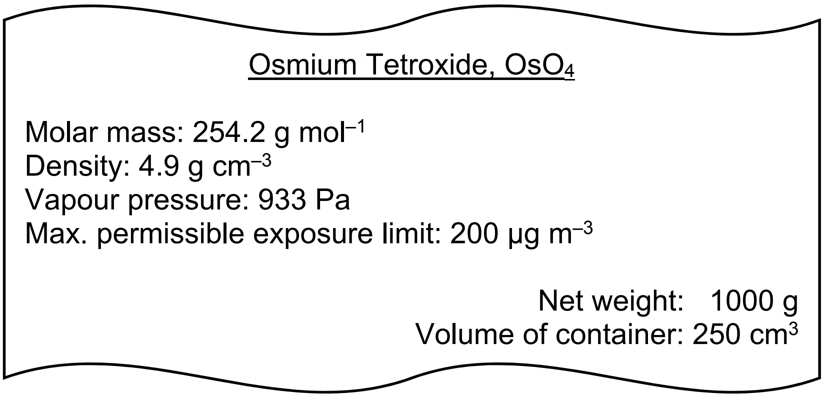
(b) **(i)** Use the standard electrode potential given and choose another appropriate equation from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the reaction between osmium and air. [1]

$$OsO_4 + 8H^+ + 8e^- \rightleftharpoons Os + 4H_2O \qquad E^{\ominus} = +0.84\ V$$

(ii) Hence calculate $\Delta G^{\ominus}_{cell}$ for the reaction in **(b)(i)**, leaving your answer in kJ mol^{-1}. [1]

(iii) Suggest, with reasoning, the sign for the standard enthalpy change of reaction for the reaction between osmium and air, making reference to the terms in the Gibbs free energy equation and your answer in **(b)(ii)**. [2]

The figure below shows part of a label on a bottle of osmium tetroxide.



Osmium Tetroxide, OsO_4

Molar mass: 254.2 g mol^{-1}
Density: 4.9 g cm^{-3}
Vapour pressure: 933 Pa
Max. permissible exposure limit: 200 μg m^{-3}

Net weight: 1000 g
Volume of container: 250 cm^3

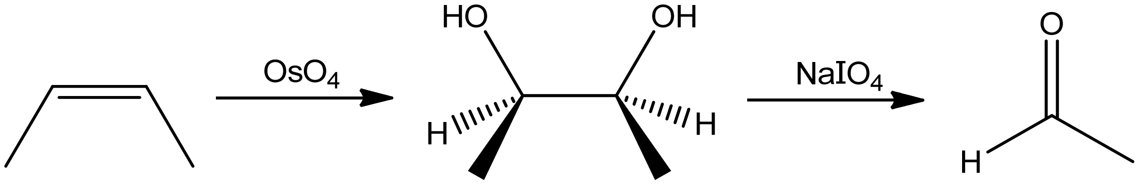
Note:
Vapour pressure – the pressure of vapour in equilibrium with its solid/liquid form.
1 μg = 1 x 10^{-6} g

(c) **(i)** Use the information above to calculate the amount of OsO_4 in the vapour phase within an unopened container of OsO_4 at room temperature. Assume ideal gas behaviour. [2]

(ii) Hence determine the concentration of OsO_4, in μg m^{-3}, in the air of a 100 m^3 laboratory where a new container is opened. Assume that the air has evenly mixed. [2]

(iii) Discuss whether it is safe for researchers to open the container in this laboratory without a proper fume cupboard, considering your answer in **(c)(ii)** and the approach used to calculate it. [1]

Osmium tetroxide, OsO_4 can oxidise alkenes to give diols. $NaIO_4$ will react further with the diol to produce carbonyl compounds.



A **B**

(d) Suggest a simple chemical test to distinguish between compounds **A** and **B** and write a balanced equation for the positive test. [3]

[Total: 20]

Name	Index Number	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/04**
Higher 2

Paper 4 Practical 7 August 2018

2 hour 30 minutes

READ THESE INSTRUCTIONS CAREFULLY

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on page 17 and 18.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
Question No.	**Marks**
1 (23 m)	
2 (12 m)	
3 (12 m)	
4 (8 m)	
TOTAL: 55 m	

This document consists of **17** printed pages and **1** blank page.

BLANK PAGE

Answer **all** the questions in the spaces provided.

1 **Determination of the value of *n* in IO_n^-**

IO_n^- is an oxoanion of iodine. It can react with iodide ions, I^-, in an acidic medium, to produce only molecular iodine and water.

This amount of iodine can be analysed via titration with sodium thiosulfate, $Na_2S_2O_3$.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

In this question, you will perform an experiment to determine the stoichiometric ratio between IO_n^- and I_2 and the value of *n* in IO_n^-.

FA 1 is solid hydrated sodium thiosulfate, $Na_2S_2O_3{\bullet}5H_2O$
FA 2 is a solution containing 0.00825 mol dm^{-3} KIO_n
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is 0.25 mol dm^{-3} potassium iodide, KI

You are also provided with starch solution.

(a) **Preparation of a standard solution of 0.0484 mol dm^{-3} sodium thiosulfate**

(i) Determine the mass of **FA 1** required to prepare 250 cm^3 of sodium thiosulfate solution with a concentration 0.0484 mol dm^{-3}.
[A_r: S, 32.1; O, 16.0; Na, 23.0; H, 1.0]

mass of **FA 1** required = ………………….. g [1]

You will follow the instructions to perform the preparation of the standard solution.

Record your measurements in Table 1.1.

(ii)
1. Using a mass balance, weigh out accurately the mass of **FA 1** determined in **(a)(i)** into a weighing bottle.
2. Dissolve **FA 1** in about 50 cm^3 of deionised water in a 100 cm^3 beaker.
3. Transfer the solution and washings into a 250 cm^3 volumetric flask, using a filter funnel.
4. Top up to the 250 cm^3 mark with deionised water.
5. Stopper the flask and shake to ensure solution is homogeneous. Label this solution as **FA 5**.

Complete Table 1.1 with your mass measurements and calculate the mass of **FA 1** that you used.

Table 1.1

Mass of weighing bottle and **FA 1** / g	
Mass of empty weighing bottle / g	
Mass of **FA 1** / g	

[2]

(b) Preparation and titration of the reaction mixture

1. Fill a burette with **FA 5**.
2. Using a 25.0 cm^3 pipette, add 25 cm^3 of **FA 2** to a 250 cm^3 conical flask.
3. Using a measuring cylinder, add 10.0 cm^3 of **FA 3**, followed by 10.0cm^3 of **FA 4** to the same conical flask and swirl quickly.
4. **Immediately** titrate the I_2 in the conical flask with **FA 5**. When a pale yellow colour is obtained, add 1 cm^3 of starch solution. The end-point is reached when the blue – black colour of the solution decolourises.
5. Repeat steps **2** to **4** until consistent results are obtained and record your results below.

Results

[5]

Obtain, from your titration results, a suitable average titre of **FA 5**. Show clearly the titres you used in calculating this average.

Average volume of **FA 5** = ……………………….. [1]

Calculations

Show your working and appropriate significant figures in all of your calculations.

(c) **(i)** Calculate the amount, in moles, of $Na_2S_2O_3$ present in the volume of **FA 5** determined in **(b)** and hence the amount of iodine produced.

Amount of I_2 = ………………………..[2]

(ii) Calculate the amount of **FA 2** used in the titration.

Amount of **FA 2** = ……………………….. [1]

(d) **(i)** Construct a balanced half-equation, in terms of *n*, for the reduction of IO_n^-.

…………………………………………………………………………………… [1]

(ii) Hence construct a balanced equation, in terms of *n*, for the reaction between IO_n^- and I^- to give I_2 and H_2O.

…………………………………………………………………………………… [1]

(iii) Determine the amount of I_2 produced by one mole of IO_n^- and determine the value of *n* in IO_n^-.

n =……………………….. [1]

(e) Planning

The reaction rate between IO_n^- and I^- in an acidic medium can be expressed in the following rate equation:

$$\text{rate} = k\,[IO_n^-]^x\,[I^-]^y\,[H^+]^z$$

If the concentrations of iodide and hydrogen ions are kept constant, the rate equation becomes

$$\text{rate} = k'\,[IO_n^-]^x$$

where $k' = k\,[I^-]^y\,[H^+]^z$

Iodine produced by the reaction gives a dark blue colour in the presence of starch solution.

A small amount of sodium thiosulfate is measured using a burette and added to the reaction mixture prior to the start of the reaction. The sodium thiosulfate reduces the iodine produced and this can be used to monitor the rate of reaction. By changing the initial concentration of IO_n^- and studying how this change influences the reaction rate, its order of the reaction with iodide ions in an acidic medium can be determined.

(i) Plan an investigation, to determine the order of reaction with respect to IO_n^-, in its reaction with iodide ions in an acidic medium.

You may assume that you are provided with
- 100 cm^3 of 0.00825 mol dm^{-3} KIO_n,
- 100 cm^3 of 0.25 mol dm^{-3} potassium iodide, KI,
- 100 cm^3 of 0.0484 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
- 0.5 mol dm^{-3} sulfuric acid, H_2SO_4,
- distilled water,
- starch solution,
- the apparatus normally found in a school or college laboratory.

In your plan you should include details of
- the reagents and apparatus that you would use,
- the procedure that you would follow and the measurements that you would take.

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……………………………………………………………………………………………….. [4]

(ii) Sketch the graph, with labelled axis, you would expect to obtain from your results in **1(e)(i)**.

Explain your answer.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[3]

(iii) Briefly describe how you would use your graph to determine the order with respect to IO_n^-.

…………………………………………………………………………………………………

…………………………………………………………………………………………………[1]

[Total: 23]

2 Determination of the enthalpy change of neutralisation, ΔH_n

FA 6 is a solution of sodium hydroxide, NaOH, of unknown concentration

According to the *Arrhenius* theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions, in aqueous solution. Using the *Arrhenius* theory, an acid-base neutralisation reaction involves reacting together these two ions to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H_n$$

In this question, you will carry out a series of experiments where different volumes of **FA 3** and **FA 6** are mixed together.

You will determine the temperature change of the mixture, ΔT of each experiment and then analyse your results graphically in order to determine the

- concentration of NaOH in **FA 6**
- maximum temperature change, ΔT_{max}
- value for the enthalpy change of neutralisation, ΔH_n

(a) Determining the change in temperature for a series of reactions between FA 3 and FA 6

(i) 1. Support the styrofoam cup in a 250 cm^3 beaker.

2. Using a measuring cylinder, place 10 cm^3 of **FA 3** into the styrofoam cup.

3. Measure the temperature of **FA 3** in the styrofoam cup. Record the initial temperature of the solution of **FA 3** as $T_{initial}$.

4. Place 40 cm^3 of **FA 6** into another measuring cylinder.

5. Tip the **FA 6** in the measuring cylinder into the styrofoam cup, stir and record the maximum temperature obtained in the reaction as T_{max}.

6. Rinse and dry the styrofoam cup and the thermometer.

7. Repeat steps **2** to **6** using volumes of **FA 3** listed in Table 2.1. Fill in Table 2.1 with the appropriate volumes of **FA 6** to be used in each experiment such that the total volume of the reaction mixture is 50 cm^3.

Table 2.1

Experiment	**1**	**2**	**3**	**4**	**5**	**6**
Volume of **FA 3** / cm^3	10	20	30	40		
Volume of **FA 6** / cm^3	40					

[1]

In an appropriate format in the space provided, prepare a table in which to record for each experiment

- the initial temperature
- the maximum temperature
- the change in temperature, ∆T

Results

[3]

(ii) Plot a graph of ΔT (y–axis) against volume of **FA 6** used (x–axis) using the data you have obtained above in **a(i)** on the grid in Fig. 2.1.

By considering the points you have plotted, carry out two more experiments (experiment **5** and **6**) which will enable you to identify the volume of **FA 6** which gives the maximum temperature change, ΔT_{max}.

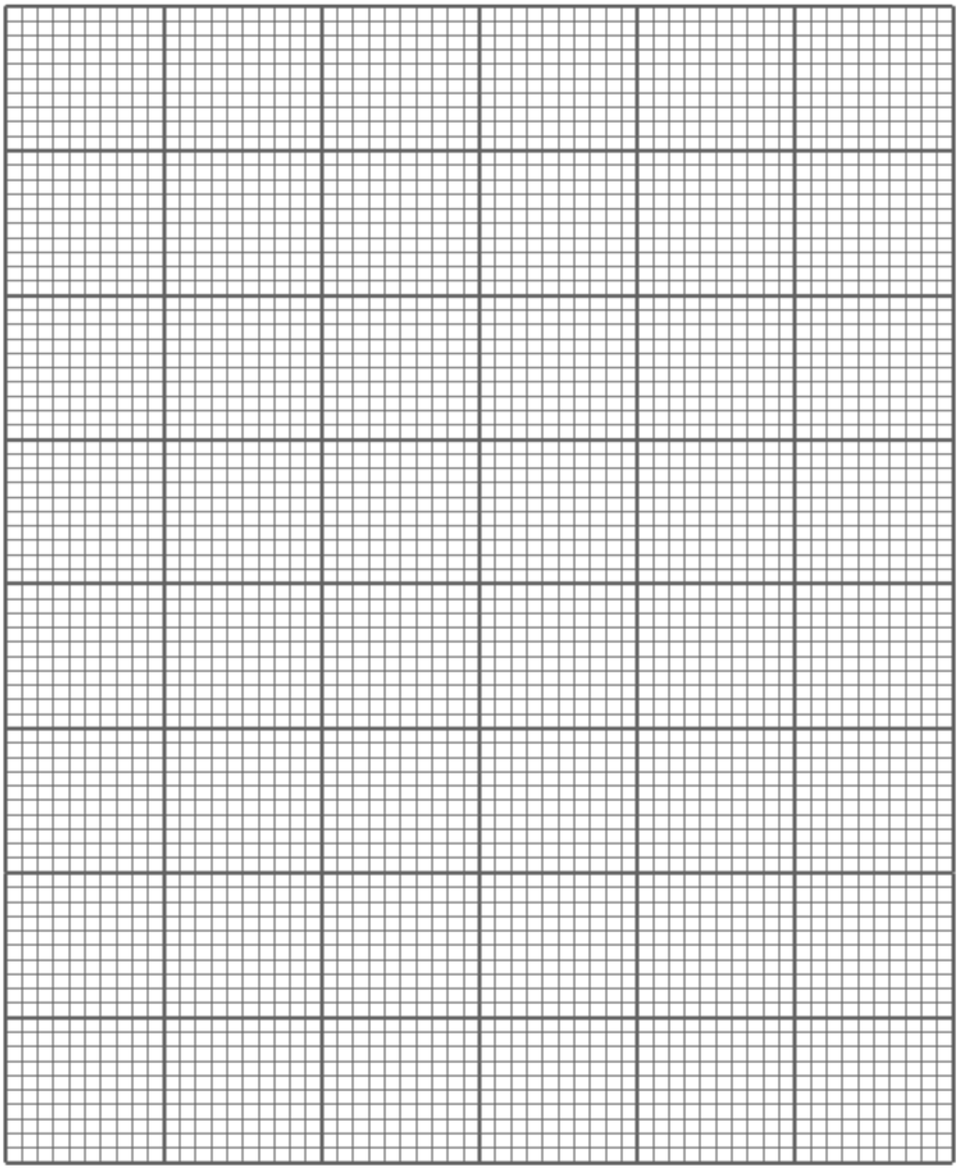

Fig. 2.1 [2]

(iii) Draw two straight lines of best fit. The first best fit line should be drawn using the plotted points where ΔT is increasing and the second best fit line should be drawn using the plotted points where ΔT is decreasing. Extrapolate these two lines until they cross. [1]

(iv) From your graph, determine the maximum temperature change, ΔT_{max}, and the volume of **FA 6** required to obtain this.

ΔT_{max} = ……………………………….^{o}C

$V_{\textbf{FA6}}$ = …...……………………...cm^3 [1]

(b) Using your answers in **a(iv)**,

(i) calculate the concentration of NaOH in **FA 6**

concentration of NaOH in **FA 6** = ……………………………….[2]

(ii) calculate the heat change at $\Delta T_{max.}$

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and that the density is 1.00 g cm^{-3}.

heat change = ……………………………….[1]

(c) Using your answers in **(b)**, calculate the enthalpy change of neutralisation, ***ΔH_n***.

ΔH_n = ……………………………….[1]

[Total: 12]

3 Qualitative Analysis

(a) You are to perform the tests given in Table 3.1 on **FA 9** and **FA 10**.

Record details of any colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should be identified by a test, described in the appropriate place in the table provided. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Table 3.1

Tests		Observations	
		FA 9	**FA 10**
1.	To 0.5 cm depth of solution in a test-tube, add equal volume of aqueous sulfuric acid. Then add three to four drops of potassium iodide solution. Then add a few drops of aqueous starch.		▨
2.	Add 2 drops of aqueous potassium manganate(VII) to a test tube followed by 2 drops of sulfuric acid. Then add about 5 drops of **FA 9**.		▨
3.	To 1 cm depth of **FA10** in a test-tube, add aqueous sodium hydroxide dropwise, until it is in excess.	▨	

4.	To 0.5 cm depth of **FA 10** in a test-tube, add aqueous silver nitrate	▨	
5.	To 0.5 cm depth of **FA 10** in a test-tube, add aqueous sodium carbonate.	▨	

[5]

(b) **(i)** **FA 9** can act both as an oxidising or a reducing agent. Based on your observations in test 1 and 2, state the role of **FA 9** in each of the tests.

role of **FA 9** in test 1……………………………………………………….........

role of **FA 9** in test 2……………………………………………………….........[2]

(ii) Give the ionic equation, with state symbols, for the reaction of the metal cation in **FA 10** with aqueous sodium hydroxide in test 3.

……………………………………………………………………………....……………[1]

(iii) The observation you made in test 4 when aqueous silver nitrate was added to **FA 10** does not allow the anion in **FA 10** to be identified with certainty.

Explain why you cannot be certain about the identity of the anion.

…………………………………………………………………………………….........

……………………………………………………………………………...….............

………………………………………………………………..............……………[1]

(iv) A student suggested that the anion in **FA 10** could be identified with more certainty if excess ammonia solution was added after the aqueous silver nitrate.

Explain why this suggestion is **not** correct.

……………………………………………………………………………………………........

……………………………………………………………………………………………........

…………………………………………………………………………......……………[1]

(v) Suggest a pH value of solution **FA 10** based on your observations in test 5. Write an equation to account for your suggested pH value.

suggested pH value………………………

equation……………………………………………………………………….……….

……………………………………………………………………………………………........

…………………………………………………………………………......……………[2]

[Total: 12]

4 Preparation of cyclohexene from cyclohexanol

Cyclohexene is prepared by dehydration of cyclohexanol using concentrated phosphoric acid as a catalyst.

$$C_6H_{11}OH(l) \longrightarrow C_6H_{10}(l) + H_2O(l)$$

Data about cyclohexanol and cyclohexene are given in the table below.

property	cyclohexanol	cyclohexene
density/ g cm^{-3}	0.96	0.81
molar mass/ g mol^{-1}	100.0	82.0
boiling point/ °C	161.0	83.3

Preparation of impure cyclohexene

0.1 mol of cyclohexanol and 3 cm^3 of concentrated phosphoric acid were added together into a round-bottomed distillation flask. The mixture was heated and the impure cyclohexene was collected by distillation. Both cyclohexanol and cyclohexene are flammable.

Purification of impure cyclohexene

The impure cyclohexene was transferred into a separating funnel and an equal volume of saturated sodium chloride solution was added. The funnel was allowed to stand for a few minutes until the layers separated out.

The cyclohexene layer was transferred into a small flask and some anhydrous calcium chloride was added. The mixture was allowed to stand until the cyclohexene became clear.

The dried cyclohexene was decanted into a clean flask and was then fractionally distilled to produce the pure cyclohexene.

(a) **(i)** Calculate the volume of cyclohexanol to be used in the preparation.

volume of cyclohexanol to be used = ………………………………cm^3 [1]

(ii) Using the information given on the previous page, outline how you would prepare a sample of impure cyclohexene from cyclohexanol.

In your answer, you should

- Give a full description of the procedures you would use to prepare the impure cyclohexene, stating clearly the apparatus used for measuring the reactants.
- State the temperature at which you would conduct the experiment.

……………………………………………………………………………………..........

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……………………………………………………………………………………..........

……………………………………………………………………………………..........

……………………………………………………………………………………..........

……………………………………………………………………………………..........

…………………………………………………………………………………... [3]

(b) **(i)** When the layers separate out in the separating funnel, suggest whether the cyclohexene will be the upper or lower layer. Hence explain how you would use the separating funnel to transfer the cyclohexene layer into a small flask.

……………………………………………………………………………………..........

……………………………………………………………………………………..........

…………………………………………………………………………………... [2]

(ii) Why is anhydrous calcium chloride added to the cyclohexene?

…………………………………………………………………………………..… [1]

(c) The percentage yield of cyclohexene in this preparation is 57.3%.

Suggest a reason why this preparation does not produce a 100% yield.

……………………………………………………………………………………........

……………………………………………………………………………………..[1]

[Total: 8]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Answer **all** the questions in the spaces provided.

1 Determination of the value of *n* in IO_n^-

IO_n^- is an oxoanion of iodine. It can react with iodide ions, I^-, in an acidic medium, to produce only molecular iodine and water.

This amount of iodine can be analysed via titration with sodium thiosulfate, $Na_2S_2O_3$.

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

In this question, you will perform an experiment to determine the stoichiometric ratio between IO_n^- and I_2 and the value of *n* in IO_n^-.

FA 1 is solid hydrated sodium thiosulfate, $Na_2S_2O_3 \bullet 5H_2O$
FA 2 is a solution containing 0.00825 mol dm^{-3} KIO_n
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4
FA 4 is 0.25 mol dm^{-3} potassium iodide, KI

You are also provided with starch solution.

(a) Preparation of a standard solution of 0.0484 mol dm^{-3} sodium thiosulfate

(i) Determine the mass of **FA 1** required to prepare 250 cm^3 of sodium thiosulfate solution with a concentration 0.0484 mol dm^{-3}.
[A_r: S, 32.1; O, 16.0; Na, 23.0; H, 1.0]

Amount of $Na_2S_2O_3 = \frac{0.0484}{1000} \times 250 = 0.0121$ mol
M_r of $Na_2S_2O_3 \bullet 5H_2O = 248.2$
Mass of $Na_2S_2O_3 \bullet 5H_2O = 0.0121 \times 248.2 = 3.003 = 3.00$ g

mass of **FA 1** required = ………………….. g [1]

You will follow the instructions to perform the preparation of the standard solution.

Record your measurements in Table 1.1.

(ii)
1. Using a mass balance, weigh out accurately the mass of **FA 1** determined in **(a)(i)** into a weighing bottle.
2. Dissolve **FA 1** in about 50 cm^3 of deionised water in a 100 cm^3 beaker.
3. Transfer the solution and washings into a 250 cm^3 volumetric flask, using a filter funnel.
4. Top up to the 250 cm^3 mark with deionised water.
5. Stopper the flask and shake to ensure solution is homogeneous. Label this solution as **FA 5**.

Complete Table 1.1 with your mass measurements and calculate the mass of **FA 1** that you used.

Table 1.1

Mass of weighing bottle and **FA 1** / g	
Mass of empty weighing bottle / g	

Mass of **FA 1** / g	3.00

[2]

Records all masses to same number of decimal places (PDO)
Records correctly all masses (PDO)
Mass of **FA 1** measured is ± 0.05 g of that determined in **(a)(i)** (MMO)

(b) Preparation and titration of the reaction mixture

1. Fill a burette with **FA 5**.
2. Using a 25.0 cm^3 pipette, add 25 cm^3 of **FA 2** to a 250 cm^3 conical flask.
3. Using a measuring cylinder, add 10.0 cm^3 of **FA 3**, followed by 10.0cm^3 of **FA 4** to the same conical flask and swirl quickly.
4. **Immediately** titrate the I_2 in the conical flask with **FA 5**. When a pale yellow colour is obtained, add 1 cm^3 of starch solution. The end-point is reached when the blue – black colour of the solution decolourises.
5. Repeat steps **2** to **4** until consistent results are obtained and record your results below.

Results

Final burette reading/cm^3		
Initial burette reading/cm^3		
Volume of FA5/ cm^3	**23.65**	**23.65**

[5]

Records all burette readings to 2 d.p. (MMO)
Has at least 2 titre values ± 0.10 cm^3 (MMO)
Table has appropriate headings and units (PDO)
Accuracy (MMO)

Obtain, from your titration results, a suitable average titre of **FA 5**. Show clearly the titres you used in calculating this average.

Average volume of **FA5** = (23.65 + 23.65)/ 2 = 23.65 cm^3

Average volume of **FA 5** = ……………………….. [1]

Selects at least 2 titre values that are ± 0.20 cm^3 and presents average titre to 2 d.p., with appropriate units (PDO)

Calculations

Show your working and appropriate significant figures in all of your calculations.

(c) **(i)** Calculate the amount, in moles, of $Na_2S_2O_3$ present in the volume of **FA 5** determined in **(b)** and hence the amount of iodine produced.

Amount of $S_2O_3^{2-}$ = conc × volume

Amount of I_2 = Amount of $S_2O_3^{2-}$ ÷ 2

Amount of I_2 = ……………………….[2]

(ii) Calculate the amount of **FA 2** used in the titration.

Amount of **FA 2** = $\frac{0.00825}{1000} \times 25 = 2.0625 \times 10^{-4}$
$= 2.06 \times 10^{-4}$ mol (ACE)

Amount of **FA 2** = ………………………. [1]

(d) **(i)** Construct a balanced half-equation, in terms of *n*, for the reduction of IO_n^-.

$IO_n^- + (2n-1)e^- + 2nH^+ \longrightarrow \frac{1}{2} I_2 + nH_2O$
……………………………………………………………………………………… [1]

(ii) Hence construct a balanced equation, in terms of *n*, for the reaction between IO_n^- and I^- to give I_2 and H_2O.

$IO_n^- + (2n-1)I^- + 2nH^+ \longrightarrow nI_2 + nH_2O$

……………………………………………………………………………………… [1]

(iii) Determine the amount of I_2 produced by one mole of IO_n^- and determine the value of *n* in IO_n^-.

Amount of I_2 produced per mole of IO_n^- = $n = \frac{\text{Answer in (c)(i)}}{\text{Answer in (c)(ii)}}$

n =………………………. [1]

(e) **Planning**

The reaction rate between IO_n^- and I^- in an acidic medium can be expressed in the following rate equation:

$$\text{rate} = k\,[IO_n^-]^x\,[I^-]^y\,[H^+]^z$$

If the concentrations of iodide and hydrogen ions are kept constant, the rate equation becomes

$$\text{rate} = k'\,[IO_n^-]^x$$

where $k' = k\,[I^-]^y\,[H^+]^z$

Iodine produced by the reaction gives a dark blue colour in the presence of starch solution.

A small amount of sodium thiosulfate is measured using a burette and added to the reaction mixture prior to the start of the reaction. The sodium thiosulfate reduces the iodine produced and this can be used to monitor the rate of reaction. By changing the initial concentration of IO_n^- and studying how this change influences the reaction rate, its order of the reaction with iodide ions in an acidic medium can be determined.

(i) Plan an investigation, to determine the order of reaction with respect to IO_n^-, in its reaction with iodide ions in an acidic medium.

You may assume that you are provided with

- 100 cm^3 of 0.00825 mol dm^{-3} KIO_n,
- 100 cm^3 of 0.25 mol dm^{-3} potassium iodide, KI,
- 100 cm^3 of 0.0484 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$,
- 0.5 mol dm^{-3} sulfuric acid, H_2SO_4,
- distilled water,
- starch solution,
- the apparatus normally found in a school or college laboratory.

In your plan you should include details of

- the reagents and apparatus that you would use,
- the procedure that you would follow and the measurements that you would take.

……………………………………………………………………………………….. [4]

- Total volume of reaction mixture is constant across different mixtures, with different volume of KIO_n used / other method to ensure concentration of IO_n^- is different in each reaction mixture

- Fixed and small (in relation to volume of KIO_n used, not marking for this) volume of $S_2O_3^{2-}$ used in each reaction mixture (to monitor a fixed amount of iodine produced by the reaction)

- Volumes of KI, KIO_n, H_2SO_4, H_2O measured using measuring cylinders of appropriate capacities

- Start taking time when either KI or KIO_n is poured into reaction mixture containing the rest of the required reagents and stop time when a blue-black colour is observed

(ii) Sketch the graph, with labelled axis, you would expect to obtain from your results in **1(e)(i)**.

Explain your answer.

…………………………………………………………………………………....……[3]

Plot lg (rate) = x lg($[IO_n^-]$) + c

y – axis is lg (rate) or lg(1/t)

- x – axis is lg($[IO_n^-]$) or lg (V_{FA2})
- c is lg *k*'
- straight line with positive gradient
- rate $\propto \frac{1}{time}$ since shorter time taken for blue colour to be seen (faster reaction with $S_2O_3^{2-}$), faster the rate of production of iodine / any other reasonable way to determine initial rate

OR

Plots the following graphs (can be drawn or described)

1. Rate vs $[IO_n^-]$ (straight horizontal line) for zero order
   OR
   1/t vs V_{FA2}
2. Rate vs $[IO_n^-]$ (linear with positive gradient) for 1st order
3. Rate vs $[IO_n^-]^2$ (linear with positive gradient) for 2nd order

- rate $\propto \frac{1}{time}$ since shorter time taken for blue colour to be seen (faster reaction with $S_2O_3^{2-}$), faster the rate of production of iodine / any other reasonable way to determine initial rate

(iii) Briefly describe how you would use your graph to determine the order with respect to IO_n^-.

Calculate the gradient of the graph in **2(c)(ii)** which will be the order

OR

Match data obtained to one of the three graphs drawn above

……………………………………………………………………………..…………..........…......

……………………....…………………………………………..…………....……………[1]

[Total: 23]

2 Determination of the enthalpy change of neutralisation, ΔH_n

FA 6 is a solution of sodium hydroxide, NaOH, of unknown concentration

According to the *Arrhenius* theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions, in aqueous solution. Using the *Arrhenius* theory, an acid-base neutralisation reaction involves reacting together these two ions to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H_n$$

In this question, you will carry out a series of experiments where different volumes of **FA 3** and **FA 6** are mixed together.

You will determine the temperature change of the mixture, ΔT of each experiment and then analyse your results graphically in order to determine the

- concentration of NaOH in **FA 6**
- maximum temperature change, ΔT_{max}
- value for the enthalpy change of neutralisation, ΔH_n

(a) Determining the change in temperature for a series of reactions between FA 3 and FA 6

(i)
1. Support the styrofoam cup in a 250 cm³ beaker.
2. Using a measuring cylinder, place 10 cm³ of **FA 3** into the styrofoam cup.
3. Measure the temperature of **FA 3** in the styrofoam cup. Record the initial temperature of the solution of **FA 3** as $\mathbf{T_{initial}}$.
4. Place 40 cm³ of **FA 6** into another measuring cylinder.
5. Tip the **FA 6** in the measuring cylinder into the styrofoam cup, stir and record the maximum temperature obtained in the reaction as $\mathbf{T_{max}}$.
6. Rinse and dry the styrofoam cup and the thermometer.
7. Repeat steps **2** to **6** using volumes of **FA 3** listed in Table 2.1. Fill in Table 2.1 with the appropriate volumes of **FA 6** to be used in each experiment such that the total volume of the reaction mixture is 50 cm³.

Table 2.1

Experiment	**1**	**2**	**3**	**4**	**5**	**6**
Volume of **FA 3** / cm³	10	20	30	40	15	25
Volume of **FA 6** / cm³	40	30	20	10	35	25

[1]

In an appropriate format in the space provided, prepare a table in which to record for each experiment

- the initial temperature
- the maximum temperature
- the change in temperature, ΔT

Results

Experiment	Initial Temperature/ °C	Final Temperature/ °C	ΔT/ °C
1	29.0	35.5	6.5
2	29.5	42.0	12.5
3	29.5	38.0	8.5
4	29.5	33.5	4.0
5	30.0	39.0	9.0
6	30.0	40.5	10.5

[3]

(ii) Plot a graph of ΔT (y–axis) against volume of **FA 6** used (x–axis) using the data you have obtained above in **a(i)** on the grid in Fig. 2.1.

By considering the points you have plotted, carry out two more experiments (experiment **5** and **6**) which will enable you to identify the volume of **FA 6** which gives the maximum temperature change, ΔT_{max}**.**

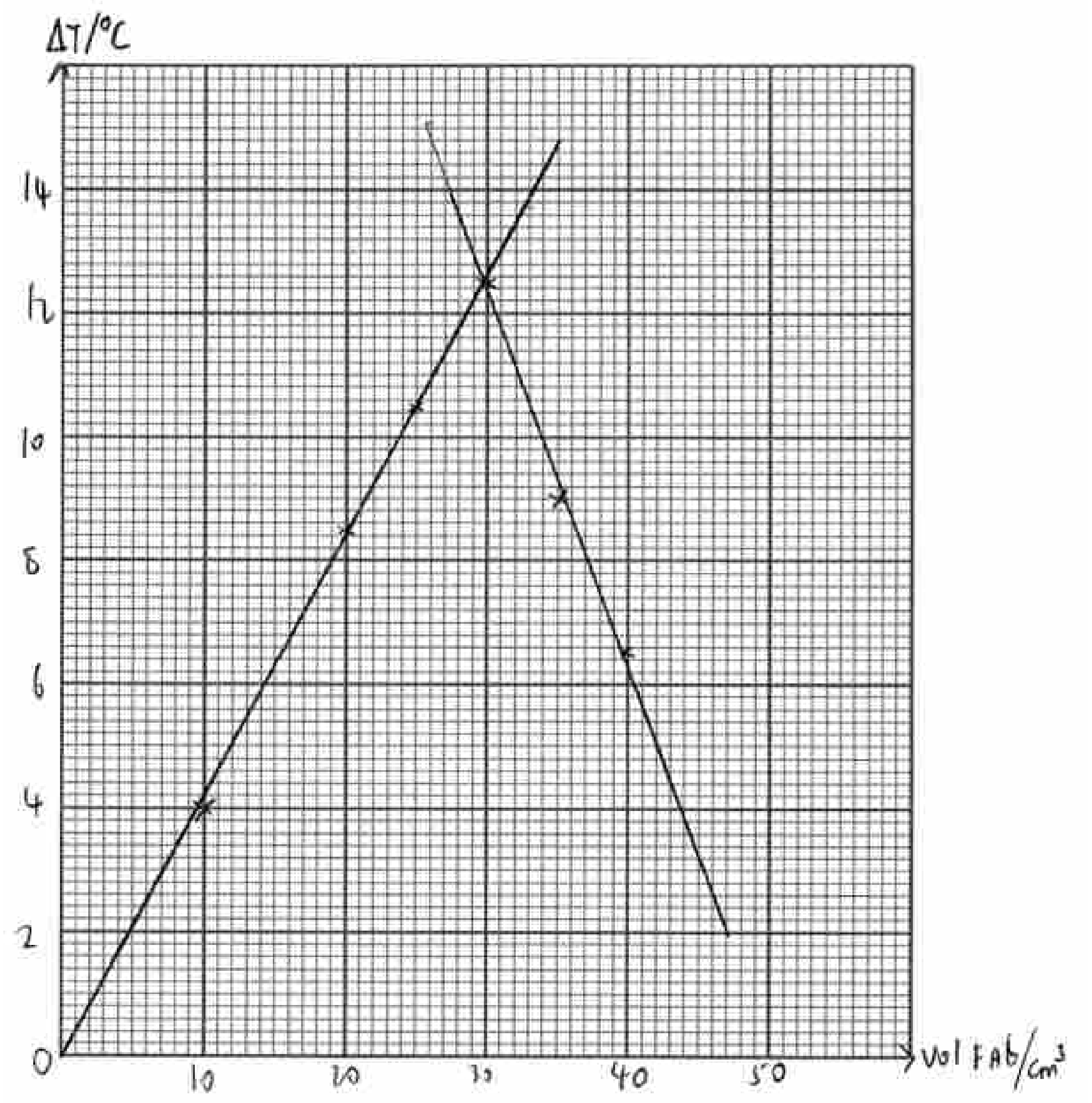


Fig. 2.1 [2]

(iii) Draw two straight lines of best fit. The first best fit line should be drawn using the plotted points where ΔT is increasing and the second best fit line should be drawn using the plotted points where ΔT is decreasing. Extrapolate these two lines until they cross. [1]

(iv) From your graph, determine the maximum temperature change, ΔT_{max}, and the volume of **FA 6** required to obtain this.

ΔT_{max} = ………12.5……………………….°C

$V_{\textbf{FA6}}$ = …..……30.0………………...cm^3 [1]

(b) Using your answers in **a(iv)**,

(i) calculate the concentration of NaOH in **FA 6**

Using V_{FA6} = 30.0 cm^3

volume of H_2SO_4 reacted = 50.0 – 30.0 = 20.0 cm^3

Amount of H_2SO_4 reacted = 20.0/1000 x 1.00 = 0.0200 mol

Amount of NaOH reacted = 0.0200 x 2 = 0.0400 mol

Concentration of NaOH = 0.0400 / (30.0/1000) = 1.33 mol dm^{-3}

concentration of NaOH in **FA 6** = …1.33 mol dm^{-3}……………………………..[2]

(ii) calculate the heat change at $\Delta T_{max.}$

You may assume that the specific heat capacity of the reaction mixture is 4.18 J g^{-1} K^{-1} and that the density is 1.00 g cm^{-3}.

heat change = 50 x 4.18 x 12.5= 2610 J

heat change = ………………………………..[1]

(c) Using your answers in **(b)**, calculate the enthalpy change of neutralisation, ***ΔH***ΔH_n.

Amount of water produced = amount of NaOH reacted = 0.0400 mol

ΔH_n = –2610/0.0400 = –65300 J mol^{-1}

ΔH_n = ………………………………..[1]

[Total: 12]

3 Qualitative Analysis

(a) You are to perform the tests given in Table 3.1 on **FA 9** and **FA 10**.

Record details of any colour changes observed, formation of any precipitate and the solubility of any such precipitate in an excess of the reagent added.

Where gases are released, they should be identified by a test, described in the appropriate place in the table provided. You should indicate clearly at what stage in a test a change occurs.

Marks are **not** given for chemical equations. **No additional tests for ions present should also be attempted**.

Table 3.1

Tests	Observations	
	FA 9	**FA 10**
1 To 0.5 cm depth of solution in a test-tube, add equal volume of aqueous sulfuric acid.	Brown gas (NO_2) is evolved	
Then add three to four drops of potassium iodide solution.	black solid/brown solution	
Then add a few drops of aqueous starch.	blue-black/dark blue colour	
2 Add 2 drops of aqueous potassium manganate(VII) to a test tube followed by 2 drops of sulfuric acid.		
Then add about 5 drops of **FA 9**.	Purple to colourless	
3 To 1 cm depth of **FA10** in a test-tube, add aqueous sodium hydroxide dropwise, until it is in excess.		Red brown ppt, insoluble in excess

4 To 0.5 cm depth of **FA 10** in a test-tube, add aqueous silver nitrate		white ppt /cream/pale yellow ppt
5 To 0.5 cm depth of **FA 10** in a test-tube, add aqueous sodium carbonate.		Reddish brown /brown ppt Effervescence seen. Gas formed white ppt in limewater. CO_2 evolved

[5]

(b) **(i)** **FA 9** can act both as an oxidising or a reducing agent. Based on your observations in test 1 and 2, state the role of **FA 9** in each of the tests.

role of **FA 9** in test 1 **oxidising agent**

role of **FA 9** in test 2 **reducing agent** [2]

(ii) Give the ionic equation, with state symbols, for the reaction of the metal cation in **FA 10** with aqueous sodium hydroxide in test 3.

$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$ [1]

(iii) The observation you made in test 4 when aqueous silver nitrate was added to **FA 10** does not allow the anion in **FA 10** to be identified with certainty.

Explain why you cannot be certain about the identity of the anion.

Difficult to distinguish the colour of the ppt due to the colour of FA 10 itself
OR
Cannot be certain whether the ppt with $AgNO_3$ is white (AgCl) or cream(AgBr) or yellow(AgI) [1]

(iv) A student suggested that the anion in **FA 10** could be identified with more certainty if excess ammonia solution was added after the aqueous silver nitrate.

Explain why this suggestion is **not** correct.

Ammonia would form ppt with Fe^{3+} ions, thus masking the effect of ammonia on the silver halide ppt
Or
Ammonia would form ppt with Fe^{3+} ions so the ppt of AgCl would not appear to dissolve. [1]

(v) Suggest a pH value of solution **FA 10** based on your observations in test 5. Write an equation to account for your suggested pH value.

suggested pH value……**Any value below 7**……

equation………………………………………………………………………………………
$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^{+}(aq)$.
…………………………………………………………………………………………

……………………………………………………………………………………[2]

[Total: 12]

4 **Preparation of cyclohexene from cyclohexanol**

Cyclohexene is prepared by dehydration of cyclohexanol using concentrated phosphoric acid as a catalyst.

$$C_6H_{11}OH(l) \longrightarrow C_6H_{10}(l) + H_2O(l)$$

Data about cyclohexanol and cyclohexene are given in the table below.

property	cyclohexanol	cyclohexene
density/ g cm^{-3}	0.96	0.81
molar mass/ g mol^{-1}	100.0	82.0
boiling point/ °C	161.0	83.3

Preparation of impure cyclohexene

0.1 mol of cyclohexanol and 3 cm^3 of concentrated phosphoric acid were added together into a round-bottomed distillation flask. The mixture was heated and the impure cyclohexene was collected by distillation. Both cyclohexanol and cyclohexene are flammable.

Purification of impure cyclohexene

The impure cyclohexene was transferred into a separating funnel and an equal volume of saturated sodium chloride solution was added. The funnel was allowed to stand for a few minutes until the layers separated out.

The cyclohexene layer was transferred into a small flask and some anhydrous calcium chloride was added. The mixture was allowed to stand until the cyclohexene became clear.

The dried cyclohexene was decanted into a clean flask and was then fractionally distilled to produce the pure cyclohexene.

(a) **(i)** Calculate the volume of cyclohexanol to be used in the preparation.

Mass = 0.1 x100 = 10.0 g
Volume = 10/0.96 = <u>10.4 cm^3</u>

volume of cyclohexanol to be used = ……………………………… cm^3 [1]

(ii) Using the information given on the previous page, outline how you would prepare a sample of impure cyclohexene from cyclohexanol.

In your answer, you should

- Give a full description of the procedures you would use to prepare the impure cyclohexene, stating clearly the apparatus used for measuring the reactants.
- State the temperature at which you would conduct the experiment.

………………………………………………………………………………….. [3]

1. **Measure 10.4 cm^3 of cyclohexanol using a 50 cm^3 measuring cylinder into a round-bottomed flask.**
2. **Using a 10 cm^3 measuring cylinder, add 3 cm^3 of concentrated phosphoric acid into the flask.**
3. **Set up the distillation apparatus with a water-cooled condenser and a thermometer in the neck of a round-bottomed distillation flask and gently heat the mixture in the flask using a water bath or an electrical heater.**
4. **When the thermometer showed about 83°C, the impure cyclohexene distilled over, cooled and is collected.**

(b) **(i)** When the layers separate out in the separating funnel, suggest whether the cyclohexene will be the upper or lower layer. Hence explain how you would use the separating funnel to transfer the cyclohexene layer into a small flask.

………………………………………………………………………………….. [2]
Upper layer is cyclohexene. Run off lower layer (to waste) by turning the tap of funnel and then pour out the upper layer into a small flask.

(ii) Why is anhydrous calcium chloride added to the cyclohexene?

…………………………………………………………………………………..… [1]
It is used as a drying agent to remove any water present in the cyclohexene layer.

(c) The percentage yield of cyclohexene in this preparation is 57.3%.

Suggest a reason why this preparation does not produce a 100% yield.

……………………………………………………………………………………………..[1]

- **Reaction may not be complete**
- **Side reactions and other products might be formed**
- **Some of the cyclohexene might have stayed in the aqueous layer.**

[Total: 8]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

ANDERSON JUNIOR COLLEGE

2018 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/01**

Paper 1 Multiple Choice **17 September 2018**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC / FIN number, **including** the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC2 PRELIM

Exam Details: H2 Chemistry / Paper 1

Date: 17/09/2018

This document consists of **13** printed pages.

1 *Use of the Data Booklet is relevant to this question.*

P and *Q* are atoms of different elements.

P has nine fewer protons than *Q*.
P has one more unpaired electron than *Q*.

What are the identities of *P* and *Q*?

1 *P* is carbon and *Q* is phosphorus.

2 *P* is nitrogen and *Q* is sulfur.

3 *P* is oxygen and *Q* is chlorine.

A 1 only

B 2 only

C 1 and 3 only

D 2 and 3 only

2 How many subshells and orbitals are there in the third shell?

	subshells	orbitals
A	2	4
B	2	8
C	3	5
D	3	9

3 An ionic compound *E*

- has an empirical formula NH_2O,
- reacts with NaOH(aq) to produce ammonia gas

How many electrons are present in the anion of *E*?

A 23 **B** 24 **C** 31 **D** 32

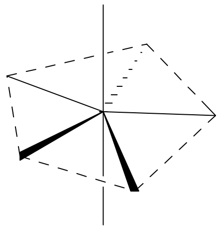
4 The shape of the PCl_5 molecule in the gas phase is trigonal bipyramidal.

The chlorine atom can be replaced one at a time by fluorine atoms, the axial chlorine atoms being replaced first, then the equatorial atoms.

Which molecule does **not** have a dipole moment?

A PCl_4F **B** PCl_3F_2 **C** PCl_2F_3 **D** $PClF_4$

5 IF_7 is an interhalogen compound where the central atom is surrounded by seven pairs of electrons arranged in an unusual pentagonal bipyramidal shape. A pentagonal bipyramidal arrangement is shown below.



Which molecule has the same maximum number of atoms in a plane as a molecule of IF_7?

A C_2H_4 **B** N_2H_4 **C** $SiCl_4$ **D** SF_6

6 Which statement about the molecule N_2F_2 is correct?

A It contains dative bonds.

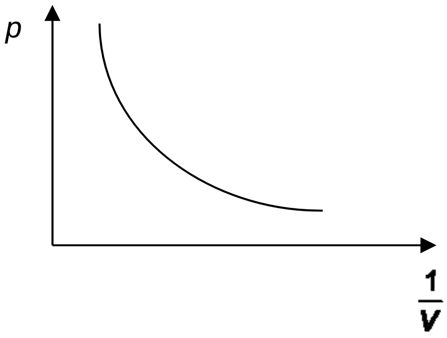
B It contains four unpaired electrons.

C It has cis–trans isomers.

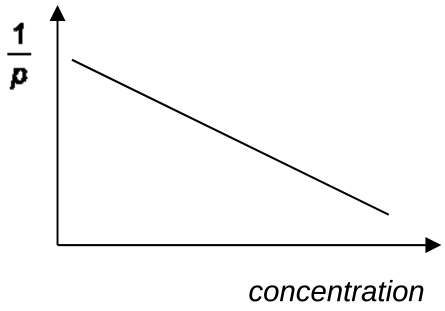
D It is linear in shape.

7 Which of the following diagrams correctly describes the behavior of a fixed mass of an ideal gas at constant *T*?

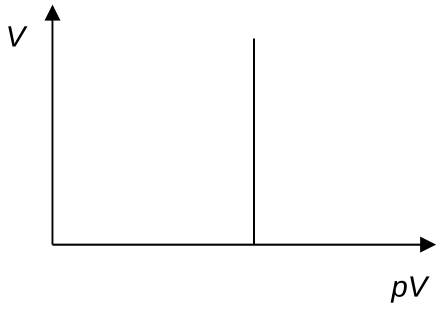
A



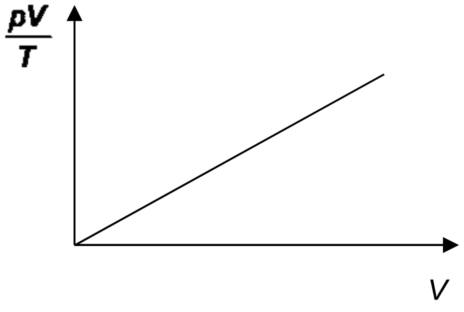
B



C



D



8 The information relates to element *Z*.

- *Z* is in Period 3 of the Periodic Table.
- *Z* has a lower electrical conductivity than Mg.
- A *Z* atom has a half–filled subshell in its ground state.
- *Z* forms an acidic oxide on exposure to air.

What is *Z*?

A Na **B** Si **C** P **D** C*l*

9 A powder was known to be either a single sodium halide or a mixture of two sodium halides.

A sample of the powder was dissolved in water and aqueous silver nitrate added. A precipitate was formed, which, on addition of excess aqueous ammonia, partly dissolved leaving a yellow solid.

What did the powder consist of?

A NaBr only

B NaI only

C a mixture of NaC*l* and NaBr

D a mixture of NaC*l* and NaI

10 Antimony can be produced in a two–stage process from its ore stibnite, Sb_2S_3.

The ore is first roasted in oxygen, producing Sb_4O_6 and SO_2.

The Sb_4O_6 is then reduced by carbon, producing Sb and CO_2.

What volume of CO_2, measured at room temperature and pressure, is produced on processing 10 moles of Sb_2S_3?

A 15 dm^3 **B** 180 dm^3 **C** 360 dm^3 **D** 720 dm^3

11 Most elements contain more than one isotope, atoms that have the same chemical properties but different masses.

Which expression correctly defines the term *relative atomic mass* of an element?

A the mass of 1 atom of an element relative to the mass of 1 atom of ^{12}C

B the mass of 1 mole of atoms of an element divided by 6.02×10^{23}

C the mass of 1 mole of atoms of an element relative to the mass of 1 atom of ^{12}C

D the mass of 1 mole of atoms of an element relative to the mass of 1 mole of ^{12}C atoms

12 The lattice energies of the compounds caesium chloride, caesium fluoride, sodium chloride and sodium fluoride are given below.

Which value corresponds to the lattice energy of caesium chloride?

A -661 kJ mol^{-1} **B** -747 kJ mol^{-1} **C** -780 kJ mol^{-1} **D** -918 kJ mol^{-1}

13 Clouds and rain form when air saturated with water vapour cools.

$$H_2O(g) \longrightarrow H_2O(l)$$

What are the correct signs of ΔH and ΔS for this reaction?

A both negative

B both positive

C ΔH negative, ΔS positive

D ΔH positive, ΔS negative

14 Which suggested mechanism is consistent with the experimentally obtained rate equation?

	rate equation	suggested mechanism
1	rate = k_1 [H_2O_2] [I^-]	$H_2O_2 + I^- \xrightarrow{slow} H_2O + OI^-$ $OI^- + H^+ \xrightarrow{fast} HOI$ $HOI + H^+ + I^- \xrightarrow{fast} I_2 + H_2O$
2	rate = k_2 [H_2] [I_2]	$H_2 \xrightarrow{slow} 2H$ $2H + I_2 \xrightarrow{fast} 2HI$
3	rate = k_3 [HBr]^2 [O_2]^{½}	$2HBr + O_2 \xrightarrow{fast} 2HBrO$ $HBrO + HBr \xrightarrow{slow} H_2O + Br_2$
4	rate = k_4 [O_3]^2 [O_2]$^{-1}$	$O_3 \xrightarrow{fast} O_2 + O$ $O_3 + O \xrightarrow{slow} 2O_2$

A 1 only

B 1 and 4 only

C 2 and 3 only

D 1, 3 and 4 only

15 An equilibrium can be represented by the following equation.

$$\boldsymbol{F}(aq) + \boldsymbol{G}(aq) \rightleftharpoons 2\boldsymbol{H}(aq) + \boldsymbol{J}(aq)$$

In a certain 1 dm^3 mixture, the equilibrium concentration of ***G*** is 10 mol dm^{-3}.

What will be the new equilibrium concentration of ***G*** if 5 mol of pure ***G*** is dissolved in the mixture?

A 15 mol dm^{-3}

B between 10 mol dm^{-3} and 15 mol dm^{-3}

C 10 mol dm^{-3}

D between 5 mol dm^{-3} and 10 mol dm^{-3}

16 Which one of the following statements is correct about a reaction for which the equilibrium constant is independent of temperature?

A The enthalpy change is zero.

B Its rate constants do not vary with temperature.

C There are equal number of moles of reactants and products.

D The forward and reverse reactions are of the same order.

17 A mixture of CO and H_2 in a 1 : 3 molar ratio was introduced into a sealed vessel and heated to 1200 K.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

At equilibrium it was found that the total pressure was 32 atm, and the mole fractions of CO and CH_4 were 0.19 and 0.12 respectively.

What is the value of the equilibrium constant, K_p?

A 4.0×10^{-4} **B** 1.0×10^{-3} **C** 1.3×10^{-1} **D** 4.0×10^{-1}

18 Values of two solubility products are given.

$$K_{sp}\ (ZnF_2) = 3.2 \times 10^{-2}\ mol^3\ dm^{-9}$$

$$K_{sp}\ (BaF_2) = 1.6 \times 10^{-7}\ mol^3\ dm^{-9}$$

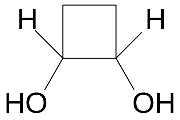
Solid zinc fluoride is shaken with water. The remaining solid is filtered off, leaving a saturated solution *M*.

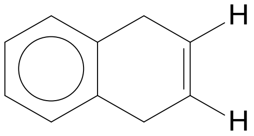
Drops of dilute aqueous barium nitrate are added to *M* until barium fluoride just precipitates.

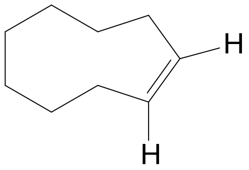
Which row of the table is correct?

	$[F^-]$ in *M* / mol dm^{-3}	$[Ba^{2+}(aq)]$ when BaF_2 just precipitates
A	2×10^{-1}	4×10^{-7}
B	2×10^{-1}	8×10^{-7}
C	4×10^{-1}	1×10^{-6}
D	4×10^{-1}	4×10^{-6}

19 Which of the following compounds exhibit cis–trans isomerism?

1 

2 

3 

A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

20 Ethane reacts with chlorine gas in the presence of ultraviolet light to form a mixture of products.

Which statements regarding this reaction are correct?

1 Both initiation and propagation steps involve homolytic fission.

2 Both initiation and propagation steps produce chlorine atom.

3 Both propagation and termination steps involve C–C*l* bond formation.

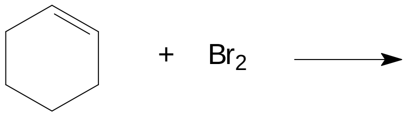
A 1 only

B 2 only

C 2 and 3 only

D 1, 2 and 3 only

21 When cyclohexene is added to bromine in an inert organic solvent, there is a fast reaction that decolourises the bromine.



Which of the following statements is correct?

1 There is σ bond in cyclohexene that is formed by 1s–2sp^2 orbital overlap.

2 There is a carbon atom that changed from being sp^2 hybridised in the reactant to being sp^3 hybridised in the intermediate formed during the reaction.

3 There are a total of 4 stereoisomers in the product mixture.

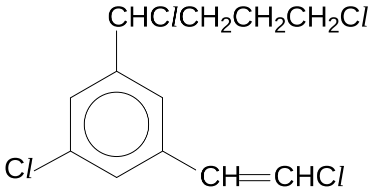
A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

22 Compound **K** has the structure as shown below.

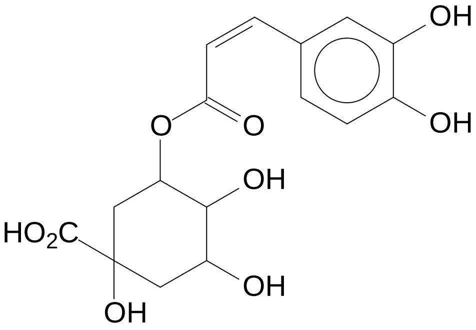


1 mol of compound **K** was heated with an excess of aqueous sodium hydroxide. The resulting reaction mixture was then cooled and acidified with dilute nitric acid. Excess aqueous silver nitrate is then added to it.

How many moles of silver chloride will be precipitated out?

A 0 **B** 1 **C** 2 **D** 4

23 Chlorogenic acid occurs naturally in coffee.



chlorogenic acid

Which of the following observations is correct?

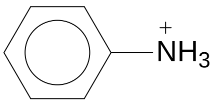
A It reacts with 2,4–dinitrophenylhydrazine to give an orange precipitate.

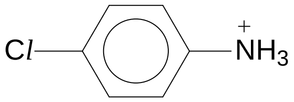
B It reacts with hot, acidified potassium manganate(VII) to produce a gas which gives a white precipitate with limewater.

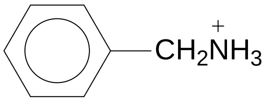
C It reacts with aqueous bromine to incorporate up to 7 atoms of bromine in each molecule.

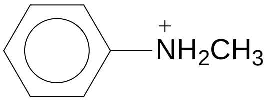
D It reacts with excess sodium metal to produce 6 mol of hydrogen gas for each mole of the molecule.

24 Consider the following four ions.

1 

2 

3 

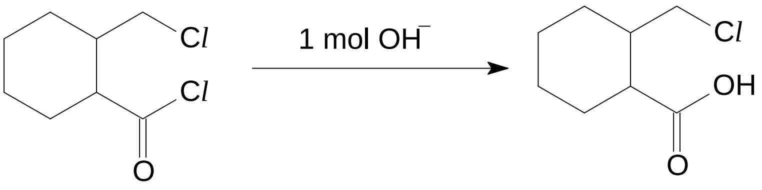
4 

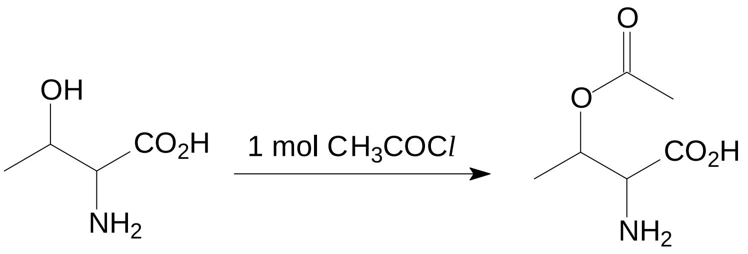
Which of the following shows the given ions arranged in order of **decreasing** pK_a?

A	3	4	1	2
B	3	4	2	1
C	4	3	1	2
D	4	2	3	1

25 Which of the reactions would **not** give the product shown?

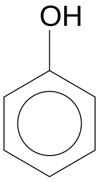
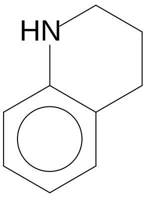
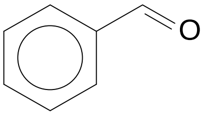
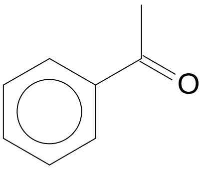
1 $ClCH_2CH_2CH_2CH_2CH_2I \xrightarrow{\text{1 mol } CH_3NH_2} CH_3NHCH_2CH_2CH_2CH_2CH_2I$

2 

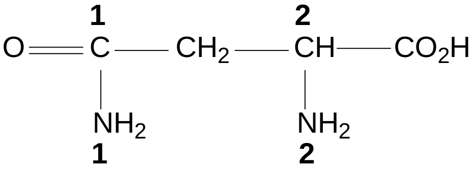
3 

- **A** 2 only
- **B** 1 and 3 only
- **C** 2 and 3 only
- **D** 1, 2 and 3

26 Which of the following reagents and conditions can be used to distinguish the pair of compounds in each set?

	Compound 1	Compound 2	Reagent and condition
A			Br_2(aq), room temperature
B	$CH_3CH_2COCI_3$	$CH_3CH(OH)CH_2CH_3$	I_2(aq), NaOH(aq), warm
C			$[Ag(NH_3)_2]^+$ in alkaline solution, warm
D	$C_6H_5CH_2CH_3$	$C_6H_5CH{=}CH_2$	$KMnO_4$(aq), dilute H_2SO_4, heat

27 *Asparagine* can be synthesised from the central metabolic pathway intermediates in human and is not required in the diet.



$$O{=}\overset{1}{\underset{\underset{1}{NH_2}}{C}}-CH_2-\overset{2}{\underset{\underset{2}{NH_2}}{CH}}-CO_2H$$

Asparagine

Which statements are correct?

1 *Asparagine* contains two sp^2 hybridised carbon atoms.

2 The single C1–N1 bond is shorter than the single C2–N2 bond.

3 One mole of *asparagine* requires two moles of HC*l* for complete neutralisation.

A 1 only

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

28 *Use of the Data Booklet is relevant to this question*.

The AgC*l* | Ag reference electrode is based on the following reaction:

$$AgCl + e^{-} \rightleftharpoons Ag + Cl^{-}$$

The reduction potential of the Fe^{2+} | Fe couple was found to be –0.64 V when measured using the AgC*l* | Ag reference electrode.

What is the reduction potential of the AgC*l* | Ag electrode with respect to the standard hydrogen electrode?

A –0.20 V **B** –1.10 V **C** +0.20 V **D** +1.10 V

29 When a large current was passed through acidified aqueous copper(II) sulfate, there was simultaneous liberation, at the cathode, of *x* mol of copper and *y* dm^3 of hydrogen gas, measured at standard temperature and pressure.

How many moles of electrons passed through the solution?

A $x + \frac{y}{22.7}$ **B** $x + \frac{2y}{22.7}$ **C** $x + \frac{4y}{22.7}$ **D** $2x + \frac{2y}{22.7}$

30 *Use of the Data Booklet is relevant to this question.*

Lithium cells are used in digital watches, hearing aids and mobile phones.

They consist of lithium and manganese(IV) oxide in non–aqueous pastes enclosed between sheets of stainless steel.

The electrode reactions are as follows.

negative electrode: $Li(s) \longrightarrow Li^{+}(s) + e^{-}$

positive electrode: $Li^{+}(s) + MnO_2(s) + e^{-} \longrightarrow LiMnO_2(s)$

The capacity of a cell is given in amp hours (Ah), which is the amount of constant current that can be drawn from the cell in one hour before it becomes discharged.

Which expression will calculate the minimum mass of lithium required to make a cell with a capacity of 1.8 Ah?

A $\frac{1.8 \times 3600 \times 6.9}{96500}$ g

B $\frac{1.8 \times 3600 \times 6.9}{1.6 \times 10^{-19}}$ g

C $\frac{1.8 \times 96500 \times 6.9}{3600}$ g

D $\frac{1.8 \times 1.6 \times 10^{-19}}{6.9 \times 3600}$ g

H2 Chemistry 9729 **AJC 2018 JC2 PRELIM** **Paper 1 – 30 marks**

Question Number	*Key*	*Question Number*	*Key*
1	**D**	16	**A**
2	**D**	17	**A**
3	**B**	18	**C**
4	**B**	19	**B**
5	**A**	20	**D**
6	**C**	21	**B**
7	**C**	22	**C**
8	**C**	23	**B**
9	**D**	24	**A**
10	**C**	25	**D**
11	**D**	26	**C**
12	**A**	27	**B**
13	**A**	28	**C**
14	**D**	29	**D**
15	**B**	30	**A**

A	**7**
B	**7**
C	**8**
D	**8**

Anderson Junior College
H2 Chemistry 9729 **2018 JC2 Prelim Paper 2 Suggested Solutions**

1 (a) (i) **$MCO_3(s) \longrightarrow MO(s) + CO_2(g)$** [1]

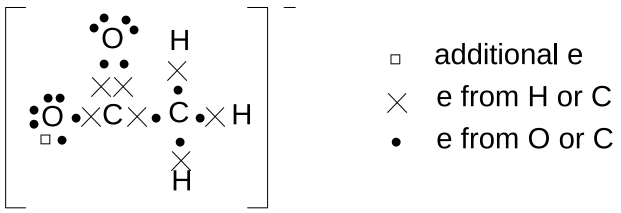
(ii) Down the group, [2]

- ionic radius of M^{2+} increases so the charge density of the M^{2+} decreases
- M^{2+} becomes less polarising
- electron cloud of CO_3^{2-} anion is less distorted so the C–O covalent bond within the CO_3^{2-} anions is less weakened down the group.

Thermal stability of carbonates increases down the group.

[1]: charge density & polarising power of M^{2+} decreases down the group
[1]: extent of distortion & weakening of (C–O) bond decreases and thermal stability increases

(b) (i) [1]



[1]: correct dot–and–cross (ignore missing legend)

(ii) Shape with respect to **C**$H_3CO_2^-$: tetrahedral [1]
Shape with respect to CH_3**C**O_2^-: trigonal planar [1]

(iii) **$CH_3CH_2COCH_2CH_3$** [1]

(iv) **A**: $CH_3CH_2COCH_3$ [1]
B: CH_3COCH_3 [1]

(c) Sample **C** contains manganese(II) ethanoate [3]
Both samples will decompose to form MCO_3 and $(CH_3)_2CO$, which gave yellow ppt with 2,4–DNPH.
As Mn^{2+}(0.088nm) has a smaller ionic radius than Pb^{2+}(0.120nm), Mn^{2+} ion is able to polarise / distort electron cloud of CO_3^{2-} anion to a greater extent. Hence, $MnCO_3$ will decompose to give $CO_2(g)$, which turned limewater cloudy.

[1]: sample **C**
[1]: quote ionic radius of both M^{2+}
[1]: link to further decomposition of $MnCO_3$ to give $CO_2(g)$

2 **(a)** Co–ordination number is the number of dative bonds attached to the central atom or ion in a complex. [1]

(b) **(i)** electrons in the 3d and 4s subshells are similar in energy [1] thus different number of these electrons are available for use in bond formation / ions formed by using different number of electrons for bonding are of similar stability [2]

[1]: close proximity in terms of energy for 3d and 4s subshell
[1]: different number of e$^-$ involved in bonding

(ii) electronic configuration of vanadium in $[V(H_2O)_6]^{2+}$ is [Ar] $3d^3$ while that in $[V(H_2O)_6]^{3+}$ is [Ar] $3d^2$ [2]

AND

thus $[V(H_2O)_6]^{2+}$ shows a higher relative paramagnetism as it has greater number of unpaired (3d) electrons than $[V(H_2O)_6]^{3+}$.
OR
there are 3 unpaired electrons in the d–orbitals of V^{2+}(aq)
and 2 unpaired electrons in the d–orbitals of V^{3+}(aq).
Hence the relative paramagnetism of the V^{2+}(aq) and V^{3+}(aq) ions is 3 : 2.

[1]: correct electronic configurations
[1]: compare number of unpaired (3d) electrons and relate to the difference in relative paramagnetism

(c) **(i)** **Reaction 1**

$$\frac{n(MnO_4^-)}{n(VO^{2+})} = \frac{0.0020}{0.010} = \frac{1}{5}$$

$\Rightarrow$ 1 mol of MnO_4^- reacts with 5 mol of VO^{2+}
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
$\Rightarrow$ Each mol of MnO_4^- gains 5 mol of e$^-$
$\Rightarrow$ 5 mol of VO^{2+} loses 5 mol of e$^-$
$\Rightarrow$ Each mol of VO^{2+} loses 1 mol of e$^-$ [1]
$\therefore$ final oxidation state of V is (+4 + 1) = +5

Reaction 2

$$\frac{n(Sn^{2+})}{n(VO^{2+})} = \frac{0.0050}{0.010} = \frac{1}{2}$$

$\Rightarrow$ 1 mol of Sn^{2+} reacts with 2 mol of VO^{2+}
$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$
$\Rightarrow$ Each mol of Sn^{2+} loses 2 mol of e$^-$
$\Rightarrow$ 2 mol of VO^{2+} gains 2 mol of e$^-$
$\Rightarrow$ Each mol of VO^{2+} gains 1 mol of e$^-$ [1]
$\therefore$ final oxidation state of V is (+4 – 1) = +3

(ii) Paramagnetism of solution **F** decreases in **Reaction 1** as the number of unpaired (3d) electrons decreases from 1 to 0. [1]

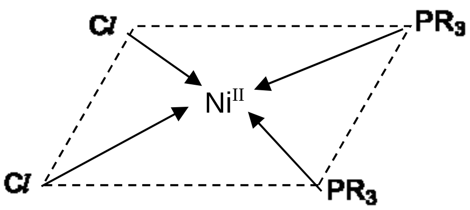
Paramagnetism of solution **F** increases in **Reaction 2** as the number of unpaired (3d) electrons increases from 1 to 2. [1]

(d) [2]

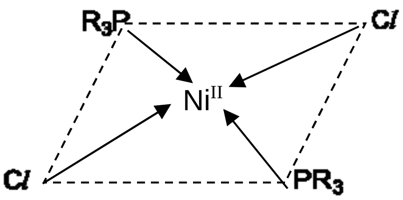
formula of complex	**geometry of complex**	**spin state of Ni^{2+} in complex**
$[NiCl_4]^{2-}$	tetrahedral	
$[Ni(CN)_4]^{2-}$	square planar	low spin

[1]: both correct geometry
[1]: correct spin state

(e) [2]



G



H

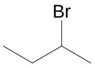
where R = (-CH_2CH_3) and *lone pair is on P atom*
G has a net dipole moment while **H** does not (dipoles cancel out).

(accept **G** in tetrahedral shape)
[1]: correct structure

3 **(a)** **(i)** elimination [1]

(ii) It behaves as a Lewis base because it is an <u>electron pair donor</u> / uses its <u>lone pair of electrons</u> on O^- to <u>form a dative bond</u> with H^+. [1]

(iii) [3]

Let the order of reaction with respect to  be x.

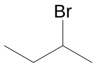
Comparing experiments 1 & 2 in which $[CH_3CH_2O^-]$ is kept constant,

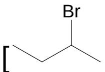
$$\frac{(0.060)^x}{(0.050)^y} = \frac{1.00}{0.833}$$

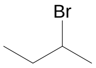
$$\left(\frac{6}{5}\right)^x = \frac{6}{5}$$

x = <u>1</u>

<u>OR</u>

when [] increases <u>6/5 times</u>, the relative initial rate also decreases 1.00/0.833 ≈ <u>6/5 times</u>.

Rate of reaction is directly proportional to [].

Hence, order of reaction with respect to  is <u>1</u>.

Let the order of reaction with respect to $CH_3CH_2O^-$ be y.
Comparing experiments 2 & 3,

$$\frac{(0.060)^x(0.050)}{(0.050)^x(0.040)} = \frac{0.833}{0.667}$$

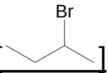
$$\left(\frac{6}{5}\right)^x = 0.999 \approx 1$$

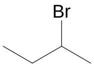
$$x = 0$$

$$\frac{(0.060)^y(0.050)}{(0.050)^y(0.040)} = \frac{0.833}{0.667}$$

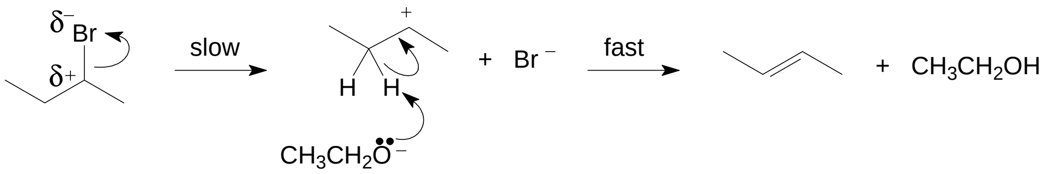
$$\left(\frac{6}{5}\right)^y = 0.999 \approx 1$$

y = <u>0</u>

Hence, <u>rate = *k* []</u>

[1]: order of reaction wrt 
[1]: order of reaction wrt $CH_3CH_2O^-$
[1]: rate law

(iv) [2]



[1]: correct electron pairs movement for both slow and fast step, including showing lone pair on O
[1]: correct intermediate and product generated

(v) The rate of reaction will be <u>slower</u> when 2–chlorobutane is used instead of 2–bromobutane. [2]
This is because C–C*l* bond is <u>stronger</u> than C–Br bond. More energy required to break the C–C*l* bond (higher E_a) and reaction is slower.

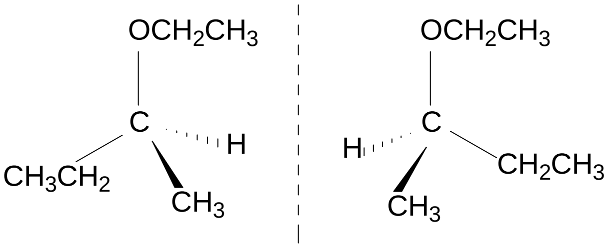
[1]: faster rate
[1]: stronger C–C*l* bond

(b) **(i)** (unimolecular) <u>nucleophilic substitution</u>, S_N1 [1]

(ii) The carbocation is trigonal <u>planar</u> wrt the electron deficient C. [1]
$CH_3CH_2O^-$ acted as a nucleophile and approached the electron–deficient carbon atom from <u>either side</u> with <u>equal probability</u>, producing <u>equimolar mixture of both enantiomers</u> and gives an optically inactive racemic mixture.

[1]: equal probability of attack from either side of planar C^+

(iii) [2]



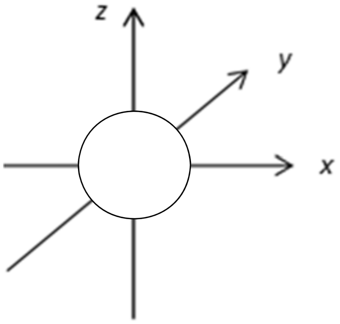
[1]: correct by–product
[1]: enantiomers shown correctly

(iv) The catalyst <u>restricts</u> the nucleophile to <u>attack</u> the electron deficient carbocation <u>from only one side</u>. Hence, one enantiomer to be produced preferentially / no racemic mixture is produced. [1]

4 **(a)** **(i)** First ionisation energies decreases down the group. [2]
Down the group, nuclear charge increases.
However, valence electron is added to the next electron shell and is further away and more shielded from nucleus.
Thus, valence electron experiences weaker electrostatic attraction from the nucleus and less energy is required to remove the valence electrons.

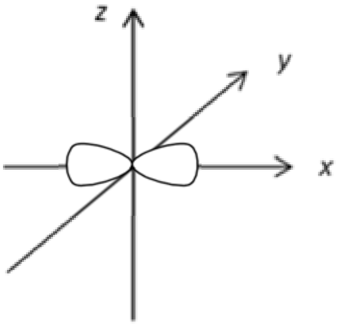
[1]: increase in nuclear charge, distance and shielding / screening effect
[1]: weaker attraction and less energy / decreasing trend

(ii) electronic configuration of P : $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3}$ [2]

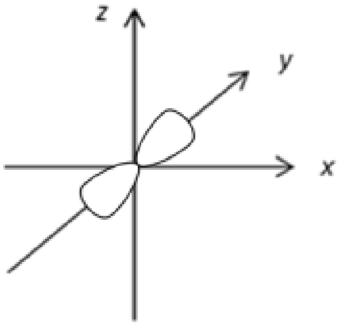


3s

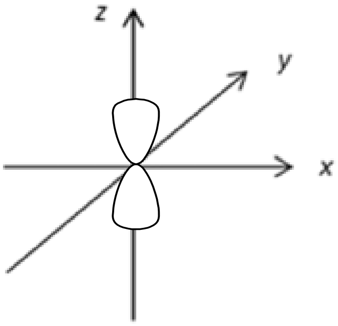
either $3p_x$, $3p_y$ or $3p_z$



$3p_x$



$3p_y$



$3p_z$

[1]: electronic configuration
[1]: show both 3s and 3p orbitals

(b) **(i)** $$\mathbf{PH_3(g) \longrightarrow \frac{1}{4}P_4(g) + \frac{3}{2}H_2(g)}$$ [1]

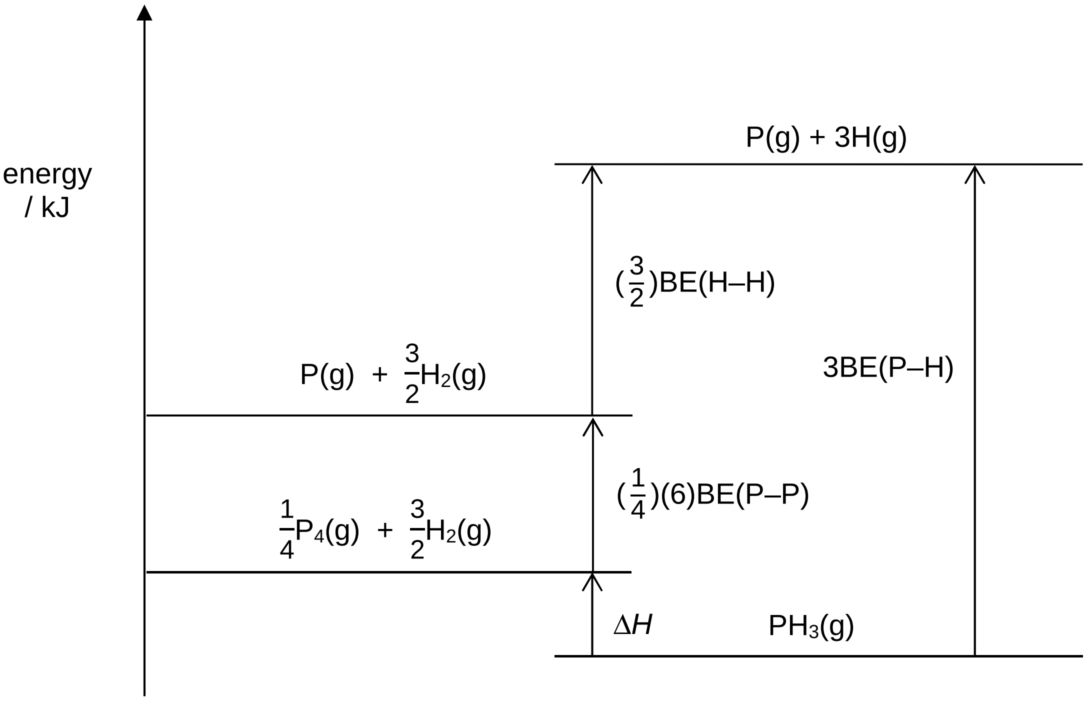
ignore state symbols

(ii) By Hess Law, [2]

$$\Delta H = 3BE(P–H) – [(\tfrac{1}{4})(6)BE(P–P) + (\tfrac{3}{2})BE(H–H)]$$
$$= 3(320) – [(\tfrac{1}{4})(6)(200) + (\tfrac{3}{2})(436)]$$
$$= \underline{+6 \text{ kJ mol}^{-1}}$$

[1]: correct application of Hess' Law
[1]: correct answers with units

(iii) [2]



[1]: correct compounds at the 3 other energy levels with corresponding stoichiometry and state symbols
[1]: correct enthalpy terms (or values) and corresponding arrow directions

(iv) $k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{35.0}$ [2]

$= \underline{0.0198\ \text{s}^{-1}}$

[1]: correct answer
[1]: correct units

(v) When volume of P_4(g) collected reaches 99% of its expected concentration, 1 % of PH_3 is left. [1]

$$1 \longrightarrow \frac{1}{2} \longrightarrow \frac{1}{4} \longrightarrow \frac{1}{8} \longrightarrow \quad \longrightarrow \frac{1}{100}\ [(\frac{1}{2})^n]$$

$\frac{C}{C_o} = (\frac{1}{2})^n$, where n = no. of half–life undergone

$\frac{1}{100} = (\frac{1}{2})^n$

$n = \ln\frac{1}{100} \div \ln\frac{1}{2}$

$= 6.64$

estimated time taken for 99 % of P_4 collected = 6.64 x 35.0
= <u>233 s</u>

(accept 6.5 x 35 = 227.5 s because $\frac{1}{100}$ is between $\frac{1}{64}$ and $\frac{1}{128}$, i.e. 6th and 7th half–life)

(c) **(i)** high temperature and low pressure [1]

(ii) [2]

$$n(PH_3) = \frac{36.0}{31.0 + 3(1.0)}$$
$$= 1.059 \text{ mol}$$

$$pV = \text{nRT}$$
$$V = \frac{\text{nRT}}{p}$$
$$= \frac{1.059(8.31)(273+327)}{1.34 \text{ x } 10^{7}}$$
$$= 3.94 \text{ x } 10^{-4} \text{ m}^3$$
$$= \underline{394 \text{ cm}^3}$$

[1]: correct volume in m^3
[1]: correct conversion from m^3 to cm^3

(iii) PH_3 behaves non–ideally and volume calculated in **(a)(ii)** is smaller than the volume of the container. [2]

under high pressure,
the volume of the PH_3 molecules is not negligible / significant. Hence the actual free volume between the gas molecules is smaller.

[1]: recognise that PH_3 is behaving non–ideally and volume is smaller
[1]: correct explanation

5 **(a)** **(i)** dilute HCl / dilute H_2SO_4 / $NaOH(aq)$ / $KOH(aq)$ (any suitable dilute acid / alkali) [1]
heat under reflux for several hours

(ii) recommended daily amount of protein = 65 x 1.4 [1]
= 91 g

(iii) mass of whey protein powder to be consumed = $\frac{91}{84}$ x 100 g [1]
= 108 g

(accept using per serving = $\frac{91}{21}$ x 25 g)

(iv) amount of energy contributed by whey protein powder = $\frac{108}{100}$ x 1740 [1]
= 1879 kJ

amount of energy contributed by other food source = $\frac{80}{20}$ x 1879
= 7516 kJ

(accept using per serving = $\frac{108}{25}$ x 435 x $\frac{80}{20}$ kJ)

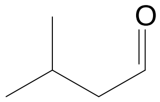
(v) To each of the 2 samples, add $K_2Cr_2O_7$, dilute H_2SO_4 and heat. [2]
Orange solution remains for phenylalamine while orange solution turns green for threonine.

(accept $I_2(aq)/OH^-$ and the corresponding observations – yellow ppt observed for threonine but not phenylalamine)

[1]: correct reagent and condition
[1]: both observations

(b) **(i)** Step I: nucleophilic addition [1]
Step IV: hydrolysis [1]

(ii) [1]



(c) **(i)** When 15.0 cm³ of NaOH(aq) was added, a buffer at its MBC is formed. [1]
pK_{a2} = pH
= 9.60

$K_{a2} = 10^{-9.60}$
$= 2.5 \times 10^{-10}$ mol dm^{-3} (shown)

(ii) $\mathbf{RCH(NH_2)CO_2^- + H_2O \rightleftharpoons RCH(NH_3^+)CO_2^- + OH^-}$ [1]

$[OH^-] > [H^+]$ and pH > 7 at point **T**

(iii) At 20 cm^3 (i.e. 2nd equivalence point), solution contains RCH(NH$_2$)COO$^-$ which is a basic salt [2]

$$K_b = \frac{10^{-14}}{2.5 \times 10^{-10}}$$
$$= 4.00 \times 10^{-5}$$

$$n(\text{RCH(NH}_2\text{)CO}_2^-) \text{ formed} = \frac{10}{1000} \times 1.00$$
$$= 0.0100 \text{ mol}$$

$$[\text{RCH(NH}_2\text{)CO}_2^-] \text{ at 20 cm}^3 = \frac{0.0100}{(10+20)} \times 1000$$
$$= \underline{0.3333 \text{ mol dm}^{-3}}$$

$$K_b = \frac{[\text{OH}^-][\text{RCH(NH}_3^+\text{)CO}_2^-]}{[\text{RCH(NH}_2\text{)CO}_2^-]}$$

$$[\text{OH}^-] \approx \sqrt{4.00 \times 10^{-5} \times 0.3333}$$
$$= 3.65 \times 10^{-3} \text{ mol dm}^{-3}$$

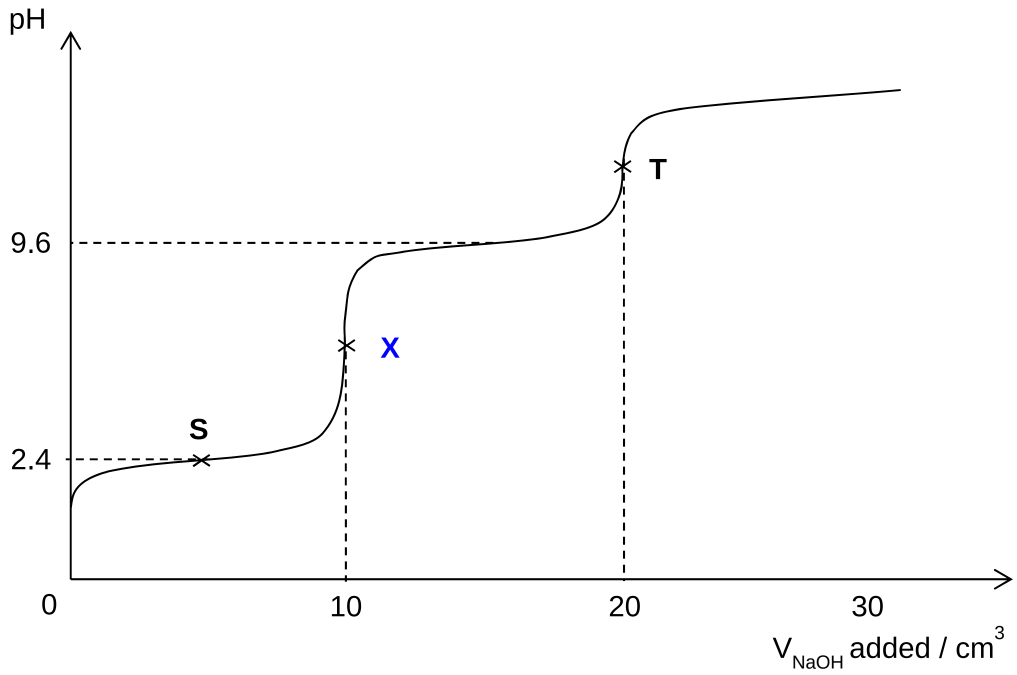
pOH = 2.44

pH = $\underline{11.6}$

[1]: [RCH(NH$_2$)COO$^-$]

[1]: pH

(iv) [1]



[1]: isoelectric point at 10 cm^3

(v) (CH$_3$)$_2$CHCH$_2$CH(NH$_3$)$^+$CO$_2$H and (CH$_3$)$_2$CHCH$_2$CH(NH$_3$)$^+$CO$_2^-$ [1]

(accept answer in abbreviated form)

[1]: both

(vi) **RCH(NH$_3^+$)COO$^-$ + H$^+$ $\longrightarrow$ RCH(NH$_3$)$^+$COOH** [1]

Or

RCH(NH$_3$)$^+$COO$^-$ + H$_3$O$^+$ $\longrightarrow$ RCH(NH$_3^+$)COOH + H$_2$O

(vii) $[OH^-]$ at 30 cm^3 = $\dfrac{10 \times 1.00}{(10+30)}$ [1]

= 0.250 mol dm^{-3}

pOH = 0.60

pH = 13.4

(d) The $-CO_2^-$ group formed from dissociation of α–CO_2H is closer to the electron withdrawing NH_3^+ group. This disperses the negative charge of the anion to a greater extent and further stabilises the anion. Thus, the ionisation of H^+ is more favoured for the α–CO_2H. [2]

[1]: closer to EW $-NH_3^+$

[1]: greater dispersal of negative charge and stabilisation of conjugate base/anion

ANDERSON JUNIOR COLLEGE

2018 JC 2 PRELIMINARY EXAMINATIONS

NAME:__________________________ **PDG:**____ /17

CHEMISTRY **9729/02**

Paper 2 Structured Questions **12 September 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 2	1	/ 12
	2	/ 13
	3	/ 14
	4	/ 17
	5	/ 19
Total		/ 75

This document consists of **18** printed pages.

Answer **all** the questions.

1 **(a)** **(i)** Write an equation to show the thermal decomposition of Group 2 metal carbonate, MCO_3.

…………………………………………………………………………………………………..[1]

(ii) Describe and explain the trend in the thermal stabilities of the carbonates of magnesium, calcium and barium.

………………………………………………………………………………………………......

………………………………………………………………………………………………......

………………………………………………………………………………………………......

…………………………………………………………………………………………………..[2]

(b) MixAlco^{TM} process is a patented technology that converts biodegradable material into mixed alcohol fuels.

This process first uses an anaerobic, mixed–culture fermentation to convert lignocellulosic biomass to carboxylate salts. These salts are then concentrated by evaporation and thermally decomposed at 450 ^{o}C into its corresponding carbonyl compounds.

The following shows the thermal decomposition of a carboxylate salt, calcium ethanoate.

$$Ca(CH_3CO_2)_2 \longrightarrow CaCO_3 + (CH_3)_2CO$$

(i) Draw a dot–and–cross diagram to show the bonding in ethanoate ion, $CH_3CO_2^-$. In your diagram use the symbols '•' and 'x' to distinguish electrons from the central atoms and those from the outermost atoms, and the symbol '□' for any additional electrons responsible for the overall negative charge.

[1]

(ii) Hence, suggest the shape with respect to **each** of the two carbon atoms in $CH_3CO_2^-$.

Shape with respect to $\mathbf{C}H_3CO_2^-$: ………………………………………………..

Shape with respect to $CH_3\mathbf{C}O_2^-$: ……………………………………………….. [2]

(iii) Suggest the organic product formed when a sample of $Ca(CH_3CH_2CO_2)_2$ undergoes the same decomposition.

[1]

(iv) In one such MixAlco™ process, three organic compounds are obtained from a 1 : 1 molar mixture of $Ca(CH_3CH_2CO_2)_2$ and $Ca(CH_3CO_2)_2$.

On purification, only two of the organic compounds, **A** and **B** give yellow precipitate with aqueous alkaline iodine. The mole ratio of **A** and **B** formed is 2 : 1.

Draw the structural formulae of **A** and **B**.

A	**B**

[2]

(c) Two samples of carboxylate salt, **C** and **D**, each containing either manganese(II) ethanoate or lead(II) ethanoate, were heated strongly.

For both samples, a solid residue and a gaseous product which gave a yellow precipitate with 2,4–dinitrophenylhydrazine were obtained. Only sample **C** gave another colourless gas which turned limewater cloudy.

By quoting suitable data from the *Data Booklet*, explain which of the samples, **C** or **D**, contains manganese(II) ethanoate.

Sample: ………………………..

Explanation: ……………………………………………………………………………………..

………………………………………………………………………………………………….

………………………………………………………………………………………………….

………………………………………………………………………………………………….[3]

[Total: 12]

2 *Use of the Data Booklet is relevant to this question.*

(a) Transition metals form complexes with different co–ordination numbers. Explain what is meant by the *co–ordination number* of a complex.

……………………………………………………………………………………………………..

……………………………………………………………………………………………………[1]

(b) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

Table 2.1 below shows the relative paramagnetism of aqua complexes of vanadium in two different oxidation states.

Table 2.1

formula of complex	**relative paramagnetism**
$[V(H_2O)_6]^{2+}$	3
$[V(H_2O)_6]^{3+}$	2

(i) Explain why transition metals can show variable oxidation states.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………[2]

(ii) With reference to the electronic configurations of vanadium in the two complexes, suggest an explanation for the difference in the relative paramagnetism of the complexes in Table 2.1.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………[2]

(c) Vanadium(IV) ions, VO^{2+}, are also paramagnetic.

Two reactions were carried out to investigate the changes in paramagnetism of a solution **F** containing 0.010 mol VO^{2+} ions.

Reaction 1
A sample of solution **F** is found to react completely with an acidified solution containing 0.0020 mol of $KMnO_4$.

Reaction 2
Another sample of solution **F** is reduced by 0.0050 mol of Sn^{2+}(aq).

(i) Using the data provided, deduce the final oxidation states of vanadium in the **Reaction 1** and **Reaction 2**. Show your working clearly.

[2]

(ii) Hence suggest the changes in the paramagnetism of solution **F** in **Reaction 1** and **Reaction 2**. Explain your answers.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(d) Paramagnetism is also observed in complexes of nickel. Nickel forms many complexes with a co–ordination number of 4. Complexes with a co–ordination number of 4 can take on either the tetrahedral or the square planar geometry.

Table 2.2 shows the relative paramagnetism of two nickel complexes with **different** geometry, which contain Ni^{2+} ion with a co–ordination number of 4.

Table 2.2

formula of complex	**relative paramagnetism**
$[NiCl_4]^{2-}$	2
$[Ni(CN)_4]^{2-}$	0

Fig. 2.1 shows how the d–orbitals of a transition metal ion such as nickel are split in complexes with these two different geometry.

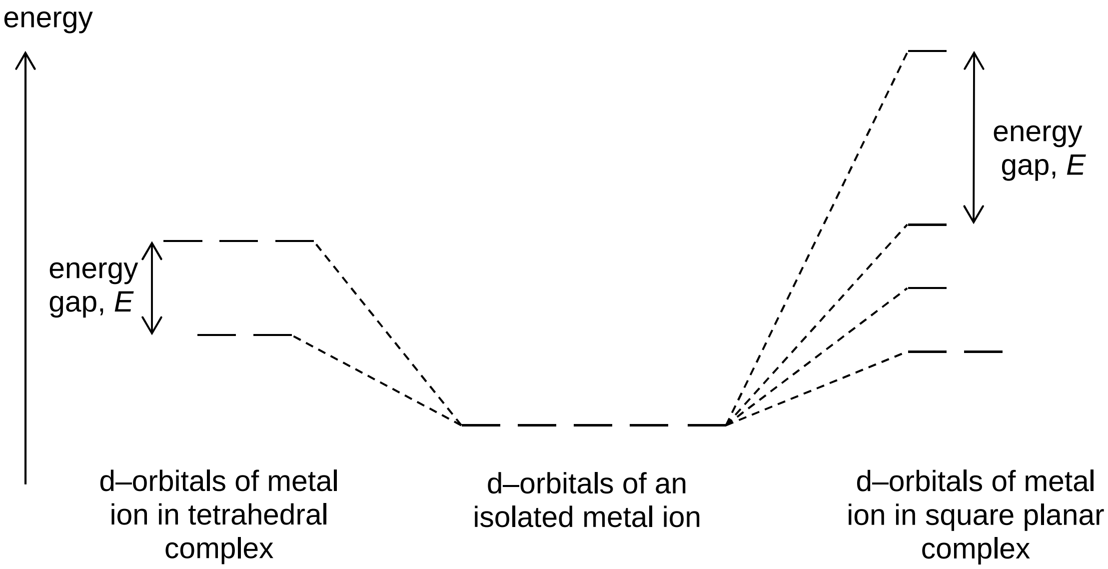


Fig. 2.1

The distribution of electrons in the d–orbitals of the transition metal ion depends on the spin state of the complex.

In a ‘high spin’ state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

In a ‘low spin’ state, the lower energy d–orbitals are filled first, by pairing up if necessary, before the higher energy d–orbitals are used.

The different distribution of electrons in the two spin states in the two complexes of nickel above give rise to different number of unpaired electrons, hence the observed relative paramagnetism.

Using the information and Fig. 2.1 given on page 6, deduce the geometry of the two nickel complexes and the spin state of Ni^{2+} in $[Ni(CN)_4]^{2-}$.

formula of complex	**geometry of complex**	**spin state of Ni^{2+} in complex**
$[NiCl_4]^{2-}$		▨
$[Ni(CN)_4]^{2-}$		

[2]

(e) Nickel(II) chloride forms a 4–coordinated complex, $Ni(R_3P)_2Cl_2$, with the monodentate organic ligand, triethylphosphine (where R = CH_3CH_2–). The complex can occur in two forms, **G** and **H**, where **G** has an overall dipole and **H** has none.

Draw the structures of **G** and **H** to account for the difference in their dipole moment.

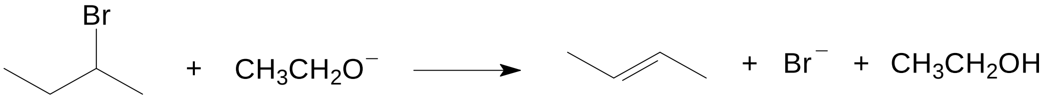
G	**H**

[2]

[Total: 13]

3 The presence of lone pair of electrons on the oxygen atom of alkoxides (RO^-) enables them to act either as a base or a nucleophile in organic reactions.

(a) 2–bromobutane reacts with CH_3CH_2ONa in ethanol according to the following equation.



(i) Name the type of reaction that occurred.

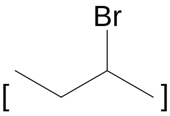
……………………………………………………………………………………………….[1]

(ii) Explain why $CH_3CH_2O^-$ behaves as a Lewis base in the above reaction.

……………………………………………………………………………………………….[1]

(iii) The kinetics of this reaction was studied and Table 3.1 contains the experimental results obtained.

Table 3.1

experiment	[ Br] / mol dm^{-3}	[$CH_3CH_2O^-$] / mol dm^{-3}	relative initial rate
1	0.060	0.060	1.00
2	0.050	0.060	0.833
3	0.040	0.050	0.667

Use the data given above to deduce the rate law.

[3]

(iv) Hence, propose a mechanism for the above reaction given that the reaction proceeds via the following 2 steps.

- rate–determining step yields a carbocation,
- followed by acid–base reaction between H in the carbocation and $CH_3CH_2O^-$.

Describe the mechanism using the above information, including curly arrows to show the movement of electrons and all charges.

[2]

(v) Explain how the rate of reaction will be affected when 2–chlorobutane is used instead of 2–bromobutane.

…………………………………………………………………………………………………......

…………………………………………………………………………………………………......

………………………………………………………………………………………………...[2]

(b) The reaction of 2–bromobutane with CH_3CH_2ONa in ethanol also produced a racemic mixture of an organic by–product. The by–product has the molecular formula of $C_6H_{14}O$. It did not give white fumes when reacted with anhydrous phosphorus pentachloride.

(i) Name the type of reaction 2–bromobutane undergone.

……………………………………………………………………………………………..[1]

(ii) With reference to the mechanism you have described in **(a)(iv)**, suggest how the racemic mixture was formed.

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………..[1]

(iii) Draw the structures of the organic by–product present in the racemic mixture, showing their isomerism.

[2]

(iv) Quaternary carbon stereocentres are carbon atoms with four distinct carbon substituents attached. These carbon stereocentres are common features of molecules found in nature. However, production of such compounds provide a daunting challenge for chemical synthesis because a racemic mixture is often obtained.

Recently, researchers at Harvard University made use of a novel catalyst to overcome this concern. This method promotes the formation of a carbocation and binds the catalyst to one side of the carbocation.

Suggest why this method can overcome the challenge and forms only an enantiomer with specific optical activity.

……………………………………………………………………………………………......

……………………………………………………………………………………………..[1]

[Total: 14]

4 Both nitrogen and phosphorus are Group 15 elements.

(a) **(i)** Describe and explain the general trend in first ionisation energies down a group.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………...[2]

(ii) Give the full electronic configuration of phosphorus and draw the shapes of the two types of occupied valence orbitals.

electronic configuration of P: ………………………………………………………………

[2]

(b) Under standard conditions, nitrogen exists as diatomic gas, N_2, while phosphorus occurs in one of a number of forms, including 'white' phosphorus, P_4 which contain **six** P–P single bonds.

Some of the physical properties of the compounds of nitrogen and phosphorus are also different. For example, ammonia, NH_3, is thermally stable, whereas phosphine, PH_3, is unstable to heat. Upon heating, gaseous PH_3 decomposes to give gaseous 'white' phosphorus, P_4 and hydrogen gas.

(i) Write the balanced equation for the thermal decomposition of one mole of PH_3.

…………………………………………………………………………………………….[1]

(ii) Use the bond energies given in the *Data Booklet*, determine the enthalpy change of the above reaction.

[2]

(iii) Draw arrows on the energy diagram below to show each of the energy terms involved in the steps you have used in your calculations in **(b)(ii)**.

Label each level with the appropriate formulae.

[2]

The thermal decomposition of phosphine is a first–order reaction. The half–life of the reaction is 35.0 s at 680 ^{o}C.

(iv) Calculate the rate constant for this reaction and state its units.

[2]

(v) Estimate the time taken for the gaseous phosphorus to reach 99% of its expected concentration.

[1]

(c) Free volume, *V*, refers to the **volume of space** between gas molecules. For an ideal gas, free volume is essentially the same as the volume of the container and can be calculated using the ideal gas equation.

$$pV = nRT$$

(i) Under what conditions of temperature and pressure would you expect the behaviour of a real gas to be most like that of an ideal gas?

……………………………………………………………………………………………[1]

(ii) The pressure of a gaseous sample of 36.0 g of phosphine, PH_3, in a container of volume 400 cm^3 is measured to be 1.34×10^7 Pa at 327 ^oC.

Using the ideal gas equation, calculate the free volume of this gaseous sample. Express your answer in cm^3.

[2]

(iii) Explain, in terms of the properties of PH_3 molecules, why the volume you have calculated in **(c)(ii)** differs from that of the volume of the container.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

[Total: 17]

5 **(a)** Amino acids are the building blocks of protein in our body. Our body can synthesise certain amino acids, but others, called essential amino acids, must come from protein–containing foods in our diet. These essential amino acids are histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine.

Protein is required to build, repair and maintain muscle tissue. According to dieticians, the amount of protein for any one individual depends on many factors, including their activity level, age, muscle mass, physique goals and current state of health. Table 5.1 shows the recommended daily intake for protein a sedentary person, a marathoner and a bodybuilder of the same age needs given that all other factors are the same.

Table 5.1

	Recommended Daily Intake for Protein (g / kg of body weight)
Sedentary person	0.8
Marathoner	1.4
Bodybuilder	1.8

Many athletes and bodybuilders also choose to add a protein supplement to their diets to increase their protein intake. Whey protein powder is a widely available protein supplement which typically consists 80% protein by weight with small amounts of carbohydrate and fat. The nutritional information of a particular brand of whey protein powder is shown in Fig. 5.1 below.

Serving Size – 1 scoop (25 g)

Servings Per Container – 40 (1 kg), 100 (2.5 kg), 200 (5 kg)

Nutritional Information

	Per 100 g	**Per Serving**
Energy	1740 kJ	435 kJ
Fat	7.5 g	1.9 g
of which saturates	5.0 g	1.3 g
Carbohydrates	4.0 g	1.0 g
of which sugars	4.0 g	1.0 g
Protein	84 g	21 g
Salt	0.50 g	0.13 g

Fig. 5.1

(i) State the reagents and conditions required to hydrolyse a protein non–enzymatically.

……………………………………………………………………………………………[1]

(ii) Calculate the recommended daily intake of protein for a marathoner who is 65 kg.

[1]

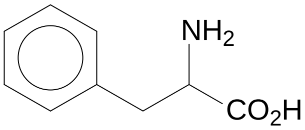
(iii) Use information from Fig 5.1 to calculate the mass of whey protein powder that the marathoner will need to consume in a day to meet the recommended daily intake of protein.

[1]

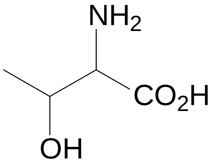
(iv) Given that the whey protein powder contributes 20 % of the total daily energy intake of the marathoner, calculate the amount of energy contributed by his other food sources.

[1]

(v) Suggest a simple chemical test to distinguish between phenylalanine and threonine. Describe your observations.



phenylalanine



threonine

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………[2]

Branched Chain Amino Acids (BCAAs) are the essential amino acids consisting of leucine, isoleucine and valine. BCAAs supplements usually offers a 2 : 1 : 1 ratio of leucine to isoleucine and valine, which is an effective combination for performance, muscle maintenance and growth benefits.

(b) Valine, an important BCAA, can be produced using the Strecker amino–acid synthesis. This is a series of chemical reactions that converts an aldehyde into an α–amino acid. The synthesis of valine, shown in Fig. 5.2, is thought to proceed through the following stages.

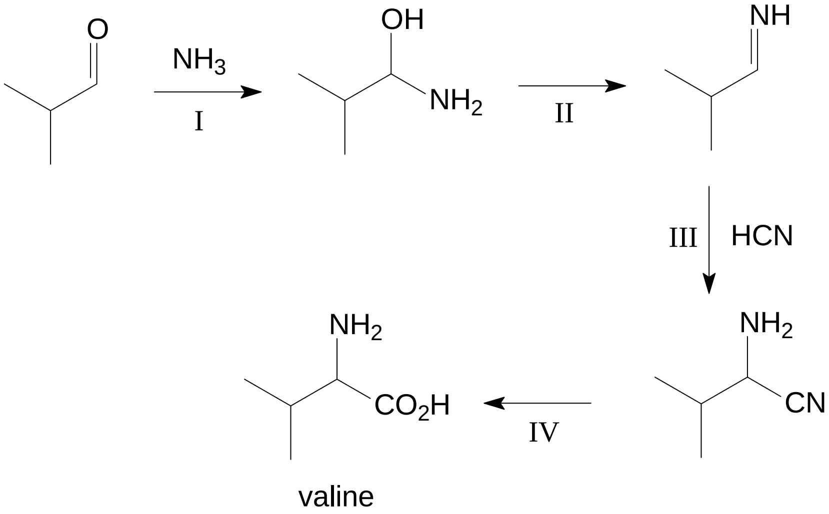


Fig. 5.2

(i) State the type of reaction in steps I and IV.

Step I: …………………………………………………………………………………...

Step IV: …………………………………………………………………………………[2]

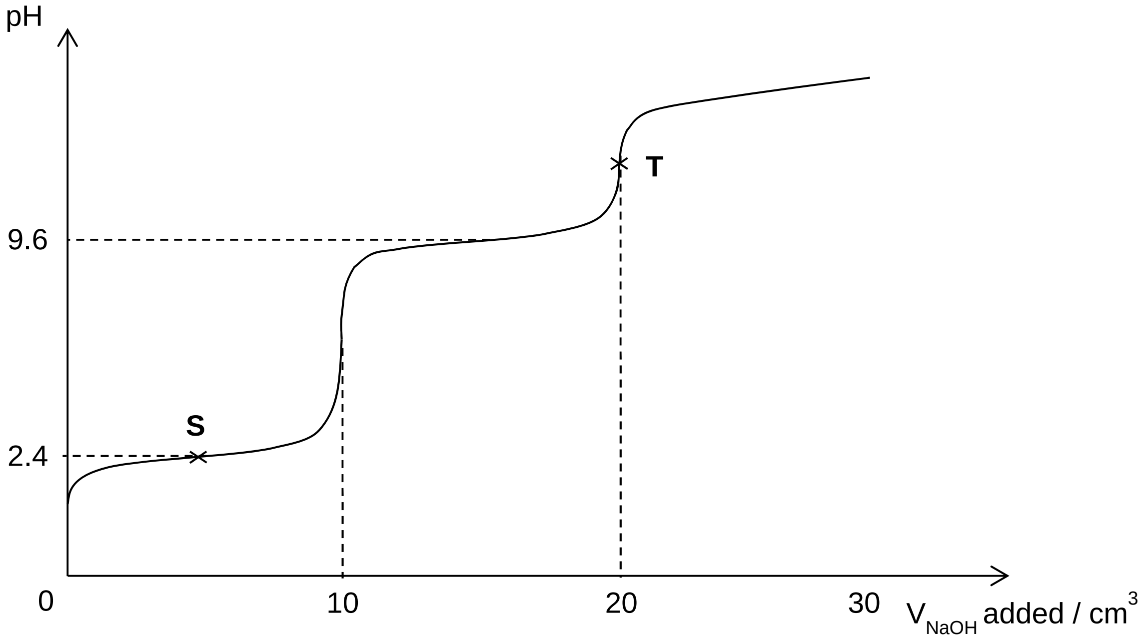
(ii) Suggest the **skeletal** formula of the starting compound if leucine is to be synthesised via the Strecker synthesis.

$(CH_3)_2CHCH_2CH(NH_2)CO_2H$
leucine

[1]

(c) There are two K_a values associated with the fully protonated form of leucine, $(CH_3)_2CHCH_2CH(NH_3^+)CO_2H$.

When 10.0 cm^3 of 1.00 mol dm^{-3} $(CH_3)_2CHCH_2CH(NH_3^+)CO_2H$ is titrated with 30 cm^3 of 1.00 mol dm^{-3} NaOH(aq), the following pH–volume added graph is obtained. You may represent the structure of protonated leucine as $RCH(NH_3^+)CO_2H$ in your answers.



(i) Show that the K_{a2} of leucine is equal to 2.5 x 10^{-10} mol dm^{-3}.

[1]

(ii) Write an equation to explain why the pH of the solution is above 7 at point **T**.

…………………………………………………………………………………………………[1]

(iii) Hence, calculate accurately the pH of the solution at point **T**.

[2]

(iv) Indicate, with an "X", the isoelectric point of leucine on the graph on page 17. [1]

(v) Identify all the organic species present at point **S**.

[1]

(vi) Hence, with the aid of an equation, explain how the solution at **S** can resist a change in pH when a small amount of acid is added.

……………………………………………………………………………………………[1]

(vii) Determine the final pH of the solution after 30 cm^3 of NaOH(aq) was added.

[1]

(d) Glutamic acid is an example of an amino acid that can be synthesised by your body and so is not essential to the human diet.

There are three pK_a values associated with glutamic acid: 2.2, 4.3 and 9.7. Starting with the fully protonated form, glutamic acid undergoes the first two stages of dissociation as shown in Fig. 5.3.

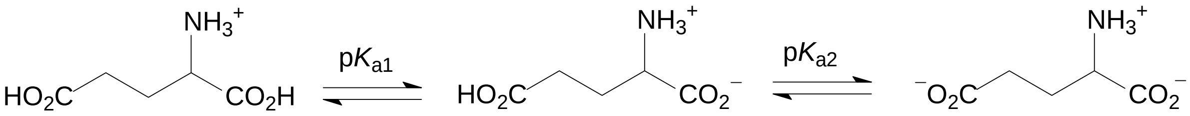


Fig. 5.3

Explain why the α–CO_2H dissociates in preference to the *R* group–COOH in the first stage of dissociation.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

[Total: 19]

Anderson Junior College
H2 Chemistry 9729 **2018 JC2 Prelim Paper 3 Suggested Solutions**

1 **(a)** **(i)** $E^{\ominus}_{cell} = 0.00 - (+1.50)$ [1]
$= -1.50\text{ V} < 0$, hence reaction is not spontaneous.

(ii) [R] $NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$ [1]
[O] $Au \longrightarrow Au^{3+} + 3e^-$

$$\mathbf{3NO_3^- + Au + 6H^+ \longrightarrow Au^{3+} + 3NO_2 + 3H_2O}$$

(iii) $Au \rightleftharpoons Au^{3+} + 3e$ —— (1) [2]

$Au^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons AuCl_4^-(aq)$ —— (2)

Due to the formation of chloroaurate(III) anions ($AuCl_4^-$) in equilibrium (2), the Au^{3+} ions are constantly removed from solution, keeping $[Au^{3+}]$ low causing position of equilibrium for equilibrium (1) to shift right.

[1]: equations showing formation of $AuCl_4^-$
[1]: explanation

(b) Amount of gold $= \dfrac{4 \times 2.18 \times 10^6}{197.0}$
$= 4.424 \times 10^4$ mol [1]

Amount of SO_2 needed $= 4.424 \times 10^4 \times \dfrac{3}{2}$
$= 6.636 \times 10^4$ mol [1] ecf

Min. volume of SO_2 needed $= 6.636 \times 10^4 \times 24.0$ [1]
$= 1.59 \times 10^6\text{ dm}^3$ ecf

(c) **(i)** linear shape [1]

(ii) $AuCl_4^-$: d^8 configuration for Au(III) [4]
In the presence of Cl^- ligands, the partially filled 3d orbitals of Au are split into two levels (non–degenerate) with a small energy gap (d orbital splitting).
When light passes through, energy is absorbed and an electron in a lower energy d–orbital is promoted to a higher energy d–orbital. (d–d transition).
The colour of the solution is the complementary colour of the light absorbed.

$Au(CN)_2^-$: d^{10} configuration / fully filled d subshell
has energy gap but no vacant higher E d orbital for d–d transition.

[1]: partially filled 3d–orbital for $AuCl_4^-$; small energy gap
[1]: d–d transition
[1]: fully filled 3d–orbital for $Au(CN)_2^-$
[1]: no d–d transition

(d) **(i)** It undergoes decomposition to form gaseous products which escape from solution, making it irreversible. As the concentration of the acids / Cl^- ions drop, aqua regia is unable to react with the metals effectively. [1]

(ii) Refer to graph [2]

[1]: correct axes and labels: conc. of NOC*l* / molecule cm^{-3} vs time / s
[1]: correctly plotted points

(iii) Rate when conc. of NOC*l* = 1.5×10^{23} molecule cm^{-3} [2]

$$\text{Gradient of tangent} = \frac{1.5 \times 10^{23}}{3.7 \times 10^{3}}$$
$$= 4.05 \times 10^{19} \text{ molecule cm}^{-3}\text{ s}^{-1}$$

Rate when conc. of NOC*l* = 0.75×10^{23} molecule cm^{-3}

$$\text{Gradient of tangent} = \frac{1.2 \times 10^{23}}{11.0 \times 10^{3}}$$
$$= 1.09 \times 10^{19} \text{ molecule cm}^{-3}\text{ s}^{-1}$$

When conc. of NOC*l* is doubled, rate is approximately quadrapled.
Rate of reaction is directly proportional to (conc. of NOC*l*)^2
Order of reaction wrt NOC*l* is $\underline{2}$

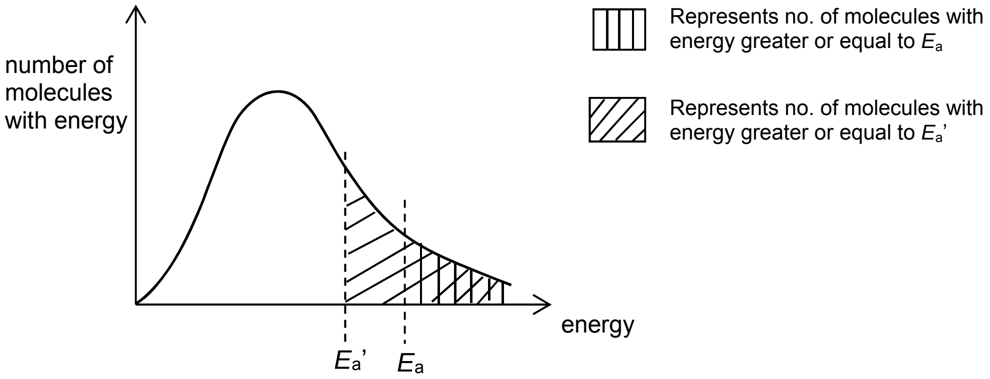
[1]: find rate at 2 different points
[1]: conclude that rate α [NOC*l*]^2

(iii) Rate = k [NOC*l*]^2 [2]

$$k = \frac{\text{rate}}{[\text{NOC}l]^2}$$
$$= \frac{4.05 \times 10^{19}}{(1.5 \times 10^{23})^2}$$
$$= \underline{1.80 \times 10^{-27} \text{ molecule}^{-1}\text{ cm}^3\text{ s}^{-1}}$$
$$= \frac{1.80 \times 10^{-27}}{1000} \times 6.02 \times 10^{23}$$
$$k = \underline{1.08 \times 10^{-6} \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}}$$

[1]: k in terms of molecules^{-1} cm^3 s^{-1} / find rate and conc. in terms of mol
[1]: k in terms of mol^{-1} dm^3 s^{-1}

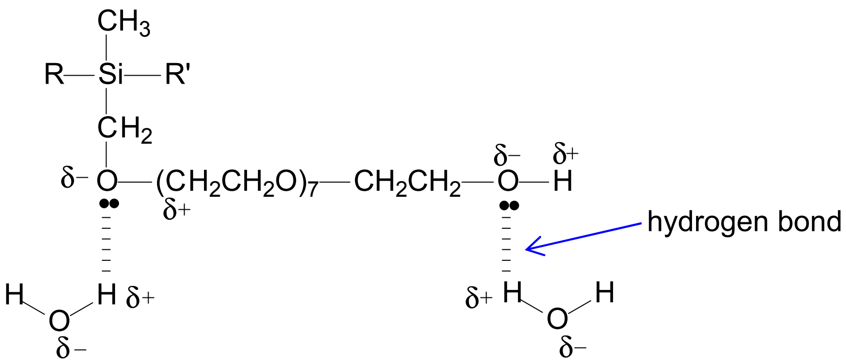
(iv) [2]



NO_2 speeds up the rate of decomposition by providing a <u>different/alternative reaction path</u> which has <u>lower activation energy</u>.
As shown on the diagram, the <u>number of NOC*l* molecules with energy greater or equal to the lowered activation energy</u> (E_a') will <u>increase</u>.
This results in an <u>increase</u> in the <u>frequency of effective collisions</u>.
Hence, the <u>rate of decomposition increases</u>.

[1]: correct axes, shape of graph (including beginning from origin) and correct shift of E_a
[1]: different reaction path with lower E_a and explanation (in terms of more molecules with energy $\geq E_a$' and frequency of effective collision increase)

2 (a) (i) [1]



[1]: polarised O–H bond, lone pair of electrons on oxygen (can be on O of H_2O) and correct atoms involved in hydrogen bonding

Sufficient to show one site for hydrogen bonding

(ii) The non–polar alkyl groups of molecule **B** forms weak instantaneous dipole–induced dipole attraction with the non–polar oil droplets.
The polar groups of molecule **B** can form hydrogen bonds with / attracted to the water molecules. [2]

Hence the dispersant can dissolve in both oil and water easily. This allows the oil to be broken down into smaller droplets and be removed more easily.

[1]: types of interactions molecule **B** form with oil and water
[1]: recognise that it can dissolve in both

(b) (i) giant molecular structure [1]

(ii) From carbon to germanium, (less energy) is required to break the decreasing strength of covalent bonds between atoms due to the decreasing bond energy / increasing atomic radius of the atom down the group. [1]

(iii) C is from period 2. It does not have energetically accessible d orbitals to accept lone pair of electrons from water molecules to form dative bonds. [1]
OR
The four large chlorine atoms shield the small carbon atom from the water molecules, making it difficult (high E_a) for the water nucleophile to attack the electrophilic C atom. (steric hindrance)

(accept explanation in terms of Si)

(iv) $GeCl_4 + 2H_2O \longrightarrow GeO_2 + 4HCl$ [2]
$GeCl_4 + 4H_2O \longrightarrow GeO_2.2H_2O + 4HCl$
$GeCl_4 + 2H_2O \longrightarrow Ge(OH)_4 + 4HCl$

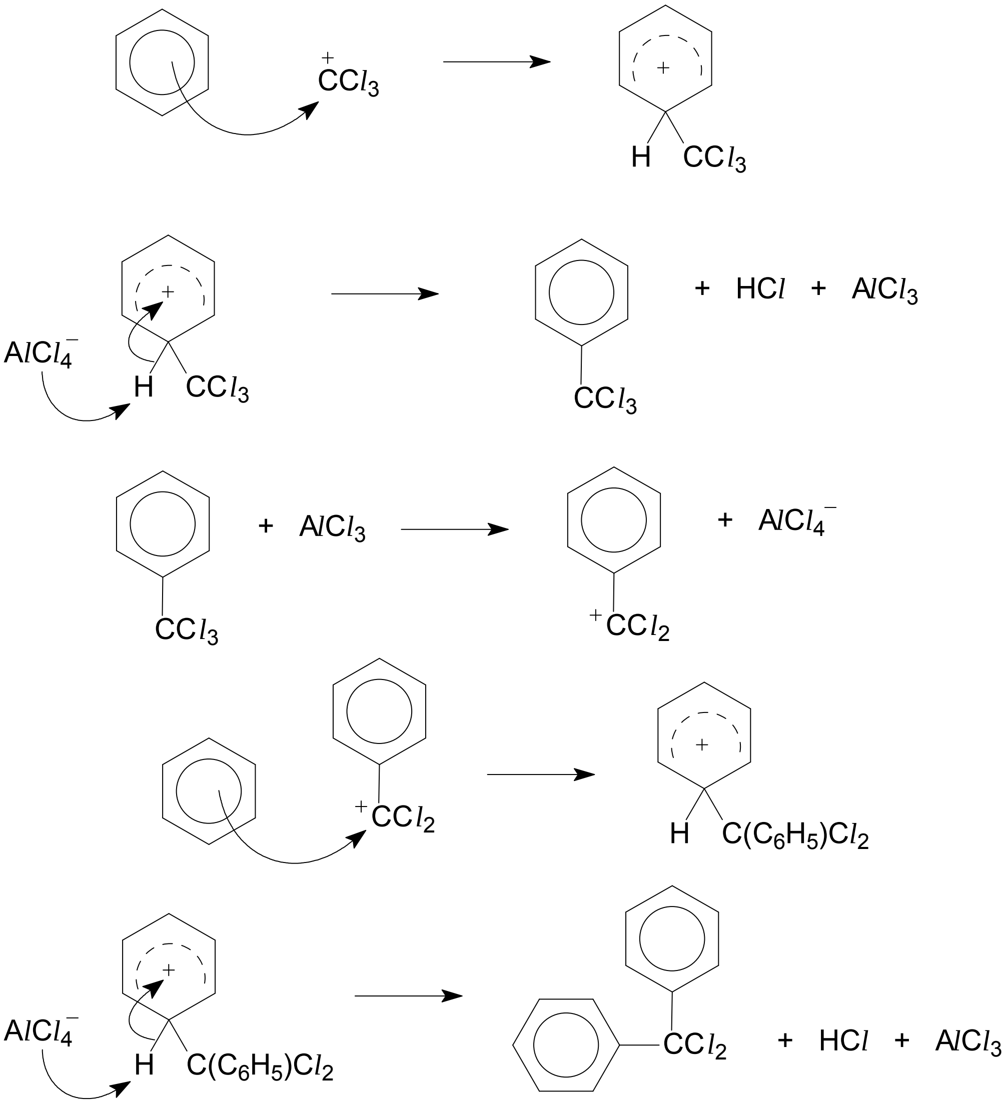
Universal Indicator solution turned red (~pH 1)

[1]: any 1 equation
[1]: observation

(c) (i) $AlCl_3$ hydrolyses in water, resulting in absence of catalyst to generate electrophile for Friedel–craft alkylation to take place. [1]

(ii) electrophilic substitution [4]

$$CCl_4 + AlCl_3 \longrightarrow \overset{+}{C}Cl_3 + AlCl_4^-$$



[1]: name of mechanism

(correct for at least one complete ES mechanism for each of the following)

[1]: charges and intermediates

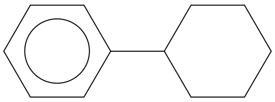
[1]: lone pairs and curly arrows

[1]: generation of electrophile and regeneration of catalyst

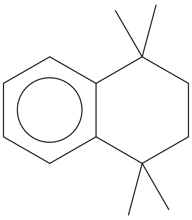
(iii) The two large phenyl groups bonded to the small carbon atom repel the 3rd phenyl group from attacking the electrophilic C atom. (steric hindrance) [1]

(accept stability of the electrophile generated due to resonance, resulting in larger E_a for further alkylation)

(iv) [2]

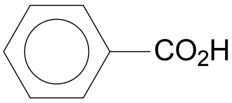


A

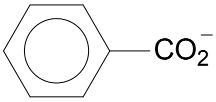


B

(v) KMnO$_4$, dil H$_2$SO$_4$ / NaOH(aq), heat [2]
A will decolourise purple KMnO$_4$. Purple KMnO$_4$ remains for **B**.



/



formed for **A**.

[1]: reagent and condition
[1]: structure of product

(vi) The <u>triphenylmethyl cation</u> generated is <u>relatively unreactive / weak electrophile</u>, [1]
due to extensive resonance charge delocalisation,
and hence can only substitute <u>highly activated aromatic rings</u> like phenol. [1]

3 **(a)** **(i)** from sp in **C**O_2 to sp^2 in R**C**O_2^- [1]

(ii) acid–base reaction [1]

(iii) **CH_3CO_2H** [1]

(iv) **$C_4H_6O_3$** [1]

FYI
F is $(CH_3CO)_2O$

(b) **(i)** Intramolecular hydrogen bonding between –OH and –CO_2H groups, resulting in less energy required to break the less extensive intermolecular hydrogen bonding between salicylic acid molecules
hence, lower m.p. [2]

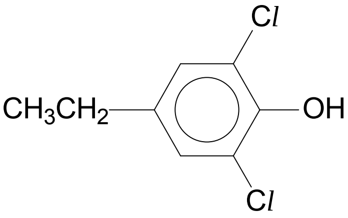
(accept explanation in terms of better packing (denser) for 4–hydroxybenzoic acid due to its more linear shape and larger surface area for id–id interactions)

[1]: recognise intramolecular hydrogen bonding result in less extensive intermolecular hydrogen bonding
[1]: less energy to overcome IMF

(ii) Salicylic acid has a lower pK_a, higher K_a / is a stronger acid than 4–hydroxybenzoic acid
Intramolecular hydrogen bonding helps to disperse the negative charge on the conjugate base, stabilising it to a greater extent. [2]

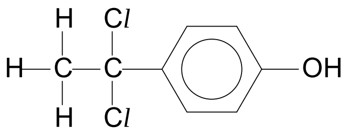
[1]: relationship between pK_{a1} and K_{a1} / strength of acid
[1]: recognise intramolecular hydrogen bonding in stabilising monoanion

(c) **(i)** [1]

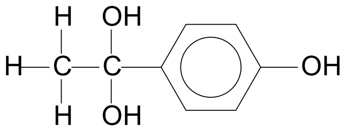


(ii) **P** is more acidic [1]
Presence of electron–withdrawing C*l* groups help to disperse the negative charge of the conjugate base and stabilising it to a greater extent. [1]

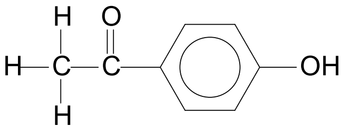
(iii) [5]



Q



R



S

[1] each correct structure

Q can undergo nucleophilic substitution with NaOH(aq) because the C*l* atoms are bonded to sp^3 C atom / it is a chloroalkane. **R** is a diol.

R undergoes elimination to form **S**. **S** is an aldehyde / ketone.

The phenolic group in **S** reacts with NaOH(aq) (acid–base reaction) to form an ionic salt and hence is soluble.

S is a ketone and undergoes condensation reaction with 2,4–DNPH but does not react with Tollens' reagent because it is not an aldehyde.

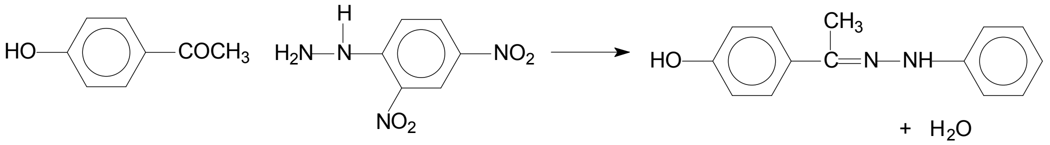
S gives a yellow precipitate with I_2(aq)/OH^-(aq) (oxidation) because it contains the CH_3COR structure.

OR

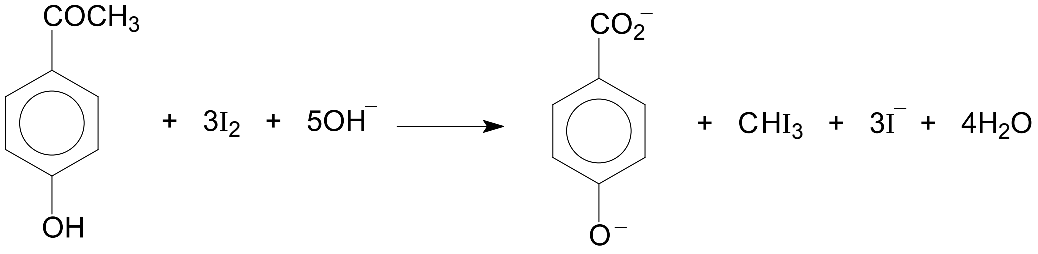
Observation	Type of reaction	Deduction
Compound **Q** reacts with NaOH(aq), followed by acidification, to give **R**, $C_8H_{10}O_3$.	nucleophilic substitution	**Q** is a chloroalkane / contains C*l* atoms bonded to sp^3 C atom. **R** is a diol.
R immediately loses water to form **S**, $C_8H_8O_2$.	elimination (of H_2O)	**S** is an aldehyde / ketone.
Compound **S** is insoluble in water but it dissolves in NaOH(aq).	acid–base reaction	**S** contains phenol or carboxylic acid group.
S reacts with 2,4–DNPH but not with Tollens' reagent.	condensation	**S** contains ketone group.
S reacts with alkaline aqueous iodine	oxidation	**S** contains $RCOCH_3$.

[2]: 8–11 points
[1]: 4–8 points

(iv) between **S** and 2,4–dinitrophenylhydrazine [1]



between **S** and alkaline aqueous iodine [1]



(v) presence of light / uv light [1]

4 **(a)** **(i)** anode: $2NH_3 + 6OH^- \longrightarrow N_2 + 6H_2O + 6e^-$ [2]

cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

(ii) $4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$ [1]

for 1 mol of NH_3,

$$\mathbf{NH_3 + \frac{3}{4}O_2 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2O}$$

(iii) $\Delta G^\ominus = -nFE^\ominus_{cell}$ [2]

$-339 \times 1000 = -(3)(96500)E^\ominus_{cell}$

$E^\ominus_{cell} = \underline{+1.17\text{ V}}$

(iv) $E^\ominus_{cell} = E^\ominus_{O_2/OH^-} - E^\ominus_{N_2/NH_3}$ [1]

$+1.17 = 0.40 - E^\ominus_{N_2/NH_3}$

$E^\ominus_{N_2/NH_3} = \underline{-0.77\text{ V}}$

(v) Ammonia is a weak <u>base</u>, will <u>react readily</u> with the <u>acidic membrane</u> to form salts, which increases the resistance of the cell rapidly. [1]

(b) **(i)** $K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$ mol² dm⁻⁶ [2]

[1]: correct expression

[1]: correct units

(ii) [2]

	$2NH_3(g)$	$\rightleftharpoons$	$N_2(g)$	+	$3H_2(g)$
initial amt / mol	2.0		0.5		0
change in amt / mol	*–1.4*		*+0.7*		*+2.1*
eqm amt / mol	0.6		1.2		2.1

$[NH_3] = \frac{0.6}{2} = \underline{0.3\text{ mol dm}^{-3}}$

$[N_2] = \frac{1.2}{2} = \underline{0.6\text{ mol dm}^{-3}}$

$[H_2] = \frac{2.1}{2} = \underline{1.05\text{ mol dm}^{-3}}$

[2]: all 3 concentrations are correct

[1] any one concentration

(iii) [1] ecf

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{0.6(1.05)^3}{(0.3)^2} = \underline{7.72}\text{ mol}^2\text{ dm}^{-6}$$

(can give credit for correct units if missing in **(i)**)

(iv) $\Delta G^\ominus = -(8.31)(670) \times \ln(7.72)$ [1]

$= \underline{-11400\text{ J mol}^{-1}}$

(v) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ [2]

$-11.4 = +92 - (670)\Delta S^\ominus$

$\Delta S^\ominus = +0.154\ \text{kJ mol}^{-1}\ \text{K}^{-1}$

$= +154\ \text{J mol}^{-1}\ \text{K}^{-1}$

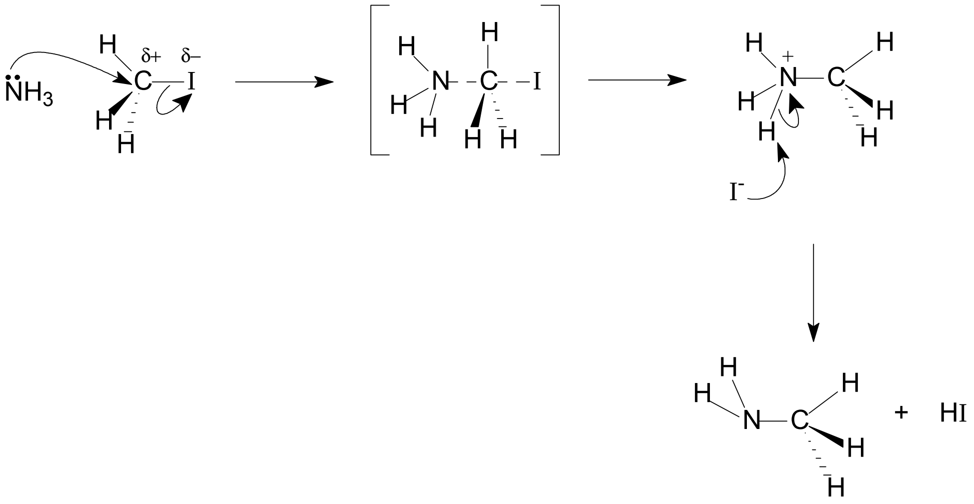
Entropy change for the reaction is positive, indicating an increase in ways of distributing energy as seen from the equation given where there is an increase in number of moles of gaseous particles.

[1]: $\Delta S^\ominus$, include units
[1]: explaining link between entropy change and disorder of reaction

(vi) Partial pressures of all gases decrease, [1]
Reaction results in greater number of moles of gaseous products and hence, a greater decrease in partial pressure on the products side,
the position of equilibrium shifts right to minimise the increased in volume.

However, as there is no change in temperature**,** K_p remains constant. [1]

(c) Bimolecular nucleophilic substitution (S_N2) [3]



[1]: type of reaction
[1]: correct dipoles and lone pair AND curly arrows to show all the relevant bond breaking/formation (ignore if missing for the last step)
[1]: correct structures for transition state, positively charged amine salt and final product

5 **(a)** [3]

$$\begin{tikzcd}
(+\ 3/2O_2)\ CO_2(g) + 3H_2(g) \arrow[r, "\Delta H^{\ominus}_{I}"] \arrow[d, "3 \times (-286)"'] & CH_3OH(g) + H_2O(g)\ (+\ 3/2O_2) \\
CO_2(g) + 3H_2O(l) & CH_3OH(g) + H_2O(l)\ (+\ 3/2O_2) \arrow[l, "-768"'] \arrow[u, "+40.8"']
\end{tikzcd}$$

By Hess' Law,

$\Delta H^{\ominus}_{I} = 3(-286) - (-768) + 40.8$

$= \underline{-49.2 \text{ kJ mol}^{-1}}$

[1]: correct conversion with correct state symbols (ignore balancing equation)
[1]: correct enthalpy change values (i.e. multiply with correct factors)
[1]: correct answer

(b) **(i)** anode: $\mathbf{CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-}$ [2]
cathode: $\mathbf{O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O}$

[1] each correct half–equations

(ii) Alkaline electrolyte reacts with (acidic) carbon dioxide produced to form an insoluble carbonate which degrades the fuel cell and leads to poor performance. [1]

(iii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$ [1]

$= -(6)(96500)(1.18)$

$= \underline{-683\ 000 \text{ J mol}^{-1}}$

(iv) $CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ [1]

$\Delta H^{\ominus}_{r} = [(-394) + 2(-286)] - (-238)$

$= \underline{-728 \text{ kJ mol}^{-1}}$

(v) $\Delta G^{\ominus}_{r} = \Delta H^{\ominus}_{r} - T\Delta S^{\ominus}_{r}$ [1]

$(-683) = (-728) - 298\Delta S^{\ominus}_{r}$

$\Delta S^{\ominus}_{r} = -0.151 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$= \underline{-151 \text{ J mol}^{-1} \text{ K}^{-1}}$

(vi) At 25 °C, $CH_3OH\mathbf{(l)} + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ [2]

At 80 °C, $CH_3OH\mathbf{(g)} + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

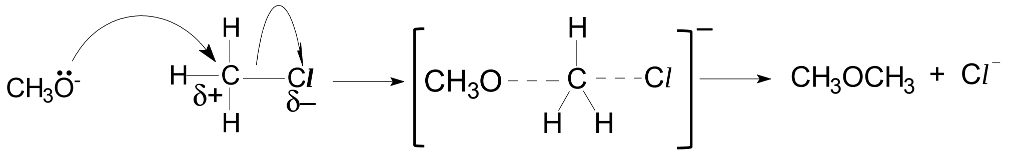
At 80 °C, methanol exists in the gaseous state.

Hence, when operating temperature 80 °C, there is a larger decrease in number gaseous molecules in the cell reaction, resulting in greater decrease in number of ways in distributing the energy. Hence ΔS_r is more negative than $\Delta S^{\ominus}_{r}$.

[1]: recognise that methanol exists in the gaseous state at 80 °C and entropy change will be more negative
[1]: explain it is due to larger decrease in number of gaseous particles

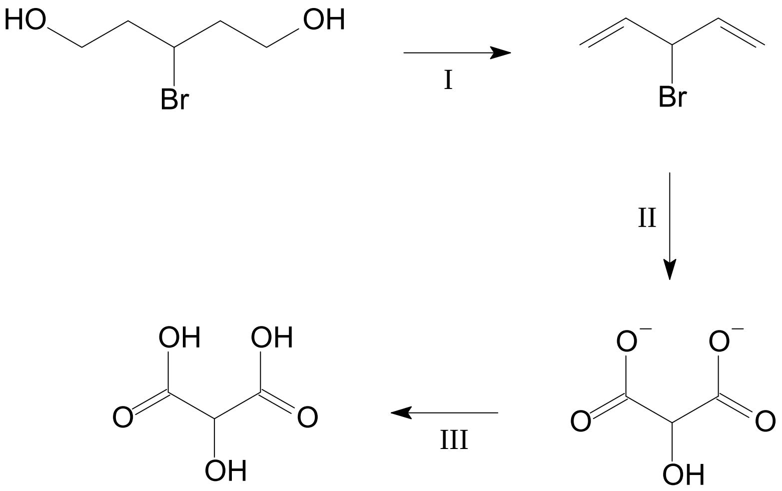
(c) **(i)** $\mathbf{CH_3OH + OH^- \longrightarrow CH_3O^- + H_2O}$ [1]

(ii) [2]



[1]: partial charges indicated + arrows correctly show electron pair on nucleophile attacking δ+ of C–C*l* bond and electrons move to C*l*
[1]: correct transition state

(d) **(i)** [3]



I: excess conc. H_2SO_4, heat (under reflux) / 180 °C

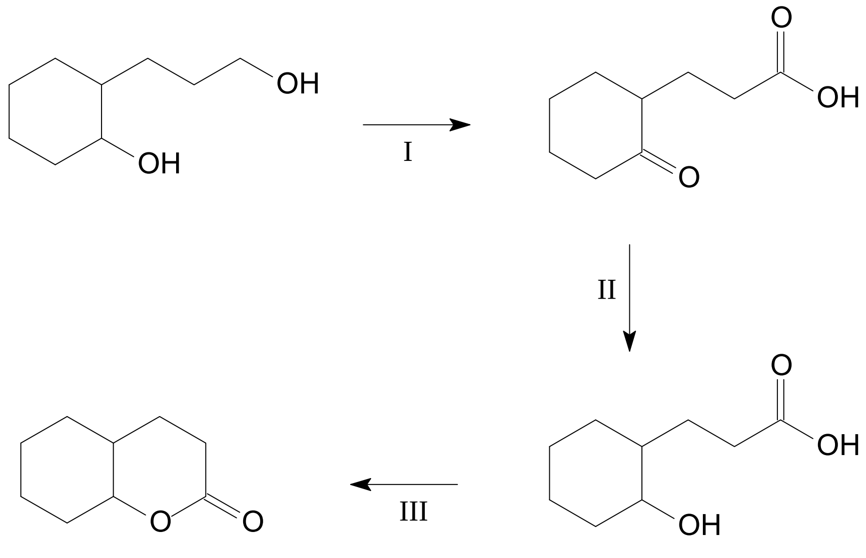
II: $KMnO_4$, NaOH(aq), heat (under reflux)

III: dilute H_2SO_4 / dilute HC*l*

[1]: correct reagent and condition for step 1 and its corresponding product
[1]: correct reagent and condition for step 2 and its corresponding product
[1]: correct reagent and condition for step 3

Do not award if Step II uses acidified $KMnO_4$, followed by NaOH(aq)/KOH(aq) with heat in Step III. This will need a Step IV to acidify to liberate the free acid.

(ii) [3]



I: $KMnO_4$, dilute H_2SO_4, heat (under reflux)

II: $NaBH_4$ (in ethanol) // H_2, Pt / Pd, r.t. // H_2, Ni, heat

III: conc. H_2SO_4, heat (under reflux)

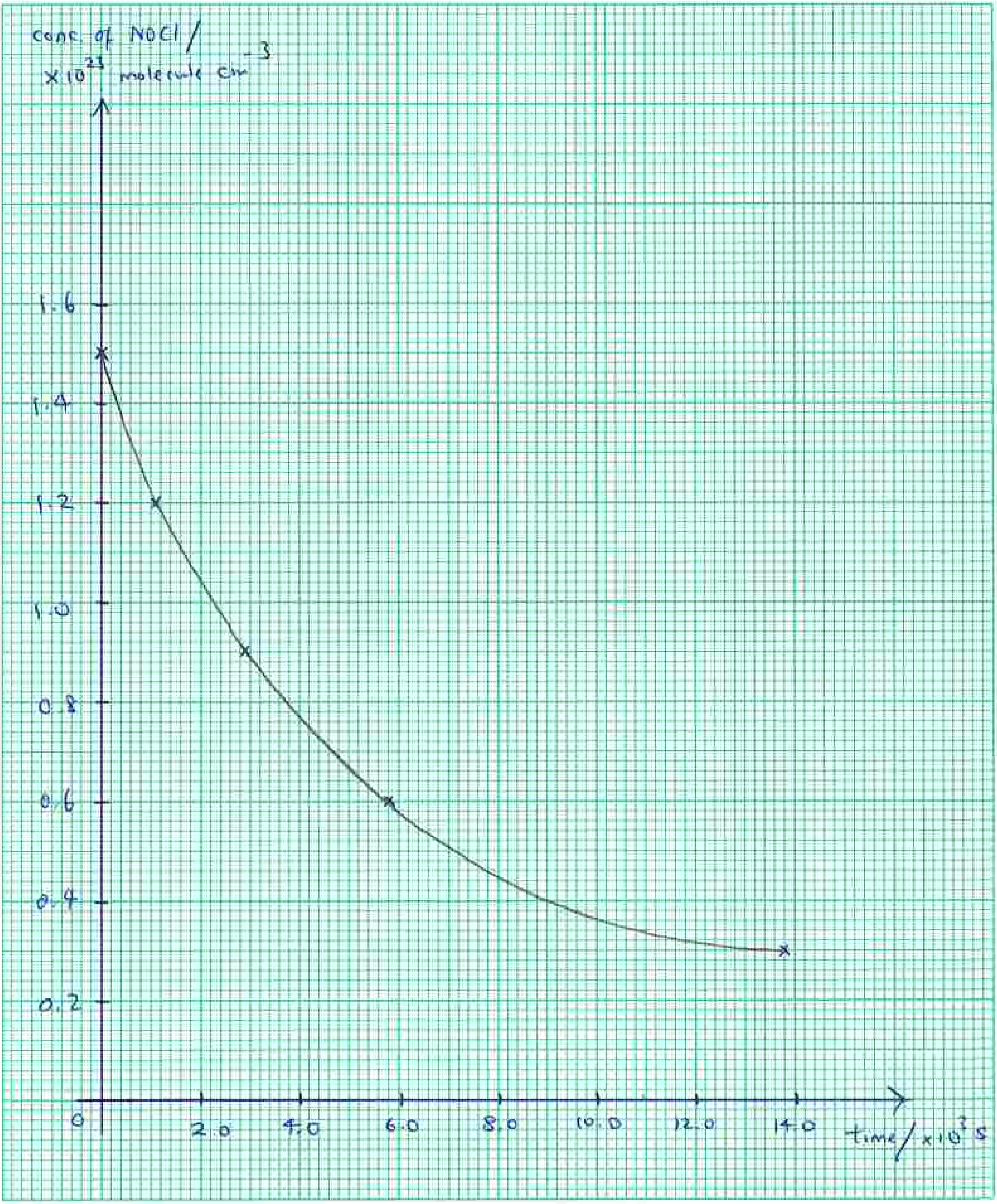
[1]: correct reagent and condition for step 1 and its corresponding product
[1]: correct reagent and condition for step 2 and its corresponding product
[1]: correct reagent and condition for step 3

Candidate Name

Subject 9729 Paper 03

Question No. 1d(ii)

Centre Number	Index Number



ANDERSON JUNIOR COLLEGE

2018 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/03**

Paper 3 Free Response **14 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Graph Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **12** printed pages.

Section A

Answer **all** the questions in this section.

1 Aqua regia is a mixture of nitric and hydrochloric acid and can be used to dissolve noble metals such as gold. Although gold is typically an inert metal and it does not dissolve in either of the acids alone, it will dissolve in aqua regia because of the unique combined action of the two acids.

The standard reduction potential of Au^{3+} to Au is given below.

$$Au^{3+} + 3e^- \rightleftharpoons Au \qquad E^\ominus = +1.50\ V$$

(a) **(i)** With the use of relevant data from the *Data Booklet*, explain why hydrochloric acid alone cannot dissolve gold. [1]

In aqua regia, nitric acid is reduced to nitrogen dioxide when it converts gold to its ionic form, Au^{3+} and hydrochloric acid provides a source of chloride which react with the gold cations to form stable tetrachloroaurate(III) anions, $AuCl_4^-$.

(ii) Write the balanced equation for the reaction between nitric acid and gold occurring in aqua regia. [1]

(iii) Explain, with the use of suitable equations, how the presence of hydrochloric acid encourages the reaction in **(a)(ii)** to take place readily. [2]

(b) If the aqua regia solution only contains gold, it may be reduced by sulfur dioxide to obtain elemental gold.

$$2AuCl_4^- + 3SO_2 + 6H_2O \longrightarrow 2Au + 12H^+ + 3SO_4^{2-} + 8Cl^-$$

Gold ore from a particular mining site is said to contain about 4.0 g of gold in one tonne of ore. In three months, the site processed 2.18×10^6 tonnes of ore. Determine the minimum volume of sulfur dioxide gas, measured at room temperature and pressure, required to extract elemental gold in three months.

[1 tonne = 1000 kg] [3]

(c) Another method of extracting gold from low–grade ore involves converting the gold to a water–soluble dicyanoaurate(I) anionic complex, $[Au(CN)_2]^-$.

$$4Au(s) + 8NaCN(aq) + O_2(g) + 2H_2O(l) \longrightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

(i) State the shape of the dicyanoaurate(I) anionic complex. [1]

(ii) Explain why the gold complex ion, $AuCl_4^-$ in **(a)** is coloured while the dicyanoaurate(I) complex ion, $[Au(CN)_2]^-$, is colourless. [4]

(d) Nitrosyl chloride, NOC*l*, is a yellow gas that is most commonly encountered as a decomposition product of aqua regia.

$$HNO_3(aq) + 3HCl(aq) \longrightarrow NOCl(g) + Cl_2(g) + 2H_2O(l)$$

Nitrosyl chloride can further decompose into nitric oxide and chlorine.

$$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$$

The decomposition of gaseous NOC*l* was studied at 125 °C and Table 1.1 shows the concentration of NOC*l* at various times.

Table 1.1

time / s	**concentration of NOC*l* / molecule cm^{-3}**
0	1.5×10^{23}
1.1×10^{3}	1.2×10^{23}
2.9×10^{3}	0.9×10^{23}
5.8×10^{3}	0.6×10^{23}
13.8×10^{3}	0.3×10^{23}

(i) Suggest why the aqua regia solution is best used to dissolve noble metals immediately after it is made. [1]

(ii) Use the data given in Table 1.1 to plot a graph of concentration of NOC*l* against time on the graph paper provided. [2]

(iii) Hence, use your graph to show that the decomposition of NOC*l* is a second order reaction. [2]

(iv) Calculate the rate constant of the reaction in $mol^{-1}\ dm^{3}\ s^{-1}$. [2]

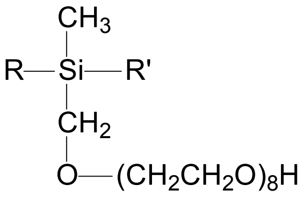
(v) It has been found that addition of nitrogen dioxide, NO_2 leads to a faster decomposition of nitrosyl chloride at the same temperature, during which the nitrogen dioxide concentration remains unchanged.

With an appropriate sketch of Boltzmann distribution, explain why the addition of nitrogen dioxide speeds up the rate of decomposition. [2]

[Total: 21]

2 **(a)** Oil spills are ecological disasters and remediating them can run into billions of dollars. One of the methods adopted to combat oil spills was the use of dispersants, which break up the oil into tiny droplets and help to spread out the droplets throughout the water.

An example of a chemical dispersant **B**, which contains both carbon and silicon, has the following structure.



B

where R and R' are alkyl groups

(i) Draw a diagram to illustrate hydrogen bonding between a molecule of **B** and a water molecule. [1]

(ii) By reference to the type of intermolecular forces, explain why this molecule of **B** is able to function as an oil spill dispersant. [2]

(b) Both carbon and silicon are among the elements of Group 14. It was observed that those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.

Table 2.1 shows the marked change in melting points after germanium.

Table 2.1

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

(i) What type of structure is present in solid carbon, silicon and germanium? [1]

(ii) Suggest why the melting points of these elements decrease from carbon to germanium. [1]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts readily with water.

(iii) Suggest an explanation for this observation. [1]

(iv) Hence, suggest a balanced equation for the reaction between $GeCl_4$ and water and state the colour observed when a few drops of Universal Indicator solution was added to the resulting mixture. [2]

(c) Friedel–craft alkylation, using $AlCl_3$ as a catalyst, is usually carried out in anhydrous conditions. In the presence of $AlCl_3$ and under suitable conditions, benzene reacts with CCl_4 to form dichlorodiphenylmethane, $(C_6H_5)_2CCl_2$.

(i) Suggest why the reaction has to be carried out under anhydrous condition. [1]

(ii) Name and describe the mechanism of the reaction, showing any intermediates. [4]

(iii) Suggest a reason why further alkylation of the product in **(c)(ii)** does not take place. [1]

Fig. 2.1 shows two examples of Friedel–craft alkylation which can be done in non–anhydrous conditions.

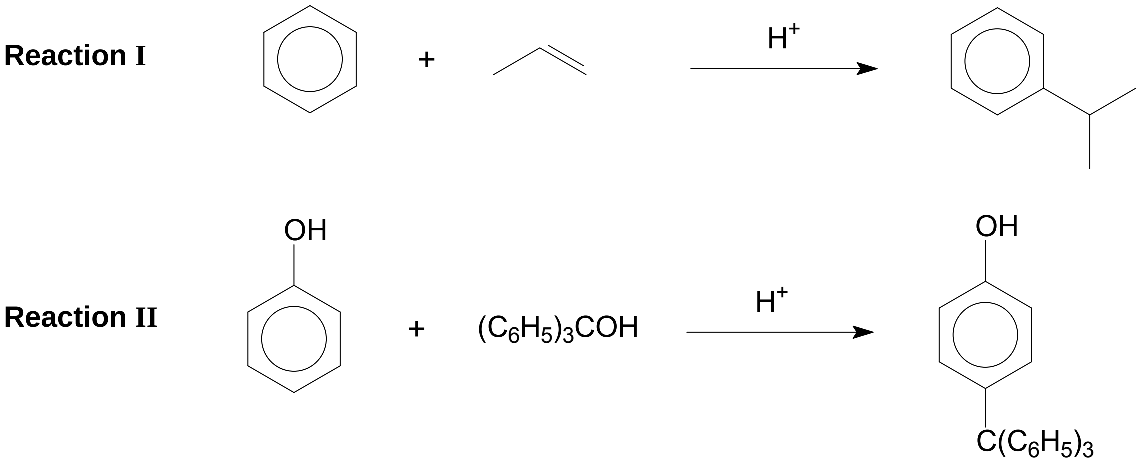
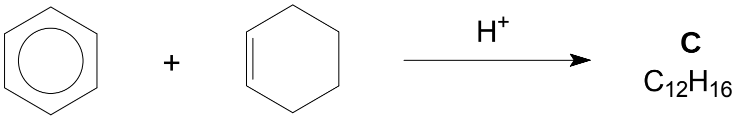
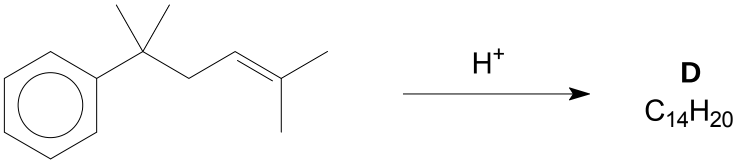


Fig. 2.1

(iv) Using the information given about **Reaction I**, predict the structure of the product of each of the following reactions.

Both compounds **C** and **D** do not react with aqueous bromine.





[2]

(v) Hence, suggest the reagents and conditions for a reaction that could be used to distinguish between **C** and **D**.
Draw the structure of the product(s) of any reactions that occur. [2]

(vi) **Reaction II cannot** take place if benzene is used instead of phenol.

With reference to the structure of the reactant and the intermediate formed, suggest why this is so. [2]

[Total: 20]

3 **(a)** The following scheme shows the synthesis of aspirin using the Kolbe process. Salicylic acid is formed as an intermediate. Study Fig. 3.1 carefully and answer the questions that follow.

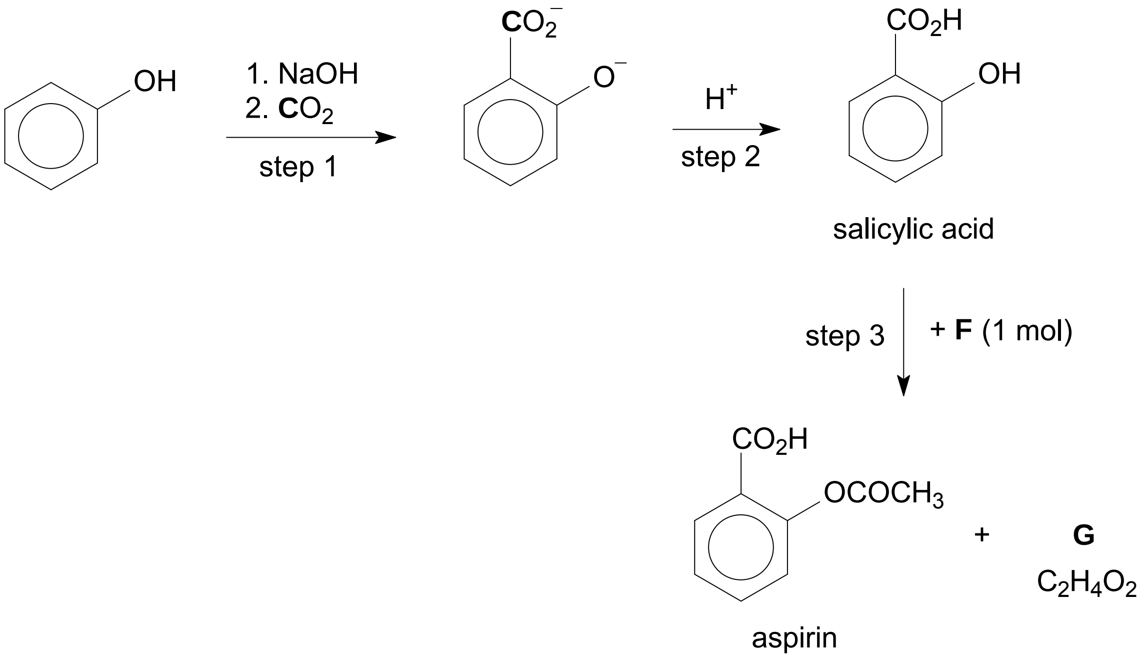


Fig. 3.1

(i) State the change in type of hybridisation with respect to the carbon atom (in **bold**), from CO_2 to the product of step 1. [1]

(ii) Suggest the type of reaction that occur in step 2. [1]

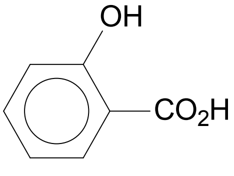
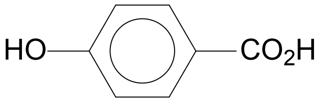
(iii) **G** forms a soluble salt with NaOH(aq).

Suggest the identity of the product **G** formed in step 3. [1]

(iv) Hence, suggest the molecular formula of the reagent **F** in step 3. [1]

(b) Table 3.1 shows the boiling point and pK_{a1} values of salicylic acid and its structural isomer, 4–hydroxybenzoic acid.

Table 3.1

compound	**melting point / °C**	**pK_{a1}**
 salicylic acid	160	3.0
 4–hydroxybenzoic acid	214	4.5

(i) Explain why the melting point of salicylic acid is lower than that of 4–hydroxybenzoic acid. [2]

(ii) Suggest a reason why the pK_{a1} value of salicylic acid is less than that of 4–hydroxybenzoic acid. [2]

(c) Depending on the conditions of the reaction, 4–ethylphenol can react with chlorine in two different ways, giving the two isomers **P** and **Q** as shown in Fig. 3.2.

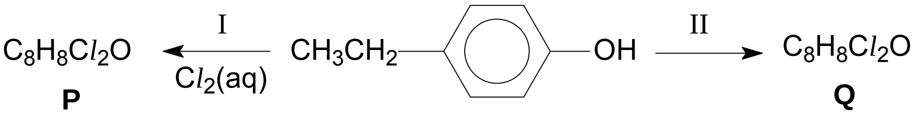


Fig. 3.2

(i) Suggest a structural formula for compound **P**. [1]

(ii) Explain whether you would expect **P** to be more or less acidic than 4–ethylphenol. [2]

Compound **Q** reacts with NaOH(aq), followed by acidification to give **R**, $C_8H_{10}O_3$, which immediately loses water to forms **S**, $C_8H_8O_2$. Compound **S** is insoluble in water but it dissolves in NaOH(aq). **S** reacts with 2,4–dinitrophenylhydrazine and with alkaline aqueous iodine, but not with Tollens' reagent.

(iii) Suggest structures for **Q**, **R** and **S**. Explain the reactions described. [5]

(iv) Write a balanced equation for each of the reaction between **S** and
- 2,4–dinitrophenylhydrazine
- alkaline aqueous iodine [2]

(v) Suggest suitable conditions for reaction II. [1]

[Total: 19]

Section B

Answer **one** question from this section.

4 **(a)** The hydrogen fuel cell gives green energy but there are problems associated with hydrogen sources and storage, limiting its use in both transportation and stationary applications. While fuel cells which use liquid alcohols pose no storage problem, they emit carbon dioxide and thus countering the move to reduce carbon footprint.

As a result, attention has turned to other alternative fuels such as ammonia and hydrazine, which on combustion gives nitrogen and water. Fig 4.1 shows a prototype of an ammonia alkaline fuel cell using aqueous potassium hydroxide membrane.

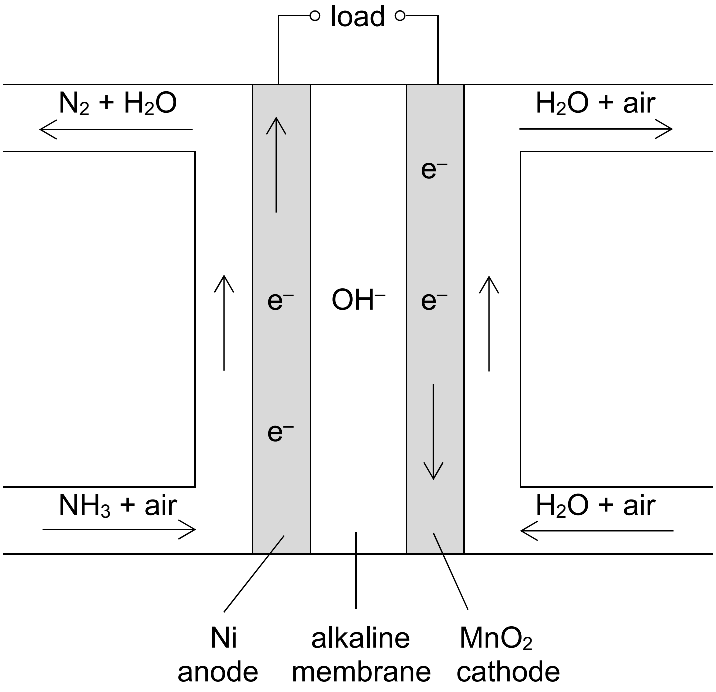


Fig. 4.1

At the anode, ammonia is oxidised to nitrogen while oxygen is reduced at the cathode.

(i) Write the equations for the reactions occurring at the anode and cathode. [2]

(ii) Hence, write the equation for the electro–combustion of one mole of ammonia. [1]

(iii) The value of $\Delta G^\ominus$ at 298 K for the equation you have written in **(a)(ii)** is –339 kJ mol^{-1}. Calculate the value for $E^\ominus_{cell}$ for the ammonia alkaline fuel cell. [2]

(iv) Using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the N_2/NH_3 electrode reaction. [1]

(v) Earlier prototypes of the ammonia fuel cell using the PEM (proton exchange membrane) was not viable. Suggest a reason for the limitation. [1]

(b) Ammonia, in aqueous or liquid form, is promising as an energy medium for hydrogen storage and generation. Under suitable conditions, ammonia decomposes to nitrogen and hydrogen gases.

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad \Delta H^\ominus = +92 \text{ kJ mol}^{-1}$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction, and state its units. [2]

A mixture of 0.5 mol of N_2 and 2.0 mol of NH_3 was introduced into a sealed 2.00 dm^3 vessel and heated to 670 K. At equilibrium, it was found that the amount of N_2 present was 1.2 mol.

(ii) Calculate the equilibrium concentration of the reactant and the two products. [2]

(iii) Use the data to calculate the value of K_c. [1]

For any reaction, $\Delta G^\ominus$ and the equilibrium constant, K_c are related according to the equation

$$\Delta G^\ominus = -RT \ln K_c$$

(iv) Use this equation and your answer to **(b)(iii)** to calculate the $\Delta G^\ominus$ of the reaction at 670 K. [1]

(v) Hence, calculate the $\Delta S^\ominus$ of the reaction at 670 K and comment on its sign with reference to the reaction. [2]

(vi) State and explain the effect on the position of equilibrium and K_c when the volume of the vessel was expanded to double the original volume at constant temperature. [2]

(c) Ammonia reacts as a nucleophile with alkyl halides to give primary amines.

Describe the mechanism for the reaction between ammonia and methyl iodide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

[Total: 20]

5 **(a)** Chemical recycling of carbon dioxide to produce renewable materials and fuels, primarily methanol, offers a powerful alternative to tackle both issues of global climate change and fossil fuel depletion. Methanol is a colourless and flammable liquid which boils at 65 °C.

In Iceland, renewable methanol is formed by reacting carbon dioxide released naturally in the atmosphere from the geothermally active areas with hydrogen over a heterogeneous catalyst.

Using copper–based catalysts, methanol can be synthesised from CO_2 as shown in (**I**) below.

$$(\mathbf{I}) \qquad CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

Some relevant enthalpy change values are given in Table 5.1.

Table 5.1

enthalpy change of combustion of H_2(g)	–286 kJ mol^{-1}
enthalpy change of combustion of CH_3OH(g)	–768 kJ mol^{-1}
enthalpy change of vapourisation of H_2O(l)	+40.8 kJ mol^{-1}

Use the data in Table 5.1 to construct an energy cycle relating the reactants and products of the forward reaction in (**I**).
Hence, calculate the standard enthalpy change of the forward reaction in (**I**), $\Delta H^{\ominus}_{\mathbf{I}}$. [3]

(b) Research has shown that the direct methanol fuel cell (DMFC) is an appropriate alternative to rechargeable battery.

The overall cell reaction of a DMFC can be expressed as follow.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

In a DMFC, methanol and water reacts at the anode to produce carbon dioxide and protons. The protons then move through an acidic conducting polymer electrolyte towards the cathode where they react with oxygen to produce water.

The electrons are transported through an external circuit from anode to cathode, providing power to connected devices like mobile phones and lap–top computers.

(i) Write the two half equations at the electrodes which results in the occurrence of the cell reaction in a typical DMFC. [2]

(ii) Explain why an alkaline electrolyte cannot be used in a DMFC. [1]

(iii) A DMFC is capable of producing a voltage of 1.18 V at standard conditions.

Hence, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the given overall cell reaction. [1]

(iv) Some relevant standard enthalpy change of formation values are given in Table 5.2.

Table 5.2

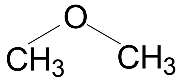
compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CH_3OH(l)$	–238
$CO_2(g)$	–394
$H_2O(l)$	–286

Use the data given to calculate the enthalpy change of the overall cell reaction of DMFC at standard conditions. [1]

(v) Hence, determine the standard entropy change, $\Delta S^{\ominus}$, for the overall cell reaction. [1]

(vi) By writing appropriate equation(s), state and explain how the entropy change for the overall cell reaction will differ from your answer in **(b)(v)** if the fuel cell is operating at 80 °C. [2]

(c) Beside its application in DMFC, methanol is also an important raw material in the production of dimethyl ether, DME.



DME

DME shows great potential as a clean high–efficiency compression ignition fuel. Its production from methanol involves the reaction between methanol and chloromethane via a nucleophilic substitution mechanism.

Step 1: Generation of a nucleophile through an acid–base reaction between methanol and a strong base, such as sodium hydroxide.

Step 2: Reaction of the nucleophile with chloromethane to form DME.

(i) Write an ionic equation to show how the nucleophile is formed in **Step 1**. [1]

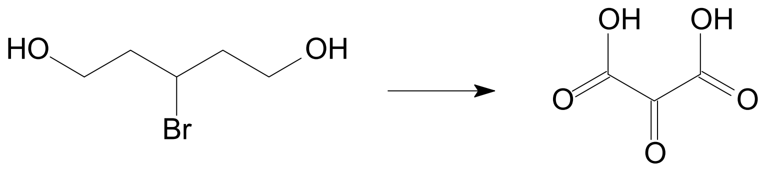
(ii) Write equation(s) to show how the nucleophile generated in **(c)(i)** reacts with chloromethane in **Step 2**.

In your answer show any relevant charges, dipoles or lone pairs of electrons you consider to be important in this step. [2]

(d) In **no more than 3 steps**, suggest how each of the following hydroxyl compounds can be transformed into the respective products.

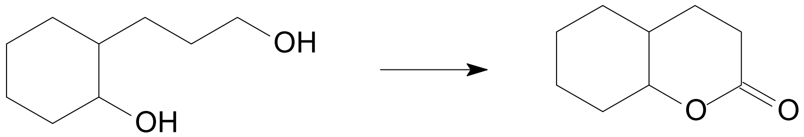
You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i)



[3]

(ii)



[3]

[Total: 20]

Preparation list (combined) **2018 JC2 Prelim Paper 4**

No.	Apparatus	Qty
1	Goggles	1
2	**Dry** weighing bottle (new bottle for each shift)	1
3	Styrofoam cup; **350** cm^3 capacity	2
4	lid for Styrofoam cup , with a central hole into which the thermometer may be inserted	1
5	thermometer (range –10 ^oC to +50 ^oC, 0.2 ^oC division)	1
6	test–tube rack	1
7	test–tube (big)	6
8	test–tube holder	1
9	250 cm^3 beaker (1 for Qn1, 1 for Qn 2 & 3)	2
10	50 cm^3 measuring cylinder	2
11	25.0 cm^3 pipette	1
12	Pipette filler	1
13	250 cm^3 graduated flask	1
14	50 cm^3 burette	2
15	Burette clips	2
16	Burette stand and clamp	1
17	250 cm^3 conical flasks	2
18	White tile	1
19	Glass stirrer	1
20	Glass funnels	3
21	Marker pen	1
22	Wash bottle containing deionised water	1
23	lighter	1
24	Weighing balances	4 per lab
25	Airpot (for hot water bath)	2 per lab
26	'container for chemical waste' – for organic waste	1 per bench
	Following items in a plastic bag	
27	Spatula	1
28	Dropping pipette (Qn1 (1), Qn 2 (3), Qn3 (4))	8
29	Paper towels	some
30	Wooden splint	some
31	Litmus paper	some
32	Filter paper	1
	Chemicals	
1	**FA 1** is 0.40 mol dm^{-3} sulfuric acid, H_2SO_4.	200 cm^3
2	**FA 2** is 0.55 mol dm^{-3} sodium hydroxide, NaOH.	250 cm^3
3	**FA 3** is Fresh anhydrous sodium carbonate, Na_2CO_3. Placed in a **dry, stoppered** test-tube.	12 g
4	**FA 5** is 2.00 mol dm^{-3} hydrochloric acid, HCl	120 cm^3
5	**FA 6** is 1.00 mol dm^{-3} sodium hydroxide, NaOH	150 cm^3
6	**FA 7** is 1.00 mol dm^{-3} sodium carbonate, Na_2CO_3	150 cm^3
7	**FA 8**: ethanol, 10% (v/v)	10 cm^3
8	**FA 9**: propanone, 10% (v/v)	10 cm^3
9	**FA 10**: ethanoic acid 10% (v/v)	10 cm^3
10	**FA 11**: glucose solution 10% (v/v) and ethanal solution 10% (v/v)	10 cm^3

	Common bench reagents	
11	Methyl orange indicator	1
12	aqueous NaOH	1
13	Iodine solution	1
14	Fehling’s solution	1
15	Magnesium powder	1
16	2,4–dinitrophenylhydrazine reagent	1
17	Nitric acid	1
18	Silver nitrate	1

There are no chemicals **FA 3** and **FA 10**. Students are not required to do the experiments.

ANDERSON JUNIOR COLLEGE

2018 JC 2 PRELIMINARY EXAMINATIONS

NAME:__________________________ **PDG:**____ /17

CHEMISTRY **9729/04**

Paper 4 Practical **28 August 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Quantitative Analysis Notes are printed on pages 22 and 23.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
Total	

This document consists of **23** printed pages.

Answer **all** the questions in the spaces provided.

1 Determination of concentration of two solutions

You are provided with the following.

FA 1 is a dilute solution of sulfuric acid, H_2SO_4.
FA 2 is a dilute solution of sodium hydroxide, NaOH.
FA 3 is solid anhydrous sodium carbonate, Na_2CO_3.
Methyl orange indicator solution.

Both sodium hydroxide and sodium carbonate are bases which will neutralise sulfuric acid.

In this question, you will prepare a standard solution of sodium carbonate, **FA 4**, using solid anhydrous sodium carbonate, **FA 3**. You will then add different volumes of **FA 4** to identical samples of dilute sulfuric acid, **FA 1**. In each case, the amount of sodium carbonate solution you add will only partially neutralise the sulfuric acid. You will then complete the neutralisation of each mixture by titration with dilute sodium hydroxide, **FA 2**.

Each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end–points.

Graphical analysis of your results will enable you to determine the concentrations of the sulfuric acid in **FA 1** and of the sodium hydroxide in **FA 2**.

(a) (i) Preparation of solution FA 4

1. Weigh a **dry** empty weighing bottle.
2. Reweigh the bottle with between 9.8 g and 10.2 g of **FA 3**.
3. Transfer the contents of the weighing bottle into a 250 cm^3 beaker and dissolve the solid in about 100 cm^3 of deionised water.
4. Transfer all of the solution to a 250 cm^3 graduated flask.
5. Make up the solution with deionised water and mix thoroughly. This is solution **FA 4**.
6. Reweigh the weighing bottle.

In an appropriate format in the space below, record all measurements of mass. Include the mass of **FA 3** used.

Results

[2]

(ii) Preparing titration mixtures and titrations

Remember, each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end–points.

1. Pipette 25.0 cm^3 of **FA 1** into a conical flask.

2. Fill a burette with **FA 4**.

3. Add 6.00 cm^3 of **FA 4** into the same conical flask. Swirl to mix the contents.

4. Fill the second burette with **FA 2**.

5. Add 2 – 3 drops of methyl orange indicator to the conical flask.

6. Titrate the mixture in the flask with **FA 2** until an orange colour is obtained.

   Record your results in Table 1.1. Make certain that your recorded results show the precision of your working.

7. Rinse the conical flask thoroughly.

8. Repeat the procedure used for steps 1 to 7 but this time, add 18.00 cm^3 of **FA 4** to 25.0 cm^3 of **FA 1**.

9. You are to perform **two additional** titrations, **each** with a **different** volume of **FA 4** added to 25.0 cm^3 of **FA 1.**

   Select **two** other suitable volumes of **FA 4** for use in two additional experiments. Your selected volumes must be between the volumes used earlier.

   Do not use volumes of FA 4 outside the range of 6 – 18 cm^3.

   Repeat the procedure in steps 1 to 7.

   You should perform your titrations in order of **increasing** volumes of **FA 4**.

Results

Table 1.1

titration number				
volume of **FA 4** used / cm^3				

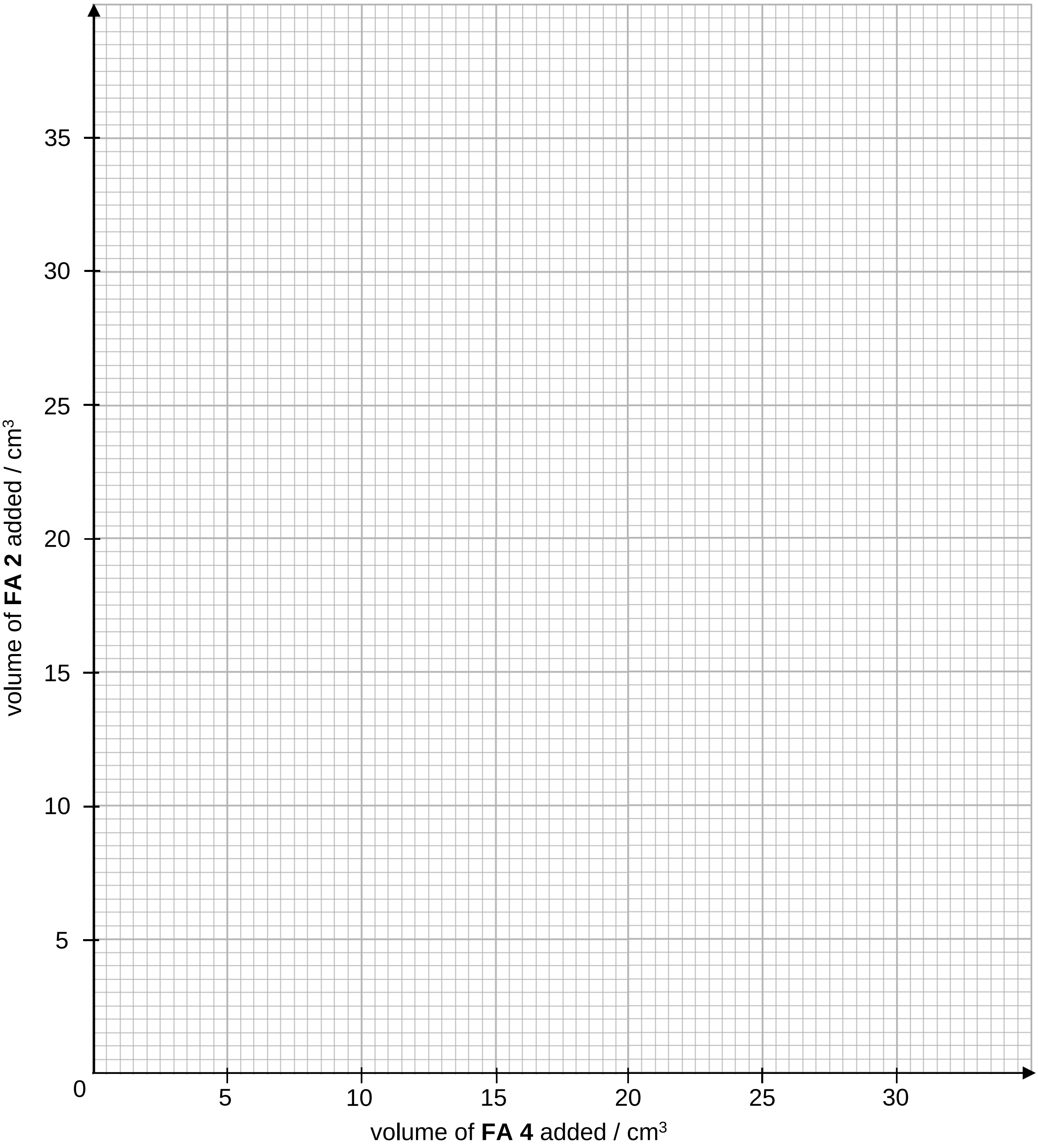
[2]

(b) Plot, on the grid below, your values for the **FA 2** titre against the volume of **FA 4** added.

The scales for the axes were chosen to allow you to determine by extrapolation

- the volume of **FA 4** required, **V_{max}(FA 4)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 2** is added;
- the volume of **FA 2** required, **V_{max}(FA 2)**, to react completely with 25.0 cm^3 of **FA 1** if no **FA 4** is added.

Draw the line of best fit, taking into account all of your plotted points. Hence, obtain values for **V_{max}(FA 4)** and **V_{max}(FA 2)**.



V_{max}(FA 4) = …………………… **V_{max}(FA 2)** = …………………… [5]

(c) Calculate the gradient of your graph line, showing clearly how you did this.

Gradient = ……………………………………….. [1]

(d) Explain, in terms of the chemistry involved, the direction of the slope of your graph.

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……………………………………………………………………………………………………. [1]

Calculations

(e) **(i)** Calculate the concentration, in mol dm^{-3}, of Na_2CO_3 in the **FA 4** solution you have prepared.

[A_r: Na, 23.0; C, 12.0; O, 16.0]

concentration of Na_2CO_3 in **FA 4** = ……………………………………….. [1]

(ii) Using appropriate data from your graph, calculate the concentration of H_2SO_4 in **FA 1**.

concentration of H_2SO_4 in **FA 1** = ……………………………………….. [2]

(iii) Using your answer to **(e)(ii)** and appropriate data from your graph, calculate the concentration of NaOH in **FA 2**.

concentration of NaOH in **FA 2** = ……………………………………….. [1]

(f) Another method to calculate the concentration of NaOH in **FA 2** is to use the expression below.

$$[\text{NaOH}] = \frac{2[\text{Na}_2\text{CO}_3]}{|\text{gradient}|}$$

Use the expression to determine the concentration of NaOH in **FA 2**.

concentration of NaOH in **FA 2** = ……………………………………….. [1]

(g) A student performs this experiment. Unknowingly, he uses a sample of **FA 3** which is slightly damp.

Suggest what effect this will have on the values of **V_{max}(FA 4)** and **V_{max}(FA 2)** he obtains. In each case, explain your answer.

Effect on **V_{max}(FA 4)** ……………………………………………………………………………

Explanation ……………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

Effect on **V_{max}(FA 2)** ……………………………………………………………………………

Explanation ……………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [2]

[Total: 18]

2 Determination of the enthalpy change of a reaction

You will follow the instructions to obtain the enthalpy changes, ΔH_1 and ΔH_2 for the following reactions.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_1$$

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

You will then use the results of your experiments to calculate the enthalpy change, ΔH_3 for the following reaction.

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l) \qquad \Delta H_3$$

You are provided with the following.

FA 5 is 2.00 mol dm^{-3} hydrochloric acid, HCl.
FA 6 is 1.00 mol dm^{-3} sodium hydroxide, NaOH.
FA 7 is 1.00 mol dm^{-3} sodium carbonate, Na_2CO_3.

(a) Reaction between FA 5 and FA 6

Record your results for this experiment in Table 2.1.

1. Using a measuring cylinder, transfer 40.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup into a second Styrofoam cup, which is placed in a 250 cm^3 beaker.

2. Stir and measure the temperature of **FA 5**.

3. Using another measuring cylinder, measure 50.0 cm^3 of **FA 6**.

4. Stir and measure the temperature of **FA 6**.

5. Slip the thermometer through the lid of the cup. Add **FA 6** from the measuring cylinder into **FA 5** in the Styrofoam cup.

6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.

Complete Tables 2.1 and 2.2 by calculating values for the weighted average initial temperature, T_{av}, for the two solutions, and the temperature change during the reaction, ΔT_{max}.

The value for T_{av} can be calculated by using the formula given below.

$$\boldsymbol{T}_{av} = \frac{(\text{volume } \textbf{FA 5} \text{ x initial temp } \textbf{FA 5}) + (\text{volume } \textbf{FA 6} \text{ x initial temp } \textbf{FA 6})}{\text{total volume of reaction mixture}}$$

Results

Table 2.1

Initial temperature of **FA 5** / °C	
Initial temperature of **FA 6** / °C	
Average temperature of **FA 5** and **FA 6,** T_{av} / °C	
Maximum temperature after reaction, T_{max} / °C	
Temperature change, ΔT_{max} / °C	

[1]

(b) Reaction between FA 5 and FA 7

Record your results for this experiment in Table 2.2.

1. Empty and rinse the Styrofoam cup used in **(a)**. Place this cup into a second Styrofoam cup which is placed in a 250 cm^3 beaker.
2. Using a measuring cylinder, transfer 40.0 cm^3 of **FA 5** into the Styrofoam cup.
3. Stir and measure the temperature of **FA 5**.
4. Rinse the measuring cylinder used for **FA 6** in **(a)** and use it to place 50.0 cm^3 of **FA 7**.
5. Stir and measure the temperature of **FA 7**.
6. Slip the thermometer through the lid of the cup. Add **FA 7** from the measuring cylinder into **FA 5** in the Styrofoam cup.
7. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record this temperature, T_{max}.

Results

Table 2.2

Initial temperature of **FA 5** / °C	
Initial temperature of **FA 7** / °C	
Average temperature of **FA 5** and **FA 7,** T_{av} / °C	
Maximum temperature after reaction, T_{max} / °C	
Temperature change, ΔT_{max} / °C	

[3]

Calculations
In the following calculations, you should assume that the

- specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1},
- density of the mixture is 1.00 g cm^{-3}.

(c) **Enthalpy change of reaction of aqueous sodium hydroxide and hydrochloric acid, ΔH_1**

(i) By reference to the volumes used, the concentrations of the solutions and the equation for the reaction, show which of the reagents **FA 5** or **FA 6** was added in excess.

[1]

(ii) Calculate the heat change, q, for your experiment in **(a)** and hence determine a value for the enthalpy change, ΔH_1, for the reaction

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

q = ……………………………………………..

ΔH_1 = ……………………………………… [2]

(d) **Enthalpy change of reaction of aqueous sodium carbonate and hydrochloric acid, ΔH_2**

(i) By reference to the volumes used, the concentrations of the solutions and the equation for the reaction, show which of the reagents **FA 5** or **FA 7** was added in excess.

[1]

(ii) Calculate the heat change, q, for your experiment in **(b)** and hence determine a value for the enthalpy change, ΔH_2, for the reaction

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

q = …………………………………………..

ΔH_2 = ……………………………………… [2]

(e) **Enthalpy change of reaction of aqueous sodium hydroxide and carbon dioxide, ΔH_3**

Use the equations

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H_1$$

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

and your calculated values of ΔH_1 and ΔH_2 to calculate the enthalpy change, ΔH_3, for the reaction

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l) \qquad \Delta H_3$$

Show your working clearly.

ΔH_3 = ………………………………………. [4]

(f) **Planning**

You will plan an additional experiment whose results, when linked to those from experiments in **(a)** and **(b)**, will enable you to determine the enthalpy change, ΔH_4, for the following reaction.

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l) \qquad \Delta H_4$$

You may assume that you are provided with the reagents and apparatus used in **(a)** and the following additional materials

- solid sodium carbonate, Na_2CO_3,
- deionised water,
- equipment normally found in a college laboratory.

In your plan, you will

- suggest the additional enthalpy change that can be used together with results from experiments in **(a)** and **(b)** and show how they can be used to determine the enthalpy change, ΔH_4,
- give a brief outline of the procedure that you would follow and the measurements that you would take.

[A_r : Na, 23.0; C, 12.0; O, 16.0]

DO NOT CARRY OUT THE PLAN.

You may show your working in the space below.

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…… [3]

[Total: 17]

3 **Organic Qualitative Analysis**

(a) You are provided with samples of **FA 8**, **FA 9**, **FA 10** and **FA 11**. Each of which is a different one of the following.

an alcohol
an aldehyde
a carboxylic acid
a ketone

Perform the tests described in the table below, and record your observations in the spaces provided in Table 3.1. You do **not** need to perform those with observations recorded.

Use a fresh sample of each solution for each test.

Table 3.1

	test	**observations**			
		FA 8	**FA 9**	**FA 10**	**FA 11**
(i)	Place about 1 cm depth of the unknown in a test tube. To the test–tube, add about 1 cm depth of 2,4–dinitrophenylhydrazine reagent. Shake and warm the test tube in a water–bath.	no observable change			

	test	**observations**			
		FA 8	**FA 9**	**FA 10**	**FA 11**
(ii)	Place about 1 cm depth of the unknown in a test tube. To the test–tube, add a small amount of magnesium powder.		no observable change		
(iii)	Place about 1 cm depth of the unknown in a test tube. To the test–tube, add 1 cm depth of Fehling's solution. Shake and warm the test–tube in a water–bath.			no observable change	
(iv)	Place about 1 cm depth of the unknown in a test tube. To this test–tube, add about 3 cm depth of iodine solution. Then add sodium hydroxide dropwise until the iodine colour has almost discharged. Warm the test–tube in a water–bath if necessary.				no observable change

[3]

(b) **(i)** From the observations, give evidence for the type of compound present in **FA 8 – FA 11**.

	compound type	**evidence**
FA 8		
FA 9		
FA 10		
FA 11		

[4]

(ii) Identify the sample in which a copper containing product is formed in test **(a)(iii)**. State the identity of the copper containing product and hence the type of reaction taking place in that test tube.

sample: ……………………………………………………………………………………….

identity: ………………………………………………………………………………………..

type of reaction: …………………………………………………………………………..... [1]

(c) **Planning**

2,4–dinitrophenylhydrazine can be synthesised from benzene by a 3–step synthesis with bromobenzene and 2,4–dinitrobromobenzene as intermediates. The preparation of organic compounds usually produces a mixture of the required compound and other impurities.

The synthesis of bromobenzene is described below. When excess bromine is used in the synthesis of bromobenzene, 1,4–dibromobenzene is formed as a by–product.

<u>Preparation and purification of bromobenzene</u>

20.0 cm^3 of benzene, 6.0 cm^3 of bromine are mixed with an iron tack to catalyse the reaction. The mixture is warmed at 50 – 55 °C. During the reaction, acidic fumes of hydrogen bromide is evolved. After about 15 min when the reaction subsides, the reaction mixture is removed from the water–bath.

The mixture is then heated to drive off unreacted bromine and cooled before doing solvent extraction. 25 cm^3 of ether is added to dissolve the mixture before shaking the ether solution with two 5 cm^3 portions of sodium hydroxide and one 10 cm^3 portion of water, keeping only the ether layer each time and disposing the aqueous layer. A spatula full of anhydrous magnesium sulfate is added to dry the ether layer for a few minutes before it is filtered away. Fractional distillation is done and only the bromobenzene fraction is collected.

The procedure above, when excess benzene was used, achieved a yield of 75%. A student would like to investigate if increasing the proportion of bromine used, by reducing amount of benzene in the reaction mixture, can raise the yield of bromobenzene.

Some relevant data are given in Table 3.2.

Table 3.2

Compound	boiling point / ^{o}C	density / g cm^{-3}	M_r
bromine	59	3.12	159.8
benzene	80	0.88	78.0
bromobenzene	156	1.50	156.9
1,4–dibromobenzene	220	1.84	235.8

(i) Write a balanced equation for the formation of bromobenzene from benzene.

……………………………………………………………………………………………….. [1]

(ii) It is also found from literature that when the amount of bromine used is twice the amount of benzene, 1,4–dibromobenzene is formed as the major product instead.

Calculate the volume of benzene that you would use to react with 6.0 cm^3 of bromine such that the amount of bromine is twice that of benzene.

[2]

(iii) The optimum ratio of bromine to benzene can be determined by repeating the experiment several times using different initial ratios of reactants each time.

Using the information given on page 18 and your answer to **(c)(ii)**, suggest the different volumes of reactants to be used in each experiment and complete Table 3.3.

Table 3.3

experiment number	volume of benzene used / cm^3	volume of bromine used / cm^3
1	20.0	6.0
2		
3		

[1]

(iv) You are required to write a plan to determine the optimum ratio of bromine to benzene to achieve the highest possible yield of bromobenzene.

Your plan should include the following:

- give a full description of the procedure that you would use to prepare and purify bromobenzene using the three different reaction mixtures in **(c)(iii)**,
- an outline of how percentage yield (with reference to amount of benzene used) would be obtained from each of the three different reaction mixtures,
- any safety precaution that you consider important.

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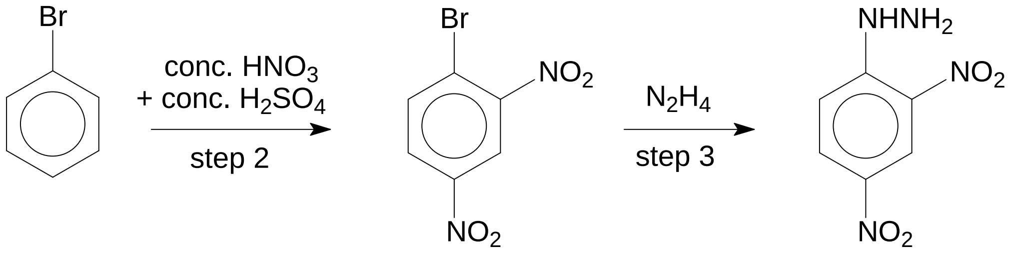
…………………………………………………………………………………………….. [6]

(v) The bromobenzene obtained is then converted to 2,4–dinitrophenylhydrazine as shown in the following reaction scheme.



Name the types of reaction that occur during each of the steps.

Step 2: ……………………………………………………

Step 3: …………………………………………………… [2]

[Total: 20]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey–green ppt. soluble in excess giving dark green solution	grey–green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red–brown ppt. insoluble in excess	red–brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off–white ppt. rapidly turning brown on contact with air insoluble in excess	off–white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange–red
iodine, I_2	black solid / purple gas	brown	purple

Anderson Junior College
H2 Chemistry 9729 **2018 JC2 Prelim Paper 4 Suggested Solutions**

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>1(a)(i)</td><td>Tabulates mass of weighing bottle and mass of weighing bottle and residual FA 3 for table and mass of FA 3 used.

Table has appropriate headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers.
Where units have not been included in the header, there should be the appropriate unit for each entry in the table.

Weighing
<table>
<tr><td>Mass of (empty) weighing bottle / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and FA 3 / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and residual FA 3 / g</td><td></td></tr>
<tr><td>Mass of FA 3 used / g</td><td></td></tr>
</table></td><td>1</td></tr>
<tr><td></td><td>Correctly calculates the mass of FA 3 used is within 9.8 to 10.2 g, both inclusive.</td><td>1</td></tr>
<tr><td>(ii)</td><td>All the final/initial burette readings for all accurate titres are recorded to the nearest 0.05 cm^3.

<i>Treat all titres as “accurate” unless labelled rough or 1st titre is of lower precision than subsequent titres</i>

Table has appropriate headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers.
Where units have not been included in the header, there should be the appropriate unit for each entry in the table.

Titration
<table>
<tr><td>titration number</td><td>1</td><td>2</td><td>3</td><td>4</td></tr>
<tr><td>volume of FA 4 added / cm^3</td><td>6.00</td><td>18.00</td><td>10.00</td><td>14.00</td></tr>
<tr><td>initial burette reading / cm^3</td><td></td><td></td><td></td><td></td></tr>
<tr><td>final burette reading / cm^3</td><td></td><td></td><td></td><td></td></tr>
<tr><td>volume of FA 2 used / cm^3</td><td></td><td></td><td></td><td></td></tr>
</table></td><td>1</td></tr>
<tr><td></td><td>Proposes two extra volumes* of FA 4 which are within the range 6 – 18 cm^3.

* gaps between adjacent FA 4 volumes should be $\geq$ 3.5 cm^3 and $\leq$ 4.5 cm^3</td><td>1</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

(b)	Plotting – all points within ±½ small square. Check all points and put tick at each point if correct.	1
	The graph line is the straight best–fit line **and** line is correctly extrapolated to intersect both axes. i.e. one continuous straight line **and** no point is further than 1 cm^3 away from the line in either direction.	1
	Accuracy mark scaled $\boldsymbol{V_{max}}$**(FA 4)** = graphical value of $\boldsymbol{V_{max}}$**(FA 4)** x $\dfrac{\text{mass of } \textbf{FA 3} \text{ used}}{10.00}$ Award this mark if the difference between the student's scaled $\boldsymbol{V}_{\mathbf{max}}$**(FA 4)**, and the teacher's scaled $\boldsymbol{V}_{\mathbf{max}}$**(FA 4)** values is no greater than ±**1.5** cm^3.	1
	Accuracy mark The value of $\boldsymbol{V}_{\mathbf{max}}$**(FA 2)** is independent of the concentration of **FA 4**, so no scaling is needed for this mark. Award this mark if the difference between the student's, and the teacher's, graphical $\boldsymbol{V}_{\mathbf{max}}$**(FA 2)** values is no greater than ±**1.0** cm^3.	1
	Student recognises that $\boldsymbol{V}_{\mathbf{max}}$**(FA 2)** and $\boldsymbol{V}_{\mathbf{max}}$**(FA 4)** are the intercept values on the *y*–axis and the *x*–axis respectively **and** these values are correctly read from the graph to ±½ small square (ignore sig figs) If the student has not shown the extrapolation on the graph, the student may still earn this mark if the values quoted correspond to correct extrapolation of the student's graph line.	1
(c)	Use clearly stated co–ordinates from graph. *Coordinates could be from* $\boldsymbol{V}_{\mathbf{max}}$ *values*. **or** Correct values of Δ*titre* and of Δ(*volume of* ***FA 4*** *used*) obtained from a clearly drawn triangle which covers at least 3 large squares in each direction (*allow measurements to ± ½ small square*). **and** • Correctly calculate gradient *with negative sign*. (ignore sig figs for this mark) ***Do not award this mark if*** • *the graph line is not straight.* *For this mark, ignore missing working and incorrect/missing units.*	1

	Minimal: Student used V_{max} (FA 4) and V_{max} (FA 2) to determine gradient without working or labeling of coordinates.	
(d)	Negative gradient because the more Na_2CO_3 / **FA 4** added, the less NaOH / **FA 2** is needed for neutralisation (or words to that effect) (owtte) • slope of graph has a negative gradient • as more Na_2CO_3 are added, amount of H_2SO_4 partially neutralised by it will increase and • hence less NaOH is required to neutralise the remaining H_2SO_4	1
(e)(i)	Correctly calculates $[Na_2CO_3]$ in **FA 4**. $[Na_2CO_3] = \frac{\text{mass of } \mathbf{FA\ 3} \text{ used}}{106.0} \times \frac{1000}{250} = \mathbf{A}\ (\text{mol dm}^{-3})$ *Do NOT award this mark if the mass of **FA 3** was incorrectly calculated in the table in part **(a)**.*	1
(e)(ii)	Student chooses to use the $\boldsymbol{V_{max}}$**(FA 4)** value and for using it effectively and correctly calculates the nNa_2CO_3 it contains $nNa_2CO_3 = \frac{V_{max}\,(\text{FA 4})}{1000} \times \mathbf{A} = \mathbf{B}\ (\text{mol})$ $[H_2SO_4] = \mathbf{B} \times \frac{1000}{25.0} = \mathbf{C}\ (\text{mol dm}^{-3})$ *Allow both marks for a correct answer, even if the working is missing. The 1st mark is for choosing to use the student's recorded value for* $\boldsymbol{V_{max}}$***(FA 4)*** *and for using it effectively.* *Note: Students who do not calculate* nNa_2CO_3*, but who incorporate all the appropriate figures in an expression which yields a correct value for **C**, should not be penalised under the 'shows working' mark because of this.*	1 1
(e)(iii)	Using $\boldsymbol{V_{max}}$**(FA 2)** to calculate [NaOH] Using $[H_2SO_4]$ = **C** $[NaOH] = 2\mathbf{C} \times \frac{25.0}{V_{max}\,(\text{FA 2})} = \mathbf{D}\ (\text{mol dm}^{-3})$ **Or** Using nNa_2CO_3, **B** $[NaOH] = 2\mathbf{B} \times \frac{1000}{V_{max}\,(\text{FA 2})} = \mathbf{D}\ (\text{mol dm}^{-3})$	1
(f)	Correctly calculates [NaOH] using the given expression.	1

(g)	effect: value of ***V***V_{max}**(FA 4)** will be higher *than expected* / greater / increase / too high explanation: presence of water means mass of Na_2CO_3 weighed out is lower than expected, so [Na_2CO_3] in **FA 4** is lower than expected, so more **FA 4** is needed to neutralise the sulfuric acid. Cannot accept: • mass of **FA 3** weighed out is lower than expected (because mass of FA 3 includes the water)	1
	effect: value of **V_{max}(FA 2)** is *same as expected* / unchanged / no effect / remains the same explanation: the volume of **FA 4** added at **V_{max}(FA 2)** is zero, so the incorrect concentration of **FA 4** has no effect.	1

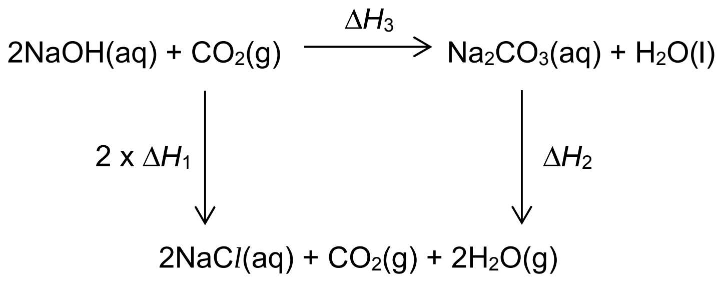
Teacher's values

Date	**Shift**	**Teacher's value**			
		V_{max}(FA4)	**mass**	**scaled**	**V_{max}(FA2)**
28/8/2018	1 (0800 – 1030)	25.50	9.958	25.39	35.50 (CL1-4) 35.00 (CL5, PL1 – 3)
	2 (1110 – 1340)	25.50 (all labs) / 26.25* (CL5, PL1–3)	10.045	25.61 (all labs) / 26.37* (CL5, PL1 – 3)	35.50 (CL1-4) 35.00 (CL5, PL1–3)
	3 (1420 – 1650)	25.50 (all labs) / 26.25* (CL5, PL1–3)	10.045	25.61 (all labs) / 26.37* (CL5, PL1–3)	35.50 (CL1-4) 35.00 (CL5, PL1–3)

Note: **V_{max}(FA2)** differ for level 2 and level 3 labs due to different stock solutions used.

$$\text{Student's/Teacher's scaled } V_{max}(\textbf{FA 4}) = \text{graphical value of } V_{max}(\textbf{FA 4}) \times \frac{\text{mass of } \textbf{FA 3} \text{ used}}{10.00}$$

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td rowspan="3">2(a), (b)</td><td>All <u>measured temperatures</u> (initial temperature of FA 5, FA 6 and T_{max} after reaction) are recorded to <u>0.1 °C</u>
and
Correctly calculate T_{av} and ΔT_{max} (to 0.1 °C or up to 2 d.p.) using the two expressions below.
$T_{av} = \frac{(\text{volume } \textbf{FA 5} \text{ x initial temp } \textbf{FA 5}) + (\text{volume } \textbf{FA 6} \text{ x initial temp } \textbf{FA 6})}{\text{total volume of reaction mixture}}$
$\Delta T_{max} = T_{max} - T_{av}$</td><td>1</td></tr>
<tr><td>All <u>measured temperatures</u> (initial temperature of FA 5, FA 7 and T_{max} after reaction) are recorded to <u>0.1 °C</u>
and
Correctly calculate T_{av} and ΔT_{max} (up to 2 d.p.) using the two expressions below.
$T_{av} = \frac{(\text{volume } \textbf{FA 5} \text{ x initial temp } \textbf{FA 5}) + (\text{volume } \textbf{FA 7} \text{ x initial temp } \textbf{FA 7})}{\text{total volume of reaction mixture}}$
$\Delta T_{max} = T_{max} - T_{av}$</td><td>1</td></tr>
<tr><td><u>Accuracy mark</u>
If ΔT for both experiments +/– 0.2 from Teacher's result
If ΔT for both experiments +/– 0.6 from Teacher's result
<i>Teacher's results</i>
<table>
<tr><th>Shift</th><th>ΔT for FA 6</th><th>ΔT for FA 7</th></tr>
<tr><td>1</td><td>7.3</td><td>1.3</td></tr>
<tr><td>2</td><td>7.2</td><td>1.3</td></tr>
<tr><td>3</td><td>6.8</td><td>1.1</td></tr>
</table></td><td>2
(max)
1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(c)(i)</td><td>Correctly calculates nHC<i>l</i> = $\frac{40.0}{1000}$ x 2.00 = 0.0800 mol
and nNaOH = $\frac{50.0}{1000}$ x 1.00 = 0.0500 mol
0.0500 mol NaOH reacts with 0.0500 mol HC<i>l</i>.
Thus, FA 5 (or HC<i>l</i>) is in excess.</td><td>1</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

(c)(ii)	Correctly calculates q = $(V_{\mathbf{FA\ 5}} + V_{FA\ 6})(1.00)\,c\Delta T$ = 90 x 1.00 x 4.18 x ΔT_{max} J (allow kJ) Ignore if q has sign or has a wrong unit or if ΔT_{max} was calculated wrongly.	1
	Recognises that the limiting reagent is HC*l* and uses nHC*l* of to determine ΔH_1. Correctly calculates $\Delta H_1 = -\frac{q}{nHCl}$ = $\underline{-\mathbf{a}}$ kJ mol^{-1} Correct sign for ΔH_1 = –ve	1
(d)(i)	Correctly calculates nHC*l* = $\frac{40.0}{1000}$ x 2.00 = 0.0800 mol and $nNa_2CO_3 = \frac{50.0}{1000}$ x 1.00 = 0.0500 mol 0.0500 mol Na_2CO_3 requires 0.100 mol HC*l* OR 0.0400 mol Na_2CO_3 reacts with 0.0800 mol HC*l* Thus, **FA 7** (or Na_2CO_3) is in excess.	1
(d)(ii)	Correctly calculates q = $(V_{\mathbf{FA\ 5}} + V_{FA\ 7})(1.00)\,c\Delta T$ = 90 x 1.00 x 4.18 x ΔT_{max} J (allow kJ) Ignore if q has sign or has a wrong unit or if ΔT was calculated wrongly.	1
	Recognises that the limiting reagent is HC*l* and uses nHC*l* of to determine ΔH_2. Correctly calculates $\Delta H_2 = -\frac{q}{nHCl}$ **x 2** = $\underline{-\mathbf{b}}$ kJ mol^{-1} Correct sign for ΔH_2 = –ve	1
(e)	Correctly calculates ΔH_3  By Hess' Law, $\Delta H_3 = 2\Delta H_1 - \Delta H_2$ = 2(–**a**) – (–**b**) = $\underline{\mathbf{b} - 2\mathbf{a}}$ kJ mol^{-1}	2
	Shows working in all calculations in **1(c), (e) – (f) and 2(c) – (d)**. All calculations must be relevant although they may not be complete or correct. *Any calculations not attempted loses this mark.*	1
	Shows appropriate significant figures (3 s.f.) in all final answers in **1(c), (e) – (f) and 2(c)(ii), (d)(ii)**. Shows appropriate units in **1(e) – (f) and 2(c) – (d)**. *Any calculations not attempted loses this mark.*	1

(f)

Recognise that enthalpy change of solution of solid Na_2CO_3, $\Delta H_{solution}(Na_2CO_3)$, is required.

1

Suitable energy cycle or working to show how the 3 enthalpy change terms can be used to determine ΔH_4

$$\begin{tikzcd}
2NaOH(aq) + CO_2(g) \arrow[r, "\Delta H_4"] \arrow[d, "2 \times \Delta H_1"'] & Na_2CO_3(s) + H_2O(l) \arrow[d, "\Delta H_{solution}(Na_2CO_3)"] \\
2NaCl(aq) + CO_2(g) + 2H_2O(g) & Na_2CO_3(aq) + H_2O(l) \arrow[l, "\Delta H_2"']
\end{tikzcd}$$

By Hess' Law,

$\Delta H_3 = 2\Delta H_1 - \Delta H_2 - \Delta H_{solution}(Na_2CO_3)$

$= \underline{\mathbf{b - 2a} - \Delta H_{solution}(Na_2CO_3)}$ kJ mol^{-1}

<u>Suggested plan</u>

2

To determine **$\Delta H_{solution}(Na_2CO_3)$**

1. Weigh a <u>fixed/known mass</u> (accurately about 5.0 g) of solid Na_2CO_3 in a weighing bottle
2. Using a (50.0 cm^3) measuring cylinder, transfer <u>50.0 cm^3 of **deionised water**</u> into <u>Styrofoam cup</u>. (Place this cup into a second Styrofoam cup which is placed in a 250 cm^3 glass beaker).
3. Record the <u>initial temperature of the water</u>.
4. Add (rapidly) solid Na_2CO_3 to the water and replace the lid, *keeping the bulb of the thermometer in the solution throughout*. *Stir* the mixture.
5. Continue to stir the mixture and record the <u>maximum change from the initial temperature</u>.
6. *Reweigh* the weighing bottle.

Marks	Requirements	Key Marking Points
[1]	Appropriate <u>quantities</u> of substances used and <u>appropriate apparatus</u> and their <u>capacities</u>	• vol of water = <u>50 cm^3</u> • water : 50 cm^3 measuring cylinder or 50 cm^3 burette • mass of Na_2CO_3 = 5 g or any known / fixed value • Styrofoam cup with lid
[1]	Essential <u>experimental details</u> to ensure <u>reliable results</u>	1. Take <u>initial</u> and <u>maximum rise / drop in temperature</u>. 2. Start reaction by <u>adding Na_2CO_3</u> and rapidly and replace lid. 3. <u>Stir</u> the reaction mixture. 4. <u>Reweigh</u> the weighing bottle. (any 3 points)

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>3(a)</td><td>See answer grid
12 possible observations

Marks allocated as follows:
<table>
<tr><td>Number of correct observations</td><td>Award (max 3)</td></tr>
<tr><td>10 – 12</td><td>3</td></tr>
<tr><td>7 – 9</td><td>2</td></tr>
<tr><td>4 – 6</td><td>1</td></tr>
</table></td><td>3</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(b)(i)</td><td>
<table>
<tr><td>FA 8</td><td>alcohol</td><td>gives negative 2,4–DNPH test in (a)(i) but positive iodoform test in (a)(iv) shows that it contains $CH_3CH(OH)–$ group and is an alcohol.</td></tr>
<tr><td>FA 9</td><td>ketone</td><td>gives a positive 2,4–DNPH test in (a)(i) but negative Fehling's test in (a)(iii) shows that it is a ketone.</td></tr>
<tr><td>FA 10</td><td>carboxylic acid</td><td>gives H_2 on reaction with Mg in (a)(ii) shows that it contains the $–CO_2H$ group / is a carboxylic acid.</td></tr>
<tr><td>FA 11</td><td>aldehyde</td><td>positive Fehling's test in (a)(iii) shows that it contains the –CHO group / is an aldehyde.</td></tr>
</table>
[1] each

for quoting of evidence, can give either the name of the reagent or the qn
for alcohol, stating the presence of $CH_3CH(OH)–$ group is essential
additional evidence (not required for identity to be deduced) is penalised</td><td>4</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(ii)</td><td>sample: FA 11
identity: Cu_2O
type of reaction: redox</td><td>1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(c)(i)</td><td>$\mathbf{C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr}$</td><td>1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(ii)</td><td>amount of bromine = $\frac{6.0 \times 3.12}{159.8}$
= 0.1171 mol
amount of benzene = $\frac{0.1171}{2}$
= 0.005857 mol
mass of benzene = 0.005857 x 78.0
= 4.568 g
volume of benzene = $\frac{4.568}{0.88}$
= 5.19 cm^3</td><td>1
1</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

(iii)

Volume of benzene used is within the range of 5.19 – 20.00 cm^3.
Volume of bromine is kept unchanged.
To keep mole ratio of benzene : bromine within 2:1 and 1:2.

Suggested answer:

n(benzene):n(Br_2)	n(benzene) / mol	n(Br_2) / mol	V(benzene) / cm^3	V(Br_2) / cm^3
1:1	0.1171	0.1171	10.0	6.0
1:1.5	0.007806	0.1171	7.0	6.0

1

(iv)

Suggested Plan

Preparation of crude bromobenzene

1. Using a 20 cm^3 measuring cylinder, measure 20.0 cm^3 (0.226 mol) of benzene, and a 10 cm^3 measuring cylinder to measure 6.0 cm^3 (0.117 mol) of bromine. Add both into a 50 cm^3 round–bottomed flask.
2. Add an iron tack to the reaction mixture.
3. Using a water bath, gently heat the flask fitted with a reflux condenser at 50 – 55 °C for about 15 minutes. Reaction should be done in a fume cupboard to remove the acidic fumes of hydrogen bromide evolved.
4. After about 15 min when the reaction subsides, remove the reaction mixture from the water bath.
5. The mixture is then transferred into a 100 cm^3 conical flask heated over a hot plate to drive off unreacted bromine until the bromine vapour above the liquid disappears (or solution turns from brown/orange to colourless). This should be done in the fume cupboard to collect the bromine gas evolved.
6. Allow the mixture to stand and cool before doing solvent extraction.
7. Using a 25 cm^3 measuring cylinder, add 25.0 cm^3 of ether to dissolve the cooled reaction mixture. Open the cover to release the pressure build-up.
8. Using a 10 cm^3 measuring cylinder, add 5 cm^3 of sodium hydroxide to the ether solution before shaking the mixture in a 100 cm^3 separatory funnel. Open the tap to release the aqueous layer.
9. Repeat step 8.
10. Using a 10 cm^3 measuring cylinder, add 10 cm^3 portion of water to the ether solution before shaking the mixture in the separatory funnel. Open the tap to release the aqueous layer.
    (Alternatively, use conical flask to shake the mixture in steps 8–10 and decant the top layer or use a dropper/ pipette to withdraw bottom aq layer)
11. Add a spatula full of magnesium sulfate to the ether layer, swirl and stand for a few minutes to dry the ether layer before it is filtered away.
12. Perform fractional distillation and collect the fraction between 140–160 °C for bromobenzene.
13. Weigh the bromobenzene collected.
14. Calculate the percentage yield of bromobenzene based on benzene. This is the yield.
15. Repeat the experiment with the sets of reagents in **(iii)** and determine the yield for these reaction mixtures.

6

Marks	Requirements	Key Marking Points
[2]	Logical flow of plan	• mixing reagents based on given quantities, warm for 15 min at specified temperature • (heat to drive off bromine) • follow steps in solvent extraction • dry the crude sample using $MgSO_4$ and filter • fractional distillation • weigh the product obtained/measure volume collected • Repeat the experiment two more times using the volumes suggested in **(iii)**. (1 mark for any 4 points, 2 marks for all points)
[1]	Appropriate apparatus and their capacities	• 50 cm^3 round bottomed flask • 10 or 25 cm^3 measuring cylinders • 100 cm^3 separatory funnel / separating funnel
[2]	Essential experimental details to ensure reliable results	• Carrying out reaction under reflux to prevent loss of volatile reagents. • Ensure unreacted Br_2 is driven off by observing the clearing of Br_2 vapour above the reaction mixture. • Collecting the bromobenzene fraction between 140–160 °C (or T between 100 and 200 °C to avoid collecting 1,4–dibromobenzene). (1 mark for any point, max. 2 marks)
[1]	Safety precautions	Carrying out the reaction in fumehood to remove the acidic HBr fume and irritant Br_2. Release the pressure from the separatory funnel occasionally. (1 mark for any point)
[1]	Calculations	Theoretical amount of bromobenzene based on benzene = n(benzene) $\% \text{ yield} = \dfrac{\text{actual amount of bromobenzene}}{\text{theoretical amount of bromobenzene}} \times 100\%$ % yield can also be in terms of mass or volume of bromobenzene. Should also show an outline of how the amount of bromobenzene are obtained from its mass or volume and/or vice versa. Note: The yield in this question is more of to determine the % conversion of benzene to bromobenzene in the given reaction mixtures and not comparing the % yield of the different reaction mixtures. The fixed reference of benzene given in the question is necessary due to changing limiting reagents in the varying proportions of benzene and bromine.

Maximum 6 marks awarded for the 7 marking points.

(v)	Step 2: electrophilic substitution Step 3: nucleophilic substitution	1 1

Mark Scheme Grid for parts 3(a)(i) – 3(a)(iv)

(a)	test	observations with			
		FA 8	**FA 9**	**FA 10**	**FA 11**
(i)	Place about 1 cm depth of the unknown in a test–tube. To the test–tube, add about 1 cm depth of 2,4–dinitrophenylhydrazine reagent. Shake and warm the test–tube in a water–bath.	no observable change	orange / yellow ppt observed (1)	no observable change (1)	orange / yellow ppt observed (1)
(ii)	Place about 1 cm depth of the unknown in a test–tube. To the test–tube, add a small amount of magnesium powder.	no observable change (1)	no observable change	effervescence observed **and** gas gives a 'pop' sound with lighted splinter (1)	no observable change (1)
(iii)	Place about 1 cm depth of the unknown in a test–tube. To the test–tube, add 1 cm depth of Fehling's solution. Shake and warm the test–tube in a water–bath.	no observable change (1)	no observable change (1)	no observable change	brick–red ppt observed (1)
(iv)	Place about 1 cm depth of the unknown in a test–tube. To this test–tube, add about 3 cm depth of iodine solution. Then add sodium hydroxide dropwise until the iodine colour has almost discharged. Warm the test–tube in a water–bath if necessary.	yellow crystals / solid observed (1)	yellow crystals / solid observed (1)	no observable change (1)	no observable change

Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/01

Paper 1 Multiple Choice

Wednesday 29 August 2018
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and NRIC/FIN number on the Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages.

1 A sample of tungsten contains four naturally occurring isotopes, ^{182}W, ^{183}W, ^{184}W and ^{186}W.

The relative atomic mass of tungsten in this sample is 183.9. What is the percentage of the isotope ^{182}W in this sample?

Isotope	**Relative Abundance (%)**
^{182}W	?
^{183}W	?
^{184}W	30.6
^{186}W	28.6

A 10.5

B 14.4

C 26.4

D 40.8

2 20 cm^3 of 0.100 mol dm^{-3} of potassium ferrate(VI), K_2FeO_4, reacts with sodium ethanedioate, $Na_2C_2O_4$, in an acidic medium to produce 144 cm^3 of carbon dioxide gas at room temperature and pressure.

The half equation of $C_2O_4^{2-}$ is shown as follows:

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-}$$

What is the final oxidation state of the iron-containing species after the reaction?

A +1 **B** +2 **C** +3 **D** +4

3 When attracted by a strong magnet, some species are able to exhibit paramagnetism. Such species contain unpaired electrons which are able to spin in a way which aligns parallel to the magnetic field.

Which of the following species in the ground state is able to exhibit paramagnetism?

1 O 2 Al^+ 3 Ti^{2+} 4 Cu^+

A 1 and 3 only

B 2 and 4 only

C 1, 3 and 4 only

D 2, 3 and 4 only

4 Phosphorus(V) chloride, PCl_5 dissolves in a suitable polar solvent to produce two ions, $[PCl_4]^+$ and $[PCl_6]^-$.

Which of the following shows the correct shape for PCl_5, $[PCl_4]^+$ and $[PCl_6]^-$?

	PCl_5	$[PCl_4]^+$	$[PCl_6]^-$
A	trigonal planar	square planar	square pyramidal
B	trigonal bipyramidal	square planar	octahedral
C	trigonal planar	distorted tetrahedral	square pyramidal
D	trigonal bipyramidal	tetrahedral	octahedral

5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
CH_3CH_2Cl	12.3
CH_3CH_2Br	34.8
CH_3CH_2I	70.0

Which of the following correctly explains the difference in the boiling point?

1 the electronegativity difference between the halogen and carbon increases from C−C*l* to C−I
2 the strength of permanent dipole-permanent dipole attraction increases from C−C*l* to C−I
3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I
4 the bond energy of C−X bond decreases from C−C*l* to C−I

A 1 and 2 only
B 2 and 4 only
C 3 only
D 3 and 4 only

6 Which of the following changes will result in the greatest decrease in the density of a fixed mass of ideal gas?

	Pressure	**Temperature/ K**
A	halves	halves
B	halves	doubles
C	doubles	halves
D	doubles	doubles

7 Consider the following reactions.

Reaction 1: $CH_3^+ + Br^- \rightarrow CH_3Br$

Reaction 2: $HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

Which of the following statement is **not** true about the reactions above?

A Both reactions are acid-base reactions.

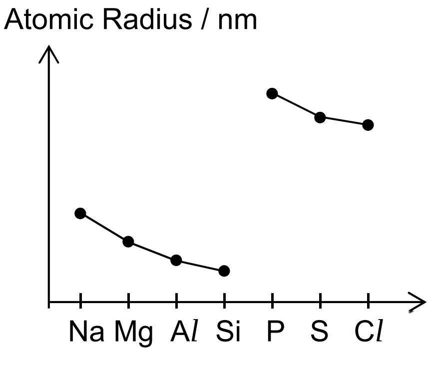
B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.

C In reaction 2, HBO_3^{2-} is the conjugate acid of $H_2BO_3^-$.

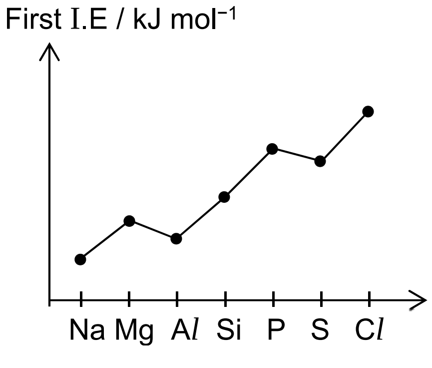
D In reaction 1, a dative covalent bond is formed between CH_3^+ and Br^-.

8 Which of the following sketches shows the correct trend in the stated property for the elements in the third period of the Periodic Table?

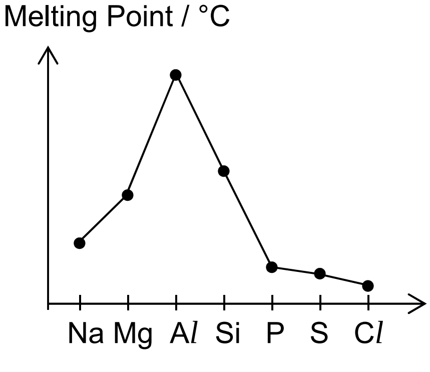
A



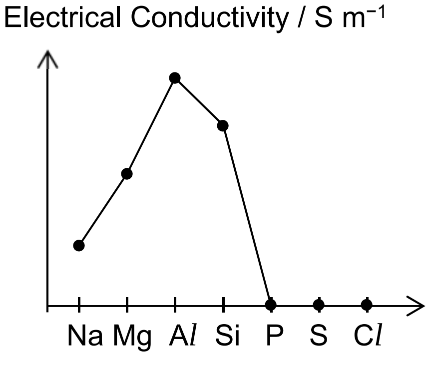
C



B



D



9 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of **increasing** resultant pH when the compounds are added to water?

A	$NaCl$, $MgCl_2$, $SiCl_4$	**C**	Al_2O_3, MgO, SO_2
B	$AlCl_3$, $SiCl_4$, PCl_5	**D**	P_4O_{10}, SiO_2, MgO

10 Phosphine reacts with hydrogen iodide to form phosphonium iodide in the reaction shown below:

$$PH_3(g) + HI(g) \rightarrow PH_4^+I^-(s) \qquad \Delta H^{\ominus} = -145.2 \text{ kJ mol}^{-1}; \Delta S^{\ominus} = -570.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Which of the following statement is true for the above reaction?

1 The products are less disordered than the reactants.

2 The reaction is non-spontaneous under standard conditions.

3 As temperature increases, the reaction becomes more spontaneous.

A 1 only

B 2 only

C 1 and 2 only

D 1, 2 and 3 only

11 The reaction of acidified aqueous potassium iodide with aqueous hydrogen peroxide:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

is thought to involve the following steps:

$$\begin{array}{ll} H_2O_2 + I^- \rightarrow H_2O + OI^- & \text{(slow)} \\ OI^- + H^+ \rightarrow HOI & \text{(fast)} \\ HOI + H^+ + I^- \rightarrow I_2 + H_2O & \text{(fast)} \end{array}$$

Which of the following conclusion can be drawn from this information?

1 The acid is acting as a catalyst only.

2 The reaction is pseudo-first order with respect to H_2O_2.

3 The reaction rate is independent of the pH of the solution.

A 1 only

B 3 only

C 1 and 2 only

D 1,2 and 3 only

12 A first-order decomposition reaction is shown below.

$$AB(g) \rightarrow A(g) + B(g)$$

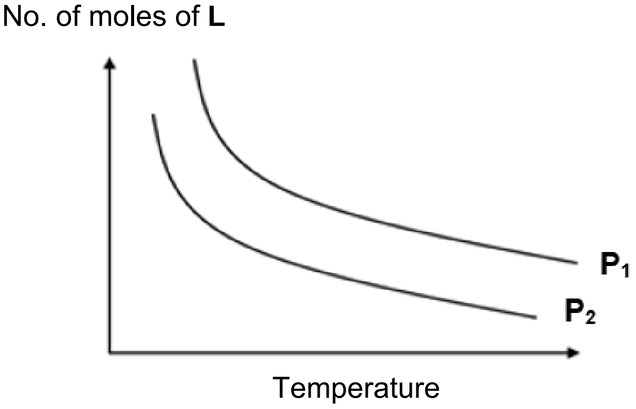
The half-life of the reaction was found to be 3.47 s.

What is the time taken for AB(g) to reach one-third of its initial concentration?

A 3.0 s **B** 3.5 s **C** 5.5 s **D** 7.0 s

13 The graph below shows how the number of moles of compound **L** varies with temperature at two different pressures of **P_1** and **P_2** respectively.
L could be any of the following compounds shown in the equation at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$



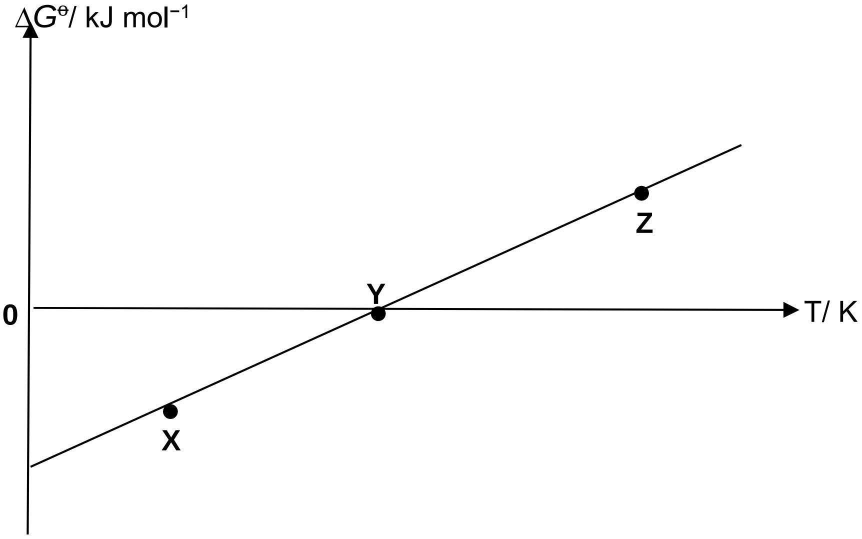
What is the correct identity of **L** and the correct magnitude of pressures **P_1** and **P_2**?

	Identity of **L**	magnitude of pressures **P_1** and **P_2**
A	SO_2	**$P_1 > P_2$**
B	SO_2	**$P_1 < P_2$**
C	SO_3	**$P_1 > P_2$**
D	SO_3	**$P_1 < P_2$**

14 When nitrogen dioxide, NO_2, and nitrogen monoxide, NO, is mixed, the gases react to form dinitrogen trioxide, N_2O_3. The reaction is shown in the following equilibrium.

$$NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$$

The graph below shows how the $\Delta G^\ominus$ varies with temperature for the above reaction.



Using the graph above, deduce which of the following statement is true about the reaction at equilibrium?

A At point **X**, more NO_2 is present as compared to that at point **Y**.

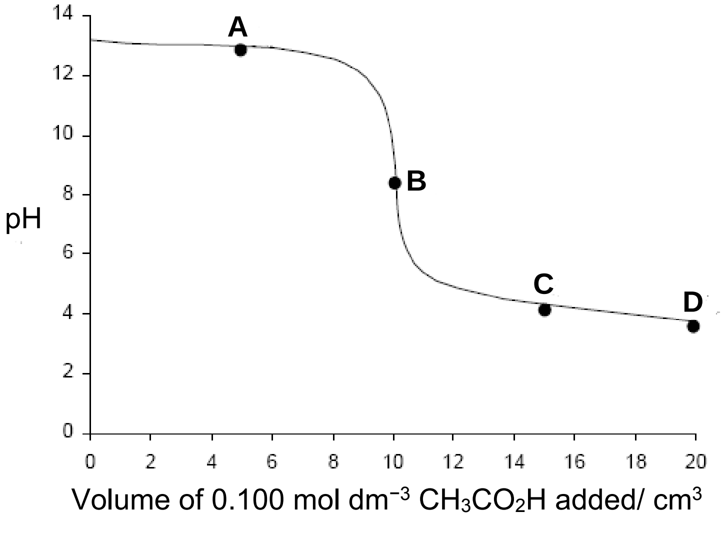
B At point **X**, the K_c value is likely to be greater than 1.

C At point **Y**, the rate of forward reaction is greater than that of backward reaction.

D At point **Z**, more N_2O_3 is present compared to that at point **Y**.

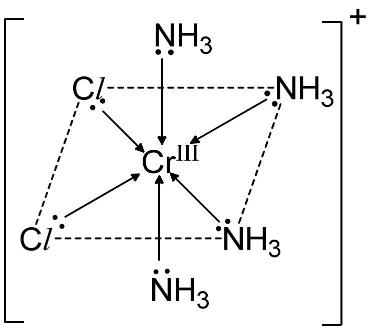
15 The pH changes when 0.100 mol dm^{-3} CH_3CO_2H is added dropwise to 10.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) as shown below.

At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of the weak acid?

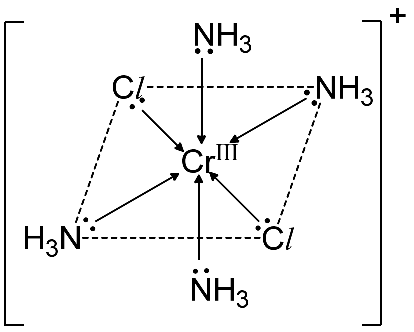


16 Coordination complexes with more than one type of ligand can exist in a number of stereoisomeric forms.

For example, the chromium(III) complex $[Cr(NH_3)_4Cl_2]^+$ can refer to the two stereoisomers as shown:



and



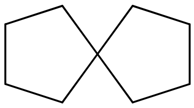
How many stereoisomers can the cobalt(III) complex $[Co(trien)Cl_2]^+$ have?
(trien = $(NH_2CH_2CH_2NHCH_2)_2$, a tetradentate ligand)

A 1 **B** 2 **C** 3 **D** 4

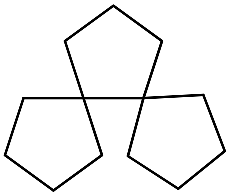
17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?

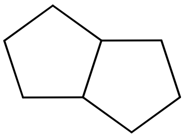
A



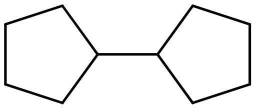
B



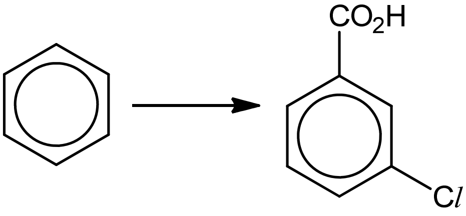
C



D



18 3-chlorobenzoic acid can be synthesized from benzene in three steps.

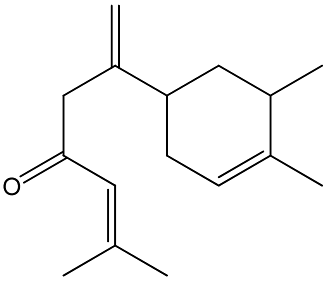


3-chlorobenzoic acid

Which of the following is the best method for this synthesis?

	Step 1	Step 2	Step 3
A	Cl_2, $AlCl_3$	CH_3Cl, $AlCl_3$	$KMnO_4$, H_2SO_4
B	Cl_2, $AlCl_3$	$KMnO_4$, H_2SO_4	CH_3Cl, $AlCl_3$
C	CH_3Cl, $AlCl_3$	$KMnO_4$, H_2SO_4	Cl_2, $AlCl_3$
D	CH_3Cl, $AlCl_3$	Cl_2, $AlCl_3$	$KMnO_4$, H_2SO_4

19 The structure of a β-atlantone derivative is shown below.

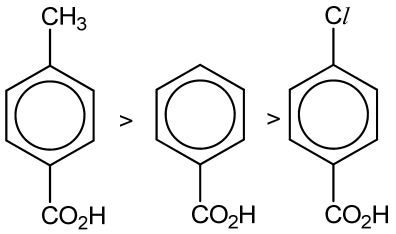


When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

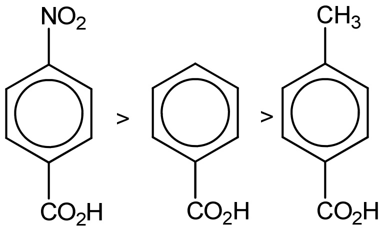
A 2 **B** 3 **C** 4 **D** 5

20 Which of the following correctly lists the compounds in order of decreasing acidity in aqueous solution?

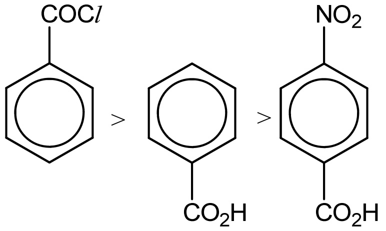
A



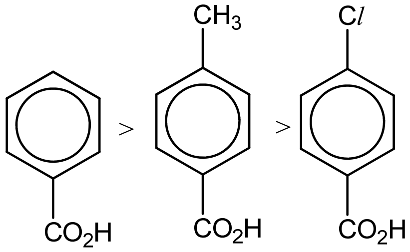
B



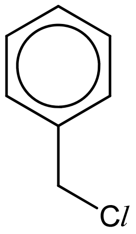
C



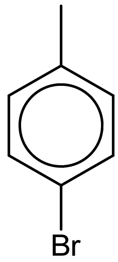
D



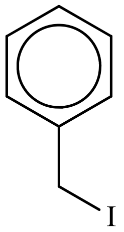
21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.



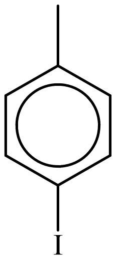
W



X



Y



Z

Which statements are correct?

1 The compounds which do not form a precipitate are **X** and **Z**.

2 The colour of the precipitate which forms the fastest is white.

3 The precipitate which forms the fastest weighs more than the other precipitate.

A 1, 2 and 3 **B** 1 and 3 only **C** 2 and 3 only **D** 1 only

22 The following reaction gives a mixture of organic products.

$$CH_3CHBrCH_2CH_3 \xrightarrow[\text{NaOH}]{\text{hot, ethanolic}}$$

Which of the following statements are true?

1 The organic products formed are mainly alcohols.

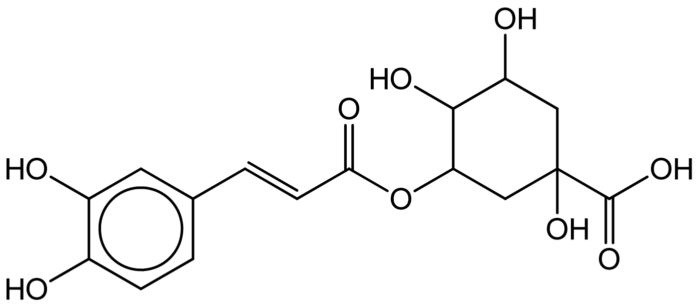
2 The predominant type of reaction occurring is nucleophilic substitution.

3 There is a pair of cis-trans isomers among the organic products.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

23 Chlorogenic acids account for up to 8% of the composition of unroasted coffee beans. More than 40 different varieties have been identified in green coffee beans, with 5-caffeoylquinic acid being the most prevalent.

The structure of 5-caffeoylquinic acid is shown below.

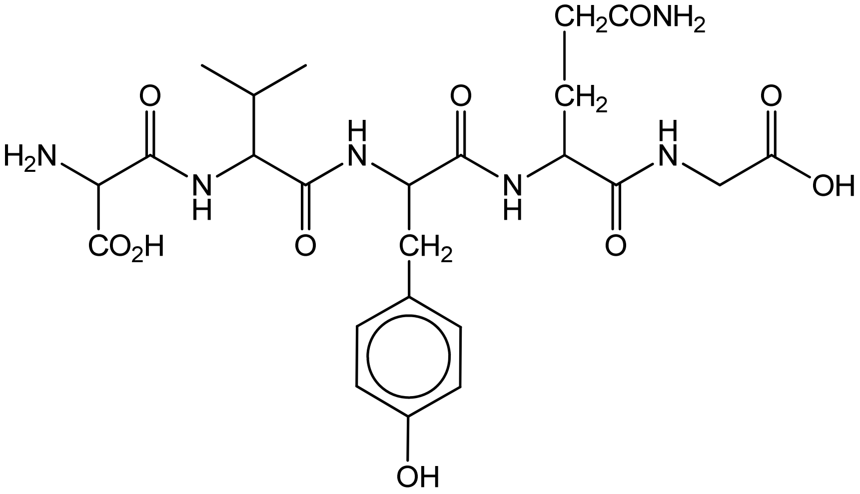


5-caffeoylquinic acid

How many moles of aqueous sodium hydroxide, sodium hydrogencarbonate and phosphorus(V) chloride will react with one mole of 5-caffeoylquinic acid at room temperature?

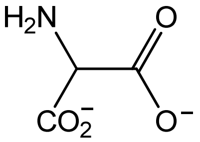
	$NaOH(aq)$	$NaHCO_3(aq)$	$PCl_5(s)$
A	6	3	6
B	5	1	3
C	4	3	4
D	3	1	4

24 The structure of a polypeptide chain is shown below.

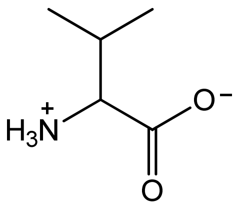


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq)?

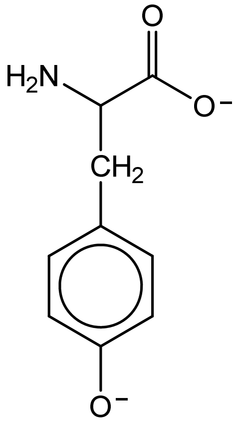
1



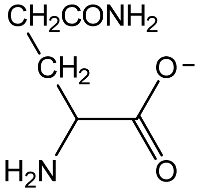
2



3



4



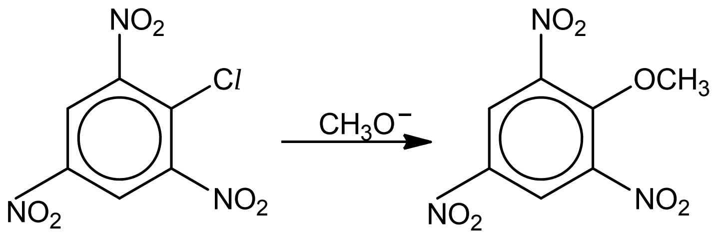
A 1 and 3 only

B 2 and 4 only

C 1, 3 and 4 only

D 1, 2, 3 and 4

25 Methoxide anion, CH_3O^-, can be generated when methanol reacts with sodium metal. The following reaction shows how methoxide anion reacts with an organic compound under suitable conditions.



Which of the following is the correct mechanism for the above reaction?

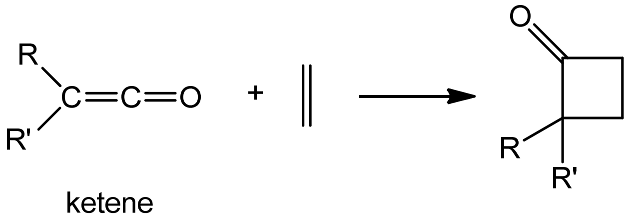
A electrophilic addition

B electrophilic substitution

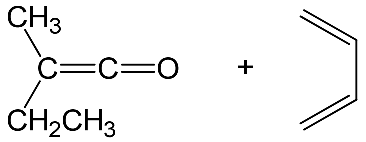
C nucleophilic addition

D nucleophilic substitution

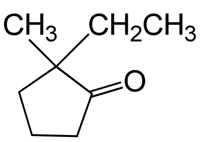
26 Ketenes contain a carbon involved in both alkene and ketone functional groups. It is a reactive compound which undergoes cycloaddition reaction readily with unsaturated compounds to form cyclic rings. One example of such a reaction is shown below.



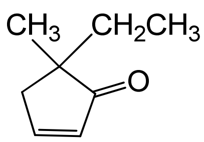
Which of the following is the correct product formed for the following cycloaddition reaction?



A



B



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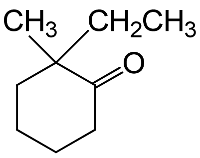
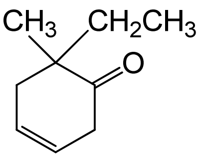


D



27 *Use of the Data Booklet is relevant to this question.*

When a current is passed through a solution of butanoic acid, $CH_3CH_2CH_2CO_2H$, the following reaction occurs at the cathode.

$$CH_3CH_2CH_2CO_2H + 4H^+ + 4e^- \rightarrow CH_3CH_2CH_2CH_2OH + H_2O$$

Oxygen is produced at the anode.

Which volume of oxygen, measured at room temperature and pressure, is produced when 0.015 mol of butanoic acid is electrolysed?

A 90 cm^3 **B** 180 cm^3 **C** 360 cm^3 **D** 720 cm^3

28 Some standard reduction potentials are given below.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V

Which oxidation is **not** feasible under standard conditions?

A chloride ions by acidified manganate(VII) ions

B bromide ions by chlorine

C manganese(II) ions by acidified dichromate(VI) ions

D chromium(III) ions by chlorine

29 A compound of chromium with the general formula $CrCl_3.6H_2O$ forms an aqueous solution. When this solution is treated with an excess of aqueous silver nitrate, only two third of the total chloride present is precipitated as AgCl.

Which of the following represents the structure of the chromium-containing ion present in the original compound?

A Cr^{3+}

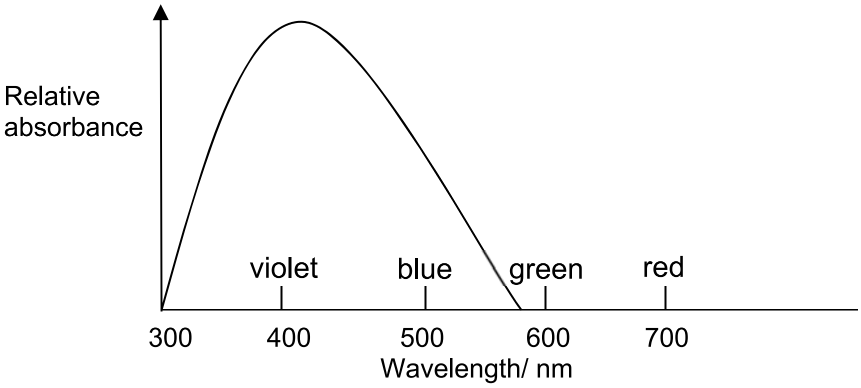
B $[Cr(H_2O)_6]^{3+}$

C $[Cr(H_2O)_5Cl]^{2+}$

D $[Cr(H_2O)_4Cl_2]^+$

30 The chromium picolinate complex is soluble in water and the visible absorption spectrum of the complex is shown below:

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



What is the most likely colour of the chromium picolinate complex?

A violet

B blue

C yellow

D green

Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY **9729/02**

Paper 2 Structured Questions **Friday 17 August 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use				**%**
Paper 1			**30**	**15**
Paper 2	**Q 1**	**15**		
	Q 2	**15**		
	Q 3	**15**		
	Q 4	**15**		
	Q 5	**15**	**75**	**30**
Paper 3	**Q 1**	**20**		
	Q 2	**20**		
	Q 3	**20**		
	Q 4 / 5	**20**	**80**	**35**
Paper 4			**55**	**20**
Total % and Grade				**100**

This document consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

1 In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.

(a) In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4. The decomposition of N_2O_5 was found to be a first-order reaction.

$$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

Table 1.1 below shows the variation of $[N_2O_5]$ with time.

Time / s	$[N_2O_5]$ / mol dm^{-3}	ln $[N_2O_5]$
0	0.910	
300	0.750	
600	0.640	
1200	0.440	
3000	0.160	

Table 1.1

(i) State the rate equation for the decomposition of N_2O_5.

.... [1]

(ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

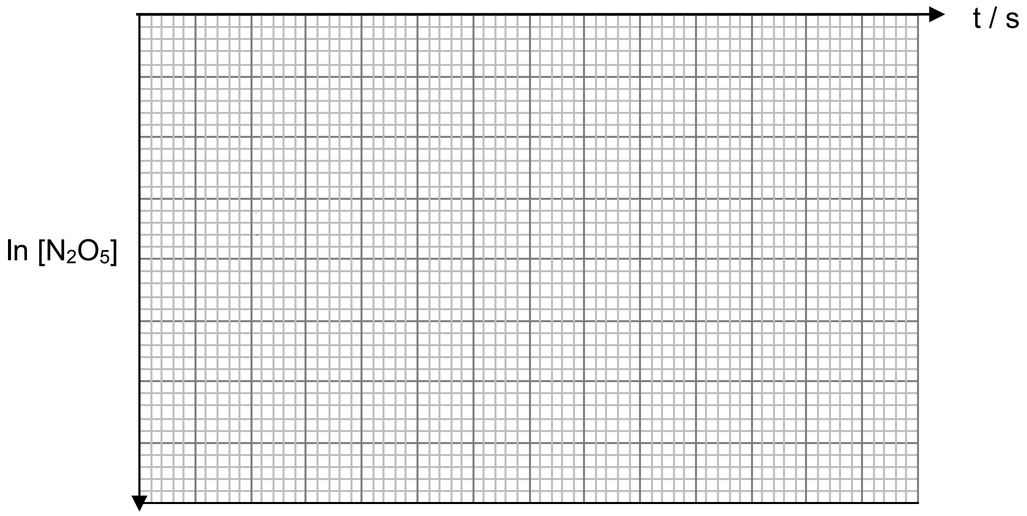
$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o$$

where $[N_2O_5]_o$ is the initial concentration of N_2O_5 and $[N_2O_5]_t$ is the concentration of N_2O_5 at time, t.

Using relevant data in Table 1.1, calculate the values for ln $[N_2O_5]$ and complete Table 1.1.

[1]

(iii) Using the following axes and relevant data in Table 1.1, plot a graph of $\ln [N_2O_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

(iv) Using your graph, determine a value for the rate constant, k, for the decomposition of N_2O_5. State the units of k clearly.

[2]

(v) Hence determine a value for the half-life of the decomposition of N_2O_5. State the units clearly.

[1]

(vi) Outline another experiment to determine the rate constant, k, for the decomposition of N_2O_5 in tetrachloromethane.

You are provided with the same solution of N_2O_5 used in the experiment described in **(a)**.

No details regarding use of specific glassware are required.

....

....

....

....

....

....

....

.... [2]

(b) The NO_2 produced in the decomposition reaction in **(a)** can exist in equilibrium with dinitrogen tetroxide (N_2O_4):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm^{-3}		Equilibrium concentration / mol dm^{-3}	
	[N_2O_4]	[NO_2]	[N_2O_4]	[NO_2]
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

(i) State *Le Chatelier's Principle*.

....

....

.... [1]

(ii) State what will be observed when the pressure in the reaction vessel is decreased.

....

.... [1]

(iii) Identify the experiment that gives the initial concentration of $N_2O_4 : NO_2$ in the ratio 15:1.

.... [1]

(iv) Based on the experiment identified in **(b)(iii)**, calculate a value for the equilibrium constant, K_c.

[1]

(v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined.

K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in **(b)(iv)** and the above expression, calculate a value for the K_p for the reversible reaction between N_2O_4 and NO_2.

[2]

[Total: 15]

2 **(a)** Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

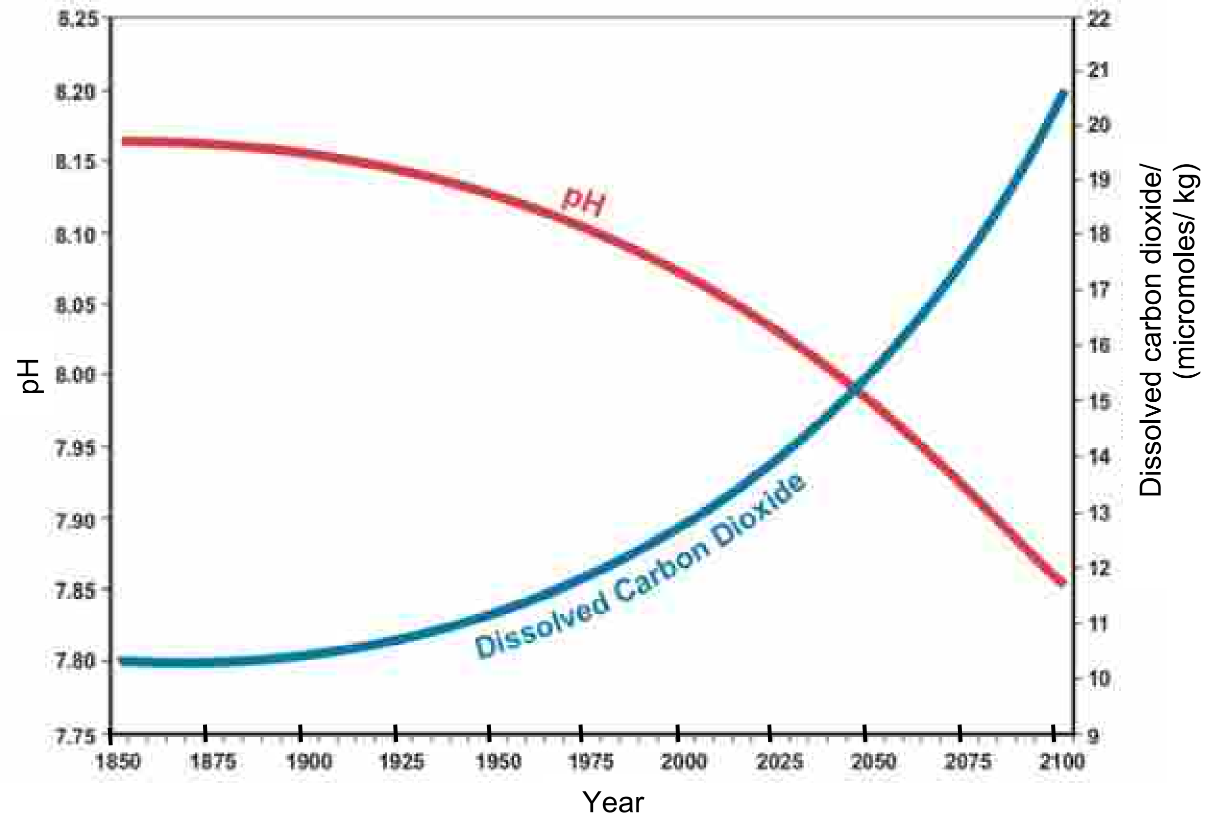


Fig. 2

(i) State what is meant by a *zwitterion*.

.... [1]

(ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

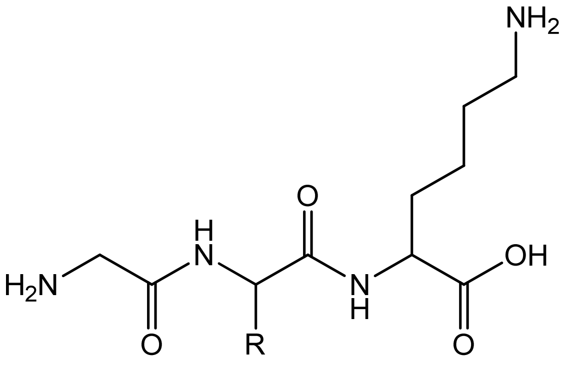
....

.... [1]

(iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO_2.

.... [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.



GHK

(iv) Circle any chiral carbon atom on the above structure, GHK. [1]

(v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.

[2]

(vi) Use the graph in Fig. 2 to determine from which year onwards, more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

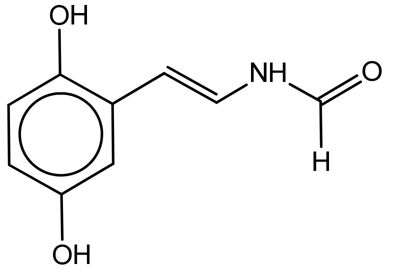
……………………………………………………………………………………………

……………………………………………………………………………………………

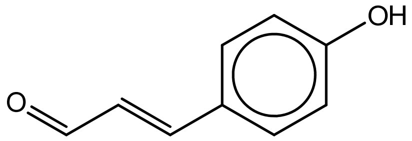
……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin



4-hydroxy cinnamaldehyde

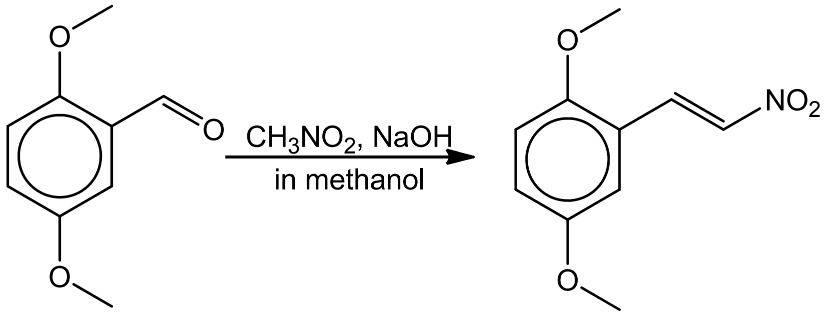
(i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………… [3]

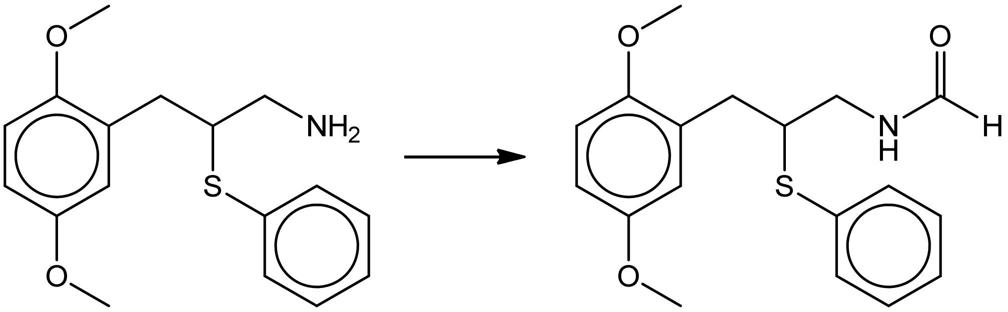
The synthesis of erbstatin involved the following step.



(ii) Given that NaOH is used as a base to form $^{-}CH_2NO_2$ as a nucleophile, suggest the type of reaction in the above step.

……………………………………………………………………………………… [1]

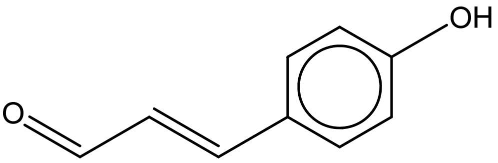
Another step in the synthesis of erbstatin is shown below.



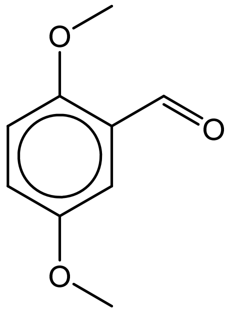
(iii) Suggest suitable reagents for the above step.

.... [1]

(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

....

....

.... [2]

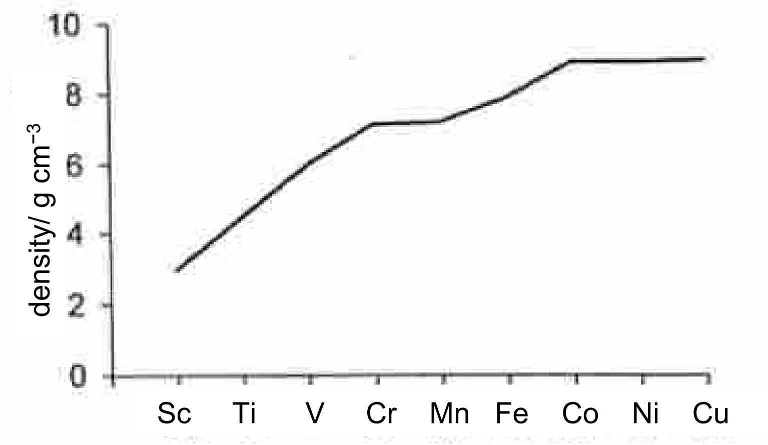
[Total: 15]

[Turn over

3 **(a)** d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

The graph below shows the densities of the elements Sc to Cu.



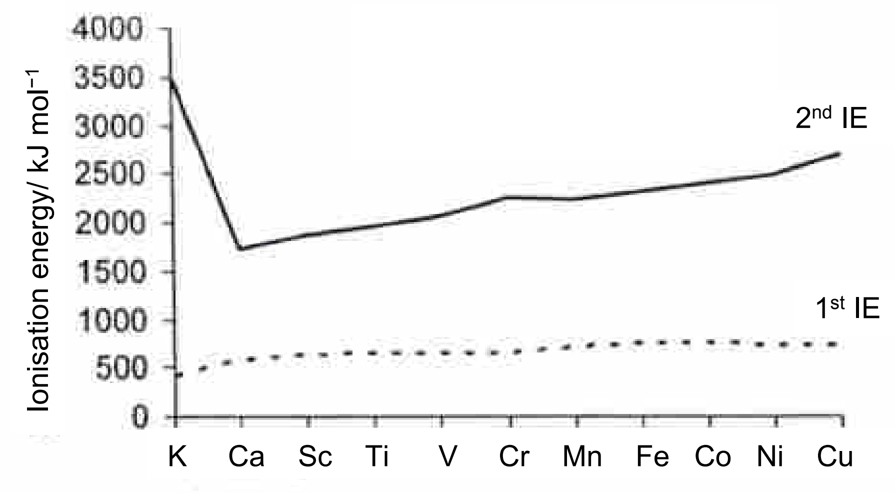
(i) Suggest why the densities of the elements increase from Sc to Cu.

....

....

.... [2]

(ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

....

....

.... [2]

(iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

....

.... [1]

(b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

....

.... [1]

(ii) State the full electronic configuration of Sc^{3+}.

....[1]

(iii) Explain why scandium is not classified as a transition element.

....

.... [1]

(c) **X** and **Y** are period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element **Y** is added to the oxide of element **X** with water.

Identify the elements **X**, **Y**, and the oxide of **Y**.

Explain the observations with the aid of relevant equations.

....

....

....

....

....

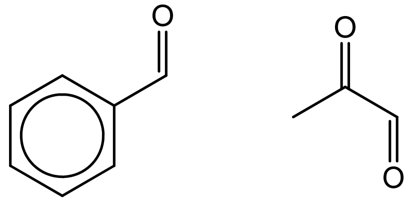
....

....

.... [7]

[Total: 15]

4 **(a)** Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



benzaldehyde 2-oxopropanal

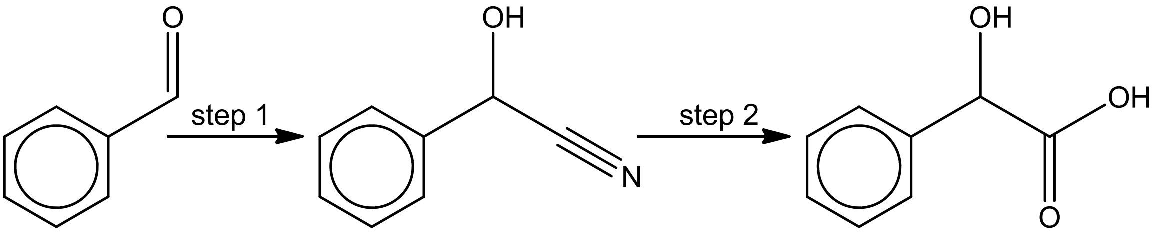
(i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: ....

	Observations:	Products:
benzaldehyde		
2-oxopropanal		

[3]

(ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



benzaldehyde mandelic acid

State the reagents and conditions for steps 1 and 2.

Step 1: ....

Step 2: ....

[2]

(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

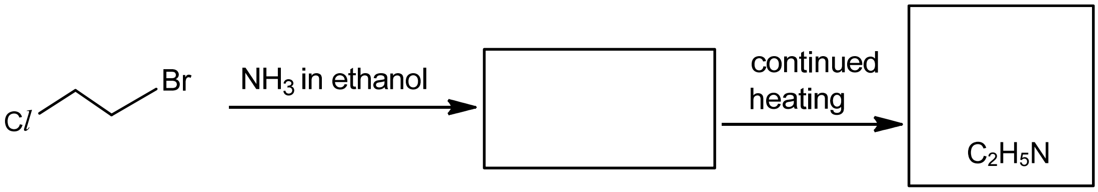
(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

....

....

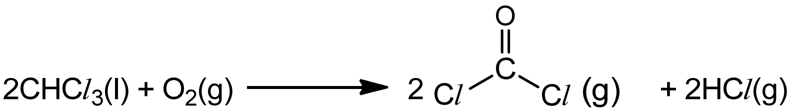
.... [1]

(ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



[2]

(c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, $COCl_2$. This reaction can also take place slowly in the presence of oxygen and light, as represented below.



$$2CHCl_3(l) + O_2(g) \longrightarrow 2\,COCl_2(g) + 2HCl(g)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $CHCl_3(l)$ is +31 kJ mol^{-1}.

[3]

(ii) Predict, with reasons, the sign of the entropy change of the reaction in **(c)(i)**.

....

....

....[2]

(iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

....

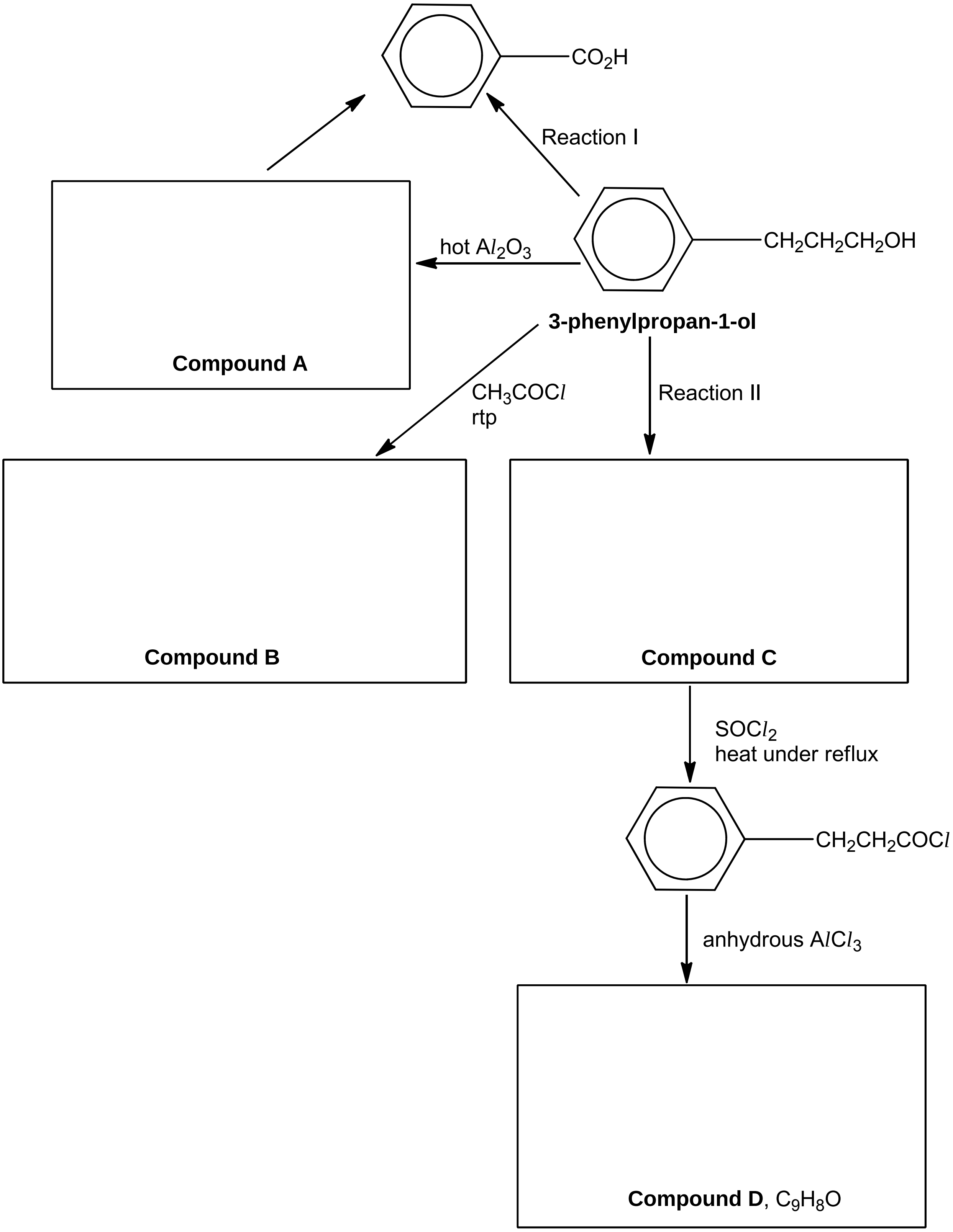
....

....[2]

[Total: 15]

5 **(a)** Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

(i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

[Turn over

(ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II.

Reaction I ……………………………………………………………

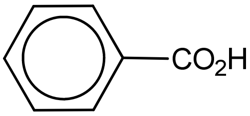
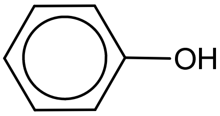
Reaction II ……………………………………………………………

[2]

(b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	**structural formula**	**K_a / mol dm^{-3}**
benzoic acid		6.3×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

(i) Draw the organic product formed when CO_2 is bubbled through a solution of aqueous sodium phenoxide.

[1]

(ii) However, no reaction occurs when CO_2 is bubbled through a solution of aqueous sodium benzoate. Explain why this is so.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………… [1]

(c) Cumene, C_9H_{12}, is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** separately under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

(i) State reagent **W**.

.... [1]

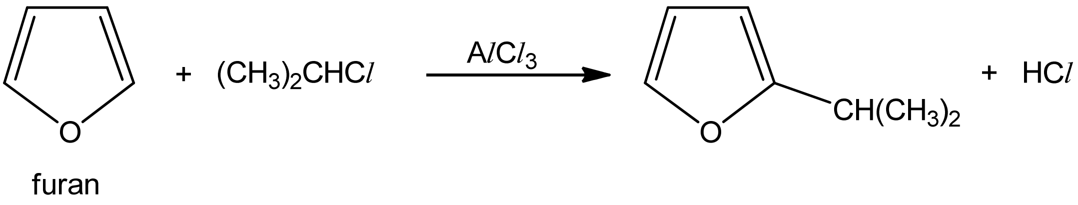
(ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**.

Compound X	**Compound Y**	**Compound Z**

[3]

(d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

Outline the mechanism of the reaction below, clearly showing all the steps involved.



[3]

[Total: 15]

Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 24 August 2018

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **10** printed pages.

Section A

Answer **all** the questions in this section.

1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

(a) When propene reacts with HBr, 2-bromopropane is produced as the major product.

$$CH_2{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$$

(i) Describe the mechanism of the above reaction, using curly arrows to show the movement of electrons. [4]

(ii) When propene reacts with BrC*l*, 1-bromo-2-chloropropane is produced as the major product.

$$CH_2{=}CHCH_3 + BrCl \rightarrow CH_2BrCHClCH_3$$

With reference to your answer in **(i)**, explain why the two reactions give major products with bromine in different positions. [2]

(iii) The product of the reaction in **(ii)** has a chiral carbon, but it is optically inactive. Explain why this is so. [2]

(b) 2-bromopropane reacts with hot aqueous sodium hydroxide, whereas 2-bromopropene does not. Suggest reasons for this difference in reactivity. [2]

(c) Propene can undergo mild oxidation in the presence of cold acidified potassium manganate(VII), to give $CH_2(OH)CH(OH)CH_3$.

(i) State the IUPAC name of the product of the above reaction. [1]

(ii) Construct the half–equation for the oxidation of propene as described above. [1]

(iii) Hence, write the equation for the overall reaction, showing clearly the stoichiometry of reaction between propene and manganate(VII) ions. [1]

(d) At room temperature and pressure, 28 cm^3 of propene was bubbled into 40.0 cm^3 of 0.0200 mol dm^{-3} acidified $KMnO_4(aq)$. The resulting solution was titrated against $Fe^{2+}(aq)$ of concentration 0.0750 mol dm^{-3}.

(i) State the colour change at endpoint for this titration. [1]

(ii) Given that 5 moles of Fe^{2+} react with 1 mole of MnO_4^-, determine the volume of $Fe^{2+}(aq)$ needed to reach endpoint. [3]

(e) A mixture of propene (M_r = 42.0) and 2-bromopropane (M_r = 122.9) kept in a vessel of volume of 3.60 dm^3 maintained at 75 °C exerts a pressure of 1.66×10^5 Pa. The mole fraction of propene in the mixture is 0.28.
Find the mass of the mixture of gases. [3]

[Total: 20]

2 Copper is a transition metal, and is one of the metals used to make coins, along with silver and gold. Most copper is used in electrical equipment such as wiring and motors. It also has uses in construction and industrial machinery.

(a) One of the characteristic properties of copper is its ability to form coloured aqueous complexes shown in Fig 2.1.

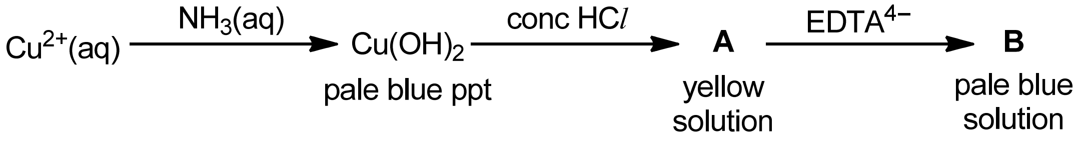


Fig. 2.1

(i) State the complex ion **A**. [1]

(ii) Draw the structure of complex ion **A**. [2]

(iii) $EDTA^{4-}$ is a hexadentate ligand. Deduce the formula of the complex ion **B**. [1]

(iv) Suggest why complex **B** is readily formed from complex **A**. [1]

(v) Explain why aqueous Cu^{2+} ions are blue in colour. [3]

(vi) The numerical value of the solubility product, K_{sp} of $Cu(OH)_2$ is 2.20 x 10^{-20} at 25 °C. Write the expression for K_{sp} and state its units. Calculate the solubility of $Cu(OH)_2$ at 25 °C. [3]

(b) When an aqueous solution of ammonia is shaken with an organic solvent, trichloromethane, at room temperature, the following equilibrium is set up between the two immiscible liquids.

$$NH_3(aq) \rightleftharpoons NH_3(organic) \qquad \textit{equilibrium 1}$$

The equilibrium constant, K_c, for this reaction is 0.04.

Water that is contaminated with copper(II) sulfate is harmful to crops, animals and humans. Some water that has been contaminated with 0.100 mol dm^{-3} copper(II) sulfate was allowed to reach dynamic equilibrium at room temperature with an excess of ammonia and trichloromethane. The aqueous layer was found to contain 0.660 mol dm^{-3} of ammonia, some of which reacted with $Cu^{2+}(aq)$ according to the following equation

$$Cu^{2+}(aq) + nNH_3 \rightarrow [Cu(NH_3)_n]^{2+}$$

The organic layer contained 0.0104 mol dm^{-3} of ammonia.

(i) Define the term *dynamic equilibrium*. [1]

(ii) Explain the relative solubility of ammonia in water and trichloromethane in terms of the intermolecular forces involved. [2]

(iii) Hence, in terms of the position of equilibrium, explain why the value of K_c for equilibrium *1* is relatively low. [1]

(iv) By calculating $[NH_3(aq)]$ present, show that the value of n in $[Cu(NH_3)_n]^{2+}$ is 4. [2]

(c) Another characteristic property of transition metal ion is its ability to catalyse reactions.
The rate of the reaction between iodide and peroxodisulfate(VI) ions

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is very slow. If a small amount of aqueous transition metal, cobalt(II) ions is added to the mixture, the rate of reaction increases.

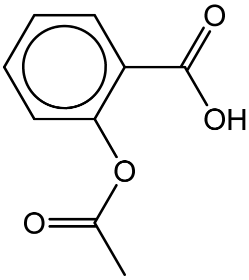
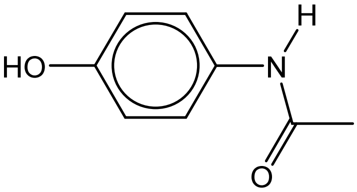
(i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]

(ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

[Total: 20]

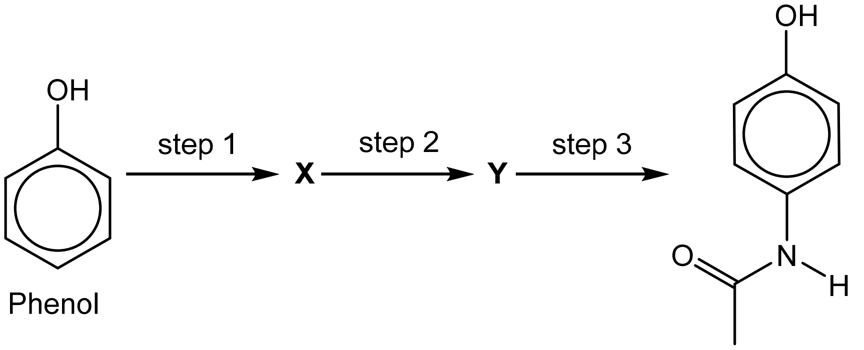
3 **(a)** Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

Table 3.1

Name of analgesic	Structure	pK_a value
Aspirin		3.49
Paracetamol		10.30

(i) Explain the difference in the pK_a values between aspirin and paracetamol. [2]

Paracetamol can be synthesised from phenol in a 3-step process shown in Fig 3.1.



Paracetamol

Fig. 3.1

(ii) Suggest the structures for intermediates **X** and **Y**. [2]

(iii) Suggest the reagents and conditions required for step 1 to 3. [3]

(b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence, buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering agents used include magnesium hydroxide, $Mg(OH)_2$, and calcium carbonate, $CaCO_3$.

Some relevant standard enthalpy change of hydration values and lattice energy of $Mg(OH)_2$, are shown in Table 3.2.

Table 3.2

Enthalpy term	Value / kJ mol^{-1}
Standard enthalpy change of hydration of Mg^{2+}(g)	–1926
Standard enthalpy change of hydration of OH^- (g)	–460
Lattice energy of $Mg(OH)_2$(s)	–2998

Using relevant data in the table above, construct an energy level diagram to determine the standard enthalpy change of solution, $\Delta H_{sol}^{\ominus}$, of $Mg(OH)_2$ in water. [3]

(c) Compound **A** is an unsaturated ester containing a benzene ring and has a molecular formula of $C_{16}H_{22}O_3$. **A** reacts with neutral $FeCl_3$ to give violet colouration. **A** reacts with H_2 in the presence of Ni to produce compound **B** ($C_{16}H_{24}O_3$). **B** exhibits enantiomerism whereas **A** does not.

On heating with acidified $KMnO_4$, **A** gives three organic products, **C**, $C_8H_6O_5$, **D**, $C_4H_{10}O$ and propanone (CH_3COCH_3). 1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HCl. Effervescence is observed when a small piece of sodium metal is added to **D**.

Suggest the structures for **A** to **D** and explain the reactions described. [10]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** The decomposition of calcium and magnesium carbonates has industrial application as flame retardants due to the endothermic nature of these reactions.

(i) Write an equation showing the thermal decomposition of calcium carbonate. [1]

(ii) Compare and explain the decomposition temperature of calcium and magnesium carbonates. [3]

(iii) Separate samples of calcium carbonate and magnesium carbonate of the same mass, were decomposed completely under constant heating and the variation of the masses of the two samples were measured.

Sketch a graph of the mass of solid against time for the two separate samples, indicating clearly the time when decomposition was complete and the final mass for each sample. No calculations are required. [2]

(iv) Besides absorption of heat to slow down the spread of a flame, suggest another reason why $CaCO_3$ acts as a flame retardant. [1]

(b) One way to study reaction mechanisms is to deduce the rate equation from kinetics experiments, such as that for the redox reaction between manganate (VII) ions and ethanedioate ions.

$$2\,MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

A study of the kinetics of this reaction was carried with a suitable catalyst and with $[C_2O_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[MnO_4^-]$ / mol dm^{-3}
0	0.0200
3	0.0160
6	0.0128
9	0.0104
12	0.0084
15	0.0068
18	0.0056

(i) Plot the data on suitable axes, using the graph paper provided. [2]

(ii) Use your graph to determine the order of reaction with respect to $[MnO_4^-]$, showing your working clearly including construction lines on your graph. [2]

(iii) Given that the reaction is first order with respect to $[C_2O_4^{2-}]$ and zero order with respect to $[H^+]$, give the rate equation for the reaction. [1]

(iv) Determine the initial rate from the graph and use it, together with your rate equation, to calculate the rate constant for the reaction, stating its units. [2]

(v) Without the initial addition of the catalyst, the reaction is initially slow then speeds up due to autocatalyst, Mn^{2+}, produced, and finally slows down due to low concentration of reactants remaining.

Sketch a graph $[MnO_4^-]$ against time if the experiment was repeated without the initial addition of catalyst. [1]

(c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

2-bromobutane undergo nucleophilic substitution with nitrile, CN^-, relatively faster, as compared to the reaction of 2-chlorobutane with nitrile, CN^-.

(i) Under suitable conditions, an initially optically pure (only one enantiomer) sample of 2-bromobutane can undergo reaction with CN^-, and produce a mixture which is almost optically inactive.

Name the mechanism that has taken place for this, and give the structures of the products formed. [2]

(ii) A suitable condition that favours the reaction mechanism in **(i)** can be the use of neutral **polar** solvent (e.g. propanone) instead of non-polar solvents. Suggest why this is the case in consideration of the mechanism stating clearly the interactions involved. [1]

(iii) Explain why 2-chlorobutane reacts more slowly with nucleophiles, relating to the steps in the mechanism in **(i)**. Quote relevant values from the *Data Booklet* to substantiate your answer. [2]

[Total: 20]

5 **(a)** The decomposition of hydrazine, N_2H_4, can be used to produce H_2 gas as shown in the following reaction.

$$N_2H_4 \rightarrow 2H_2 + N_2$$

(i) Draw a dot-and-cross diagram showing the bonding in N_2H_4. [1]

(ii) Use your diagram to suggest the shape of N_2H_4 about nitrogen atom. [1]

(iii) Use your diagram to suggest the bond angle about N atom in N_2H_4. [1]

(iv) The boiling points of hydrazine, nitrogen and ammonia are shown in Table 5.1

Table 5.1

compound	boiling point/ °C
N_2H_4	114
NH_3	–33
N_2	–196

Suggest an explanation for the difference in boiling points of these three compounds. [4]

(b) Hydrazine can be used in a fuel cell to generate electricity. At the anode, nitrogen gas is produced from hydrazine in alkaline medium. At the cathode, oxygen gas is being supplied into water.

(i) Construct half equations for the anode and cathode reactions. [2]

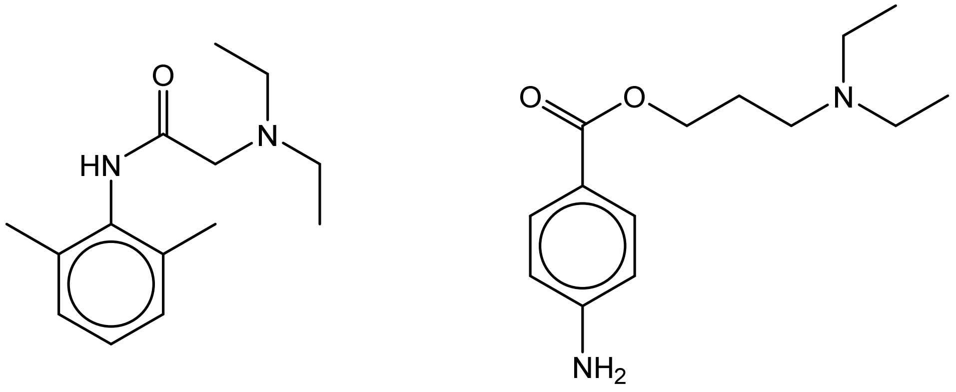
(ii) Hence, write the overall equation. [1]

(iii) The cell is capable of producing an e.m.f. of 1.56 V under standard conditions. By using suitable data from the *Data Booklet*, suggest a value of the $E^\ominus$ of the anode. [1]

(iv) Calculate ΔG for the reaction. [1]

(v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

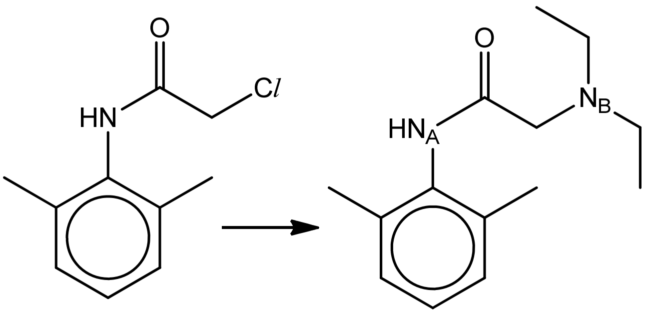
(c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1



lidocaine procaine

Fig. 5.1

The final step of the synthesis of lidocaine is shown in Fig 5.2.



lidocaine

Fig. 5.2

(i) Suggest a reagent for the above reaction. [1]

(ii) Suggest how the basicity of N_A might compare to that of N_B. Give reasons for your answers. [2]

(iii) A possible single chemical test to distinguish procaine and lidocaine involves the use of acidified potassium dichromate. Explain the chemistry involved, including any observation. Draw the structures of the products for the positive test. [3]

(iv) Suggest another reagent that can also be used to distinguish between lidocaine and procaine. [1]

[Total: 20]

Catholic Junior College

JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/04

Paper 4 Practical

Thursday 16 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your class and name on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show you working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	17
2	18
3	20
Total	55

This document consists of **15** printed pages and **1** blank page.

[Turn over

1 **Z** is an oxidising agent. You are required to use a solution of iodine in potassium iodide to determine the mass of **Z** needed to liberate 1 mole of iodine from potassium iodide.

FA3 is an aqueous solution of iodine, I_2, in potassium iodide, KI.
FA4 is a 0.100 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3.5H_2O$.
FA5 is an aqueous solution containing 2.00 g dm^{-3} **Z**, an oxidising agent.

You are to follow the following procedure and record your results as instructed.

Titration 1

1. By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask.
2. Titrate the iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette until the solution becomes colourless.
3. Repeat the titration as many times as you think necessary to obtain accurate results.
4. Record your results of titration in a suitable tabulated form below.

Titration of iodine in **FA3** with **FA4**

Summary

…………… cm^3 of **FA3** required ……………… cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[5]

(a) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with 25.0 cm^3 of **FA3**.

Moles of $Na_2S_2O_3$ = …………………………..

[1]

(b) Calculate how many moles of I_2 present in 25.0 cm^3 of **FA3** using the following equation for the reaction between iodine and thiosulfate ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Moles of I_2 = ……………………………
[1]

Titration 2

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask and then using a second pipette, add 25.0 cm^3 of **FA5**, an aqueous solution containing 2.00 g dm^{-3} of the oxidising agent, **Z**.
2 Titrate the total iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette as before until the solution becomes colourless.
3 Repeat the titration as many times as you think necessary to obtain accurate results.
4 Record your results of titration in a suitable tabulated form below.

Titration of total iodine now in **FA3** with **FA4**

Summary

……… cm^3 of **FA3** to which 25.0 cm^3 of **FA5** had been added required …………… cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[3]

[Turn over

(c) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with the total iodine in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Moles of $Na_2S_2O_3$ = …………………………..

[1]

(d) Calculate how many moles of I_2 present in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Moles of I_2 = ……………………………

[1]

(e) Calculate how many moles of I_2 were liberated from potassium iodide in the flask by 25.0 cm^3 of **FA5**.

Moles of I_2 = ……………………………

[2]

(f) Calculate the mass of **Z** present in 25.0 cm^3 of **FA5**.

Mass of **Z** = ……………………………
[1]

(g) Hence, from **(e)** and **(f)**, calculate the mass of **Z** needed to liberate 1 mole of I_2.

Mass of **Z** = ……………………………
[2]

[Total: 17]

[Turn over

2 You are required to determine the basicity of an acid by carrying out some experiments with aqueous sodium hydroxide.

FA1 is a 1.00 mol dm^{-3} aqueous sodium hydroxide, NaOH.
FA2 is a 1.00 mol dm^{-3} aqueous acid which is either monobasic with the formula **HA**, or dibasic with the formula **H_2A**.

By using the results of the following experiments, you are to going to determine the basicity of **FA2**.

You are to follow the following procedure and record your results as instructed.

Experiment 1

1 By using a measuring cylinder, pour 25 cm^3 of **FA1** into the Styrofoam cup provided and record the steady temperature. Rinse the thermometer with deionised water.
2 Use another 50 cm^3 measuring cylinder to measure 25 cm^3 of **FA2** and record its temperature.
3 Carefully add **FA2** to **FA1**, stir with the thermometer and record the highest temperature reached.
4 Record your results in the table provided below.

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial temperature of **FA1** /˚C			
Initial temperature of **FA2** /˚C			
Highest temperature /˚C			
Mean initial temperature /˚C			
Temperature rise, ΔT /˚C			

Experiment 2

Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 25 cm^3 of **FA1** and 50 cm^3 of **FA2**. Record your results in the table above.

Experiment 3

Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 50 cm^3 of **FA1** and 25 cm^3 of **FA2**. Record your results in the table above.

(a) Complete the table of results by calculating the mean initial temperature of **FA1** and **FA2** for each of the three experiments. When calculating mean initial temperatures for **Experiments 2** and **3**, ignore the fact that the volumes mixed are unequal.

Fill in the corresponding rises in temperatures, ΔT in the table provided above.

[5]

(b) Use your results to deduce the basicity of the acid.

[2]

(c) Write a full equation for the reaction between **FA1** and **FA2**. Do not omit spectator ions.

……………………………………………………………………………………………………

[1]

(d) Calculate the amount of heat evolved in **Experiment 1**.
Assume 4.3 J are required to raise the temperature of 1 cm^3 of solution by 1.0 °C.

Heat evolved = ……………………………

[1]

(e) Using your answers to **(c)** and **(d)**, calculate the enthalpy of neutralisation, ΔH_n, per mole of water formed.

ΔH_n = …………………………………..

[1]

[Turn over

Assessment of Planning Skills

You are provided with 150 cm^3 of each of three solutions, **FA6**, **FA7** and **FA8**. You are to identify which of these solutions correspond to the following solutions:

1 mol dm^{-3} sodium hydroxide, NaOH
2 mol dm^{-3} hydrochloric acid, HCl
1 mol dm^{-3} hydrochloric acid, HCl

You are also provided with the following apparatus:

A thermometer
A plastic cup
2 measuring cylinders

You are to plan a simple experiment which will allow an identification of the three solutions to be made, using only the apparatus and materials listed above and deionised water. (Note that you are **not** provided with any pH indicator).

You are **not** required to carry out the plan but you have to present your results in an appropriate manner based on your plan so that the identification can be made.

PLAN

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[3]

[Total: 18]

[Turn over

3 You are to determine the identity of **FA9**.

Carry out the following experiments on the solid **FA9** which contains the **sodium cation** and **one anion** from the following list: CO_3^{2-}, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-} and SO_3^{2-}.

In all tests, reagents should be added gradually until no further change is observed, with shaking after each addition.

Record your observations you make from them in the spaces provided.

Your answer should include
(i) details of colour change and precipitate formed, if any;
(ii) the identity of gases evolved, if any, and details of the test used to identify the gas.

You should indicate clearly at what stage in a test a change occurs.

No additional or confirmatory tests for ions present should be attempted.

Test	Observation
(a) Place one third of the solid **FA9** in a test-tube and heat strongly until the solid melts and a gas is given off. Identify the gas evolved. Continue the strong heating for 2–3 minutes then leave the tube to cool and retain the residue for test (d). (Melt a second sample of **FA9** and heat for 2–3 minutes. Leave this to cool and retain for test (h).	
(b) Using a dropper, place 1 cm depth of aqueous of sodium hydroxide into a test-tube and tip into it the remaining solid **FA9**. Warm gently and retain for test (c).	
(c) Cool the test-tube and solution from (b). Add a half spatula full of aluminium powder and warm gently.	

Test	Observation
(d) Dissolve the residue from (a) in deionised water about 3 cm depth and divide the solution into three parts. Use these tests for (e) to (g).	▨
(e) To one part of the solution from (d), add aqueous potassium iodide followed dilute sulfuric acid.	
(f) To the second part of the solution from (d), add aqueous potassium manganate(VII) followed by dilute sulfuric acid.	
(g) To the third part of the solution from (d), add aqueous sodium hydroxide and a half spatula full of aluminium powder. Warm gently.	
(h) Take the second sample of solid, heated **FA9** that you prepared in (a). Add to dilute sulfuric acid and warm gently.	

[9]

What anion is present in **FA9** before it is heated? ……………………………………………

What anion is present in **FA9** after it is heated? ……………………………………………...

In test (e), the anion is behaving as ……………………………………………………………

In test (f), the anion is behaving as ……………………………………………………………

[4]

Hence, write a balanced chemical equation for the thermal decomposition of **FA9**.

………………………………………………………………………………………………………

[1]

[Turn over

Assessment of Planning Skills

Each of the solutions **FA10**, **FA11** and **FA12** contains one of the cations Al^{3+}, Mg^{2+} and Zn^{2+} ions but not in that order.

You are provided with a set of test-tubes and the following reagents:

Aqueous ammonia, NH_3
Dilute hydrochloric acid, HCl
Aqueous sodium carbonate, Na_2CO_3
Aqueous sodium hydroxide, NaOH

You are required to devise and perform an experiment which will enable you to identify the cation present in each of the solutions **FA10**, **FA11** and **FA12**. You may only use any of the reagents provided above and **no** other reagent. **You should aim to use the minimum number of reactions**, where possible.

This space below is for you to plan your steps which should then be recorded, together with the observations you make in the table in the next page.

PLAN

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[2]

In the table below, record all of your observations, and the identity of a cation as soon as this is established.

Reagent added	Observations and identities of cations		
	FA10	**FA11**	**FA12**

[3]

Deduction

Solution **FA10** contains the cation …………………………………………………………………

Solution **FA11** contains the cation …………………………………………………………………..

Solution **FA12** contains the cation …………………………………………………………………..

[1]

[Total: 20]

[Turn over

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/01

Paper 1 Multiple Choice

Wednesday 29 August 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

WORKED SOLUTIONS

This document consists of **29** printed pages.

1 A sample of tungsten contains four naturally occurring isotopes, ^{182}W, ^{183}W, ^{184}W and ^{186}W.

The relative atomic mass of tungsten in this sample is 183.9. What is the percentage of the isotope ^{182}W in this sample?

Isotope	Relative Abundance (%)
^{182}W	?
^{183}W	?
^{184}W	30.6
^{186}W	28.6

A 10.5 **C** 26.4

B 14.4 **D** 40.8

Answer: C

Let the percentage of ^{182}W be x.

The percentage of ^{183}W would be 100 – 30.6 – 28.6 – x = 40.8 – x

Thus,

$$183.9 = \frac{182x+183(40.8-x)+184(30.6)+186(28.6)}{100}$$

$$x = 26.4$$

2 20 cm^3 of 0.100 mol dm^{-3} of potassium ferrate(VI), K_2FeO_4, reacts with sodium ethanedioate, $Na_2C_2O_4$, in an acidic medium to produce 144 cm^3 of carbon dioxide gas at room temperature and pressure.

The half equation of $C_2O_4^{2-}$ is shown as follows:

$$2CO_2 + 2e^- \rightleftharpoons C_2O_4^{2-}$$

What is the final oxidation state of the iron-containing species after the reaction?

A +1 **B** +2 **C** +3 **D** +4

Answer: C

Oxidation state of Fe in K_2FeO_4 = +6

Amt of FeO_4^{2-} reacted = $\frac{20}{1000}$ × 0.100 = 0.002 mol

Amt of CO_2 formed = 144 ÷ 24 000 = 0.006 mol

Amt of $C_2O_4^{2-}$ reacted = ½ x 0.006 = 0.003 mol

Ratio of FeO_4^{2-} : $C_2O_4^{2-}$ = 0.002 : 0.003

2 FeO_4^{2-} ≡ 3 $C_2O_4^{2-}$

3 mol of $C_2O_4^{2-}$ will produce 6 mol of e^- and 2 mol of FeO_4^{2-} will accept 6 mol of e^-.

Therefore, 1 mol of FeO_4^{2-} will accept 3 mol of e^-.

Since FeO_4^{2-} is reduced from an oxidation state of +6 to +3.

3 When attracted by a strong magnet, some species are able to exhibit paramagnetism. Such species contain unpaired electrons which are able to spin in a way which aligns parallel to the magnetic field.

Which of the following species in the ground state is able to exhibit paramagnetism?

1 O   2 Al^+ 3 Ti^{2+} 4 Cu^+

A 1 and 3 only
B 2 and 4 only
C 1, 3 and 4 only
D 2, 3 and 4 only

Answer: A (1 and 3 only)

1 O : $1s^2\ 2s^2\ 2p^4\ (2p_x^2, 2p_y^1, 2p_z^1)$ there are 2 unpaired electrons in 2p orbital
2 Al^+ : $1s^2\ 2s^2\ 2p^6\ 3s^2$ there are no unpaired electrons
3 Ti^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$ there are 2 unpaired electrons in 3d orbital
4 Cu^+ : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ there are no unpaired electrons

4 Phosphorus(V) chloride, PCl_5 dissolves in a suitable polar solvent to produce two ions, $[PCl_4]^+$ and $[PCl_6]^-$.

Which of the following shows the correct shape for PCl_5, $[PCl_4]^+$ and $[PCl_6]^-$?

	PCl_5	$[PCl_4]^+$	$[PCl_6]^-$
A	trigonal planar	square planar	square pyramidal
B	trigonal bipyramidal	square planar	octahedral
C	trigonal planar	distorted tetrahedral	square pyramidal
D	trigonal bipyramidal	tetrahedral	octahedral

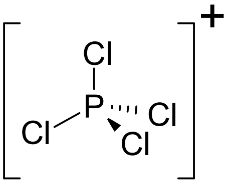
Answer: D

PCl_5 : 5 bond pairs 0 lone pairs of electrons; shape is trigonal bipyramidal

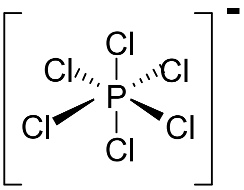
$[PCl_4]^+$: 4 bond pairs 0 lone pairs of electrons; shape is tetrahedral

$[PCl_6]^-$: 6 bond pairs 0 lone pairs of electrons; shape is octahedral

tetrahedral



octahedral



5 The table shows the boiling point of some halogenoalkanes.

compound	boiling point/ °C
CH_3CH_2Cl	12.3
CH_3CH_2Br	34.8
CH_3CH_2I	70.0

Which of the following correctly explains the difference in the boiling point?

1 the electronegativity difference between the halogen and carbon increases from C−C*l* to C−I

2 the strength of permanent dipole-permanent dipole attraction increases from C−C*l* to C−I

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I

4 the bond energy of C−X bond decreases from C−C*l* to C−I

A 1 and 2 only

B 2 and 4 only

C 3 only

D 3 and 4 only

Answer: C (3 only)

N.B. H-bonding > pd-pd> id-id only if size of electron cloud of molecules are similar.

1 the electronegativity difference between the halogen and carbon should **decrease** from C−C*l* to C−I
Statement **does not** explain for the trend of increasing boiling point from CH_3CH_2Cl to CH_3CH_2I.

2 the strength of permanent dipole-permanent dipole attraction **decreases** from C−C*l* to C−I

The statement of option 2 is **incorrect** and **does not** explain for the trend of **increasing** boiling point from CH_3CH_2Cl to CH_3CH_2I.

3 the strength of instantaneous dipole-induced dipole attraction increases from CH_3CH_2Cl to CH_3CH_2I

Statement is **correct** as the total number of electrons increases from CH_3CH_2Cl to CH_3CH_2I and due to the increase in id-id attraction, the boiling point increases from CH_3CH_2Cl to CH_3CH_2I.

4 the bond energy of C-X bond decreases from C–Cl to C–I

Statement is correct but boiling does not break the C–X bond, so this **does not** explain for the trend of **increasing** boiling point from CH_3CH_2Cl to CH_3CH_2I.

6 Which of the following changes will result in the greatest decrease in the density of a fixed mass of ideal gas?

	Pressure	**Temperature/ K**
A	halves	halves
B	halves	doubles
C	doubles	halves
D	doubles	doubles

Answer: B

Density, $\rho = \frac{m}{V}$

Hence, $\rho = \frac{pM_r}{RT}$

From the formula above, the greatest decrease in density is brought about when **pressure decreases** and **temperature increases**.

7 Consider the following reactions.

Reaction 1: $CH_3^+ + Br^- \rightarrow CH_3Br$

Reaction 2: $HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

Which of the following statement is **not** true about the reactions above?

A Both reactions are acid-base reactions.

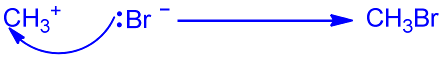
B In reaction 2, HPO_4^{2-} acts as the Brønsted-Lowry base.

C In reaction 2, HBO_3^{2-} is the conjugate acid of $H_2BO_3^-$.

D In reaction 1, a dative covalent bond is formed between CH_3^+ and Br^-.

Answer: C

For Reaction 1:



CH_3^+ behaves as the Lewis acid (electron pair acceptor) while Br^- behaves as the Lewis base (electron pair donor). Hence it is an acid-base reaction (option A is true) which involves the formation of a dative covalent bond. (option D is true)

For Reaction 2:

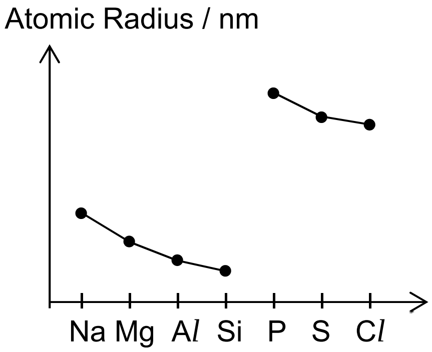
$HPO_4^{2-} + H_2BO_3^- \rightleftharpoons H_2PO_4^- + HBO_3^{2-}$

$H_2BO_3^-$ behaves as the Brønsted-Lowry acid (H^+ donor) while HPO_4^{2-} behaves as the Brønsted-Lowry base (H^+ acceptor). Hence it is an acid-base reaction. (option B is true)

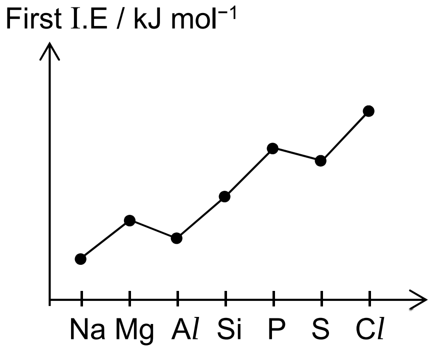
HBO_3^{2-} is the conjugate **base** of $H_2BO_3^-$ (option C is not true)

8 Which of the following sketches shows the correct trend in the stated property for the elements in the third period of the Periodic Table?

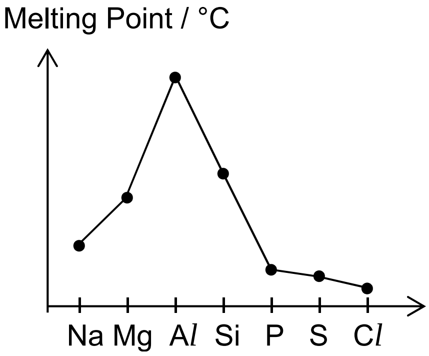
A



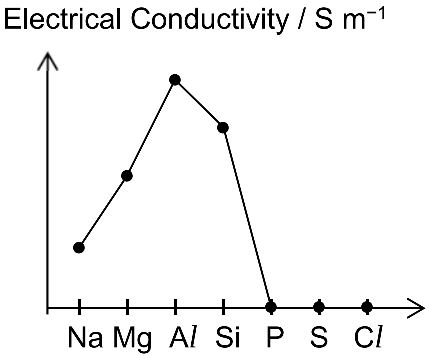
C



B

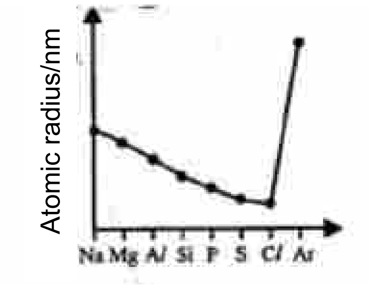


D

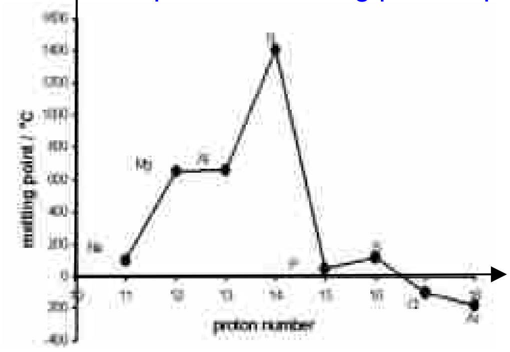


Answer: C

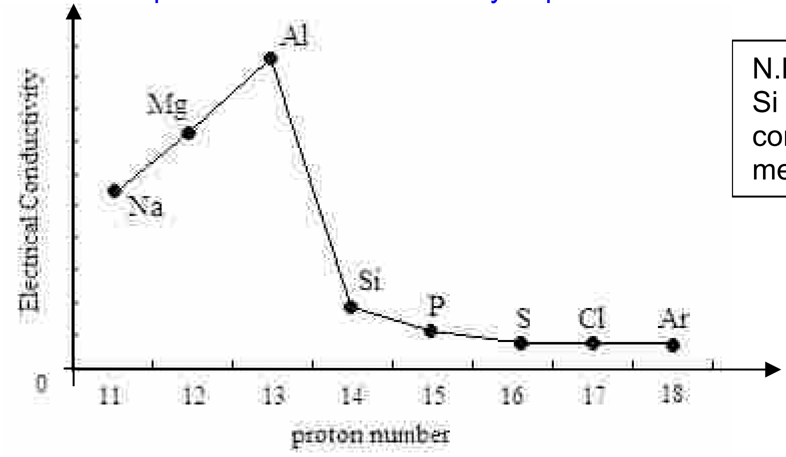
Graph A shows the trends of ionic radius across period 3 elements, not atomic radius. Atomic radius across period should be this.



Correct shape of the melting point of period 3 elements should be this:



Correct shape of electrical conductivity of period 3 elements should be this:



N.B.
Si is a semi-conductor, conductivity should be lower than metal.

9 Compounds of Period 3 elements dissolve in water to form aqueous solutions that are acidic, basic or neutral.

Which of the following sequence shows the order of **increasing** resultant pH when the compounds are added to water?

A NaC*l*, MgC*l*$_2$, SiC*l*$_4$

B A*l*C*l*$_3$, SiC*l*$_4$, PC*l*$_5$

C A*l*$_2$O$_3$, MgO, SO$_2$

D P_4O_{10}, SiO_2, MgO

Answer: D. pH 2, pH 7, pH 9

10 Phosphine reacts with hydrogen iodide to form phosphonium iodide in the reaction shown below:

$$PH_3(g) + HI(g) \rightarrow PH_4^+I^-(s) \qquad \Delta H^{\ominus} = -145.2 \text{ kJ mol}^{-1}; \Delta S^{\ominus} = -570.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Which one of the following statement is true for the above reaction?

1 The products are less disordered than the reactants.

2 The reaction is non-spontaneous under standard conditions.

3 As temperature increases, the reaction becomes more spontaneous.

A 1 only

B 2 only

C 1 and 2 only

D 1, 2 and 3 only

Answer: C

1 True. Since $\Delta S^{\theta} = -570.8$ J K^{-1} mol^{-1} (negative value), disorderness of the system has occurred.

2 True.
At 298K, $\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} = (-145.2) - (298)(-570.8/1000)$
$= +24.9$ kJ $mol^{-1} > 0$ (non-spontaneous reaction)

3 False. Since both ΔH^{θ} and ΔS^{θ} have negative values, the reaction is only spontaneous at low temperature (so that the magnitude of $-T\Delta S^{\ominus}$ (+ve) decreases).

11 The reaction of acidified aqueous potassium iodide with aqueous hydrogen peroxide:

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

is thought to involve the following steps:

$H_2O_2 + I^- \rightarrow H_2O + OI^-$ (slow)
$OI^- + H^+ \rightarrow HOI$ (fast)
$HOI + H^+ + I^- \rightarrow I_2 + H_2O$ (fast)

Which of the following conclusion can be drawn from this information?

1 The acid is acting as a catalyst only.

2 The reaction is pseudo-first order with respect to H_2O_2.

3 The reaction rate is independent of the pH of the solution.

A 1 only

B 3 only

C 1 and 2 only

D 1, 2 and 3 only

Answer: B

1 False. H^+ is consumed in Step 2 and 3 and are not regenerated. Hence the acid (H^+) is not acting as a catalyst, it is a reactant in this reaction.

2 False.
Since the first step is the slow step, the rate equation is

$$\text{rate} = k[H_2O_2][I^-]$$

The reaction is first-order with respect to both H_2O_2 and I^-. Statement 2 can only be true if a large concentration of I^- is used so that the rate equation can be simplified to

$$\text{rate} = k'[H_2O_2] \qquad \text{where } k'=k[I^-]$$

However, it is not mentioned in the question that a large concentration of I^- is used in the experiment.

3 True. The rate equation does not involve H^+, hence the pH does not affect the reaction rate.

12 A first-order decomposition reaction is shown below.

$$AB(g) \rightarrow A(g) + B(g)$$

The half-life of the reaction was found to be 3.47 s.

What is the time taken for AB(g) to reach one-third of its initial concentration?

A 3.0 s **B** 3.5 s **C** 5.5 s **D** 7.0 s

Answer: C

Using the following formula,

$\frac{c_t}{c_o} = \left(\frac{1}{2}\right)^n$, where n = no. of half-lives = $\frac{\text{time taken}}{t_{1/2}}$

If [AB] is $\frac{1}{3}$ of the initial concentration, $\frac{c_t}{c_o} = \left(\frac{1}{3}\right)$

$$\frac{1}{3} = \left(\frac{1}{2}\right)^n$$

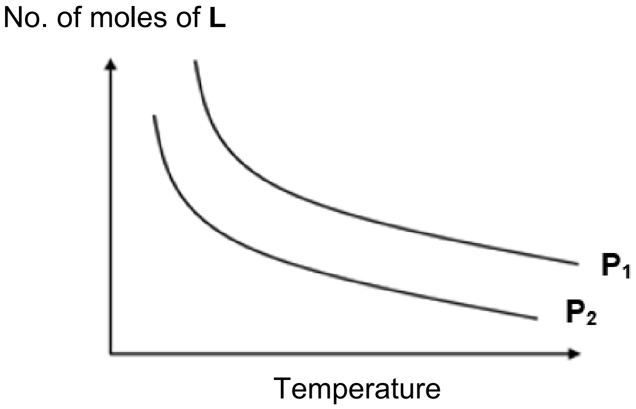
$$\lg\left(\frac{0.5}{1.5}\right) = n \lg\left(\frac{1}{2}\right)$$

n = 1.585

time taken = 1.585 x 3.47 = 5.5 s

13 The graph below shows how the number of moles of compound **L** varies with temperature at two different pressures of $\mathbf{P_1}$ and $\mathbf{P_2}$ respectively.
L could be any of the following compounds shown in the equation at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$



What is the correct identity of **L** and the correct magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$?

	Identity of **L**	magnitude of pressures $\mathbf{P_1}$ and $\mathbf{P_2}$
A	SO_2	$\mathbf{P_1} > \mathbf{P_2}$
B	SO_2	$\mathbf{P_1} < \mathbf{P_2}$
C	SO_3	$\mathbf{P_1} > \mathbf{P_2}$
D	SO_3	$\mathbf{P_1} < \mathbf{P_2}$

Answer: C

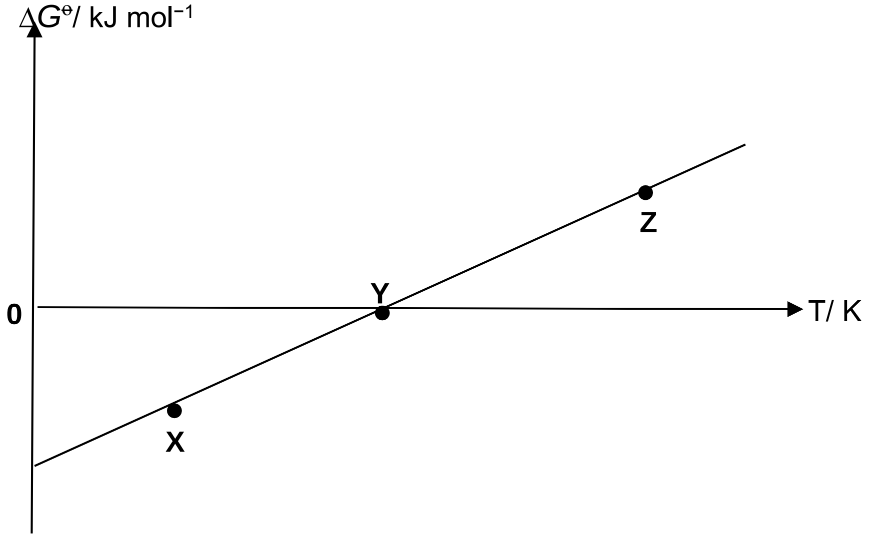
Since forward reaction is exothermic, higher temperatures will favour the backward endothermic reaction. At higher temperature, $[SO_2]$ and $[O_2]$ increases while $[SO_3]$ decreases. Thus the two downward–sloping graphs applies to SO_3.

At a higher pressure, forward reaction is favoured since the product has less moles of gaseous particles, therefore $[SO_3]$ increases.
Thus, $\mathbf{P_1} > \mathbf{P_2}$.

14 When nitrogen dioxide, NO_2, and nitrogen monoxide, NO, is mixed, the gases react to form dinitrogen trioxide, N_2O_3. The reaction is shown in the following equilibrium.

$$NO_2(g) + NO(g) \rightleftharpoons N_2O_3(g)$$

The graph below shows how the $\Delta G^\ominus$ varies with temperature for the above reaction.



Using the graph above, deduce which of the following statement is true about the reaction at equilibrium?

A At point **X**, more NO_2 is present as compared to that at point **Y**.

B At point **X**, the K_c value is likely to be greater than 1.

C At point **Y**, the rate of forward reaction is greater than that of backward reaction.

D At point **Z**, more N_2O_3 is present compared to that at point **Y**.

Answer: B

Since the reaction is at equilibrium, rate of forward reaction = rate of backward reaction for all points X, Y and Z. **(option C is incorrect)**

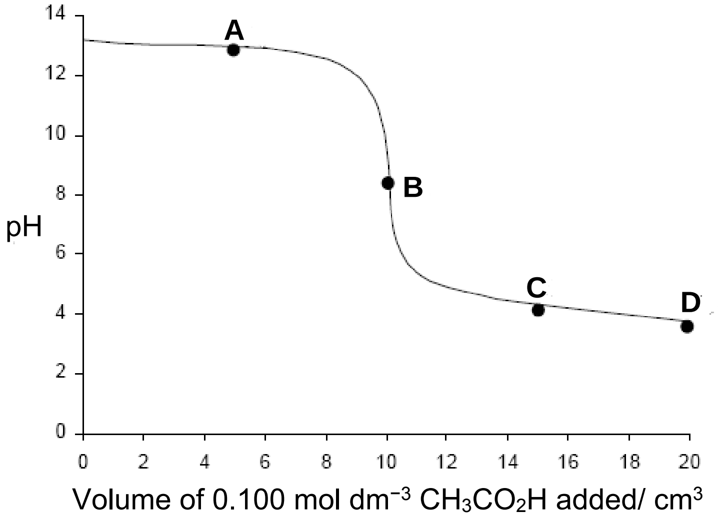
At point **X**, $\Delta G^\theta < 0$, P.O.E lies more to the right and forward reaction occurs more readily compared to backward reaction.
Since $K_c = \frac{[N_2O_3]}{[NO_2][NO]}$,
Therefore K_c value is likely to be greater than 1 at point **X**. **(option B is correct)**

At point **Y**, $\Delta G^\theta = 0$.
Comparing point **X** and **Y**, **less** NO_2 gas is present at **X** since P.O.E lies more to the right at point **X** compared to point **Y**. **(option A is wrong)**

At point **Z**, $\Delta G^\theta > 0$, P.O.E lies more to the left and backward reaction occurs more readily compared to forward reaction. K_c is lesser than 1. Therefore, at point **Z**, **less** N_2O_3 gas is present as compared to that at point **Y**. **(option D is wrong)**

15 The pH changes when 0.100 mol dm^{-3} CH_3CO_2H is added dropwise to 10.0 cm^3 of 0.100 mol dm^{-3} NaOH(aq) as shown below.

At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of the weak acid?



Answer: D

For pH = pK_a, [A^-] = [HA]

HA + NaOH → NaA + H_2O

At A, species present: NaOH and NaA

At equivalence point B, A^- ion hydrolyses in water, $A^- + H_2O \rightleftharpoons HA + OH^-$

At C, [A^-] ≠ [HA]

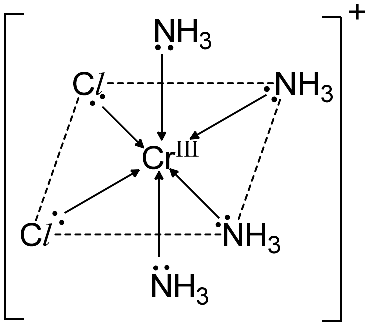
At D,

n_{HA}	= 20.00/1000 x 0.100
	= 2 x 10^{-3} mol
n_{OH-}	= 10.0/1000 x 0.100
	= 1 x 10^{-3} mol
n_{A-} formed	= 1 x 10^{-3} mol
n_{HA} unreacted	= 2 x 10^{-3} mol − 1 x 10^{-3} mol
	= 1 x 10^{-3} mol

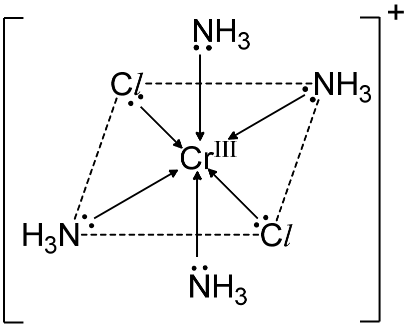
At D, [A^-] = [HA]

16 Coordination complexes with more than one type of ligand can exist in a number of stereoisomeric forms.

For example, the chromium(III) complex $[Cr(NH_3)_4Cl_2]^+$ can refer to the two stereoisomers as shown:



and

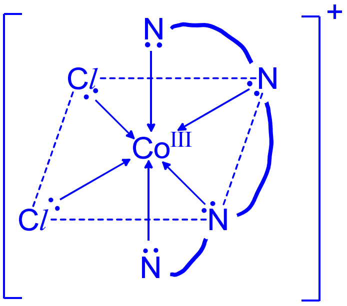


How many stereoisomers can the cobalt(III) complex $[Co(trien)Cl_2]^+$ have?
(trien = $(NH_2CH_2CH_2NHCH_2)_2$, a tetradentate ligand)

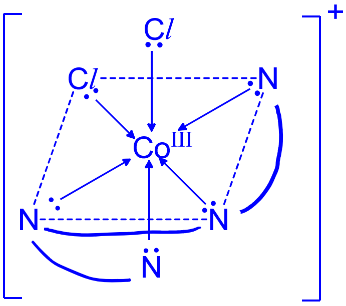
A 1 **B** 2 **C** 3 **D** 4

Answer: C

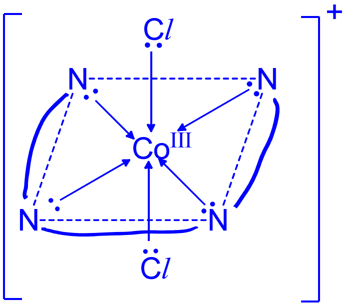
There are three stereoisomers for $[Co(trien)Cl_2]^+$.



Middle two N in same plane.



Three N in same plane.

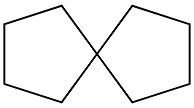


All four N in same plane.

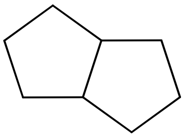
17 Cyclopentane undergoes substitution with bromine.

What is a possible by-product of this reaction?

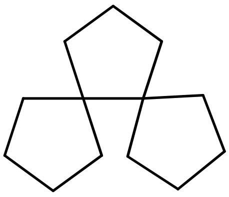
A



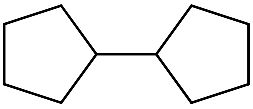
C



B



D



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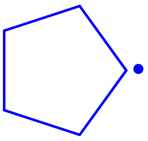
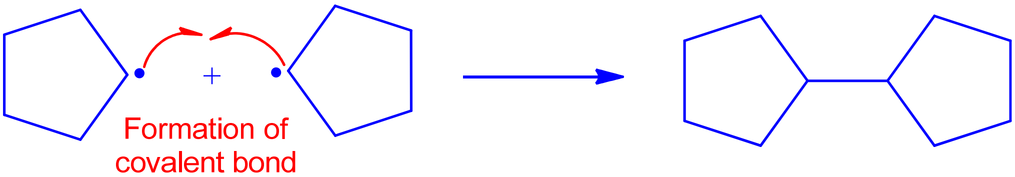
Answer: D

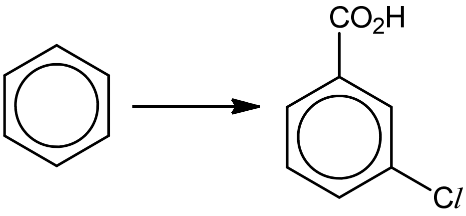
In **A**, **B** and **C**, the cyclopentane units are sharing carbon atoms, whereas in **D**, the carbon atoms of each cyclopentane unit are separate from other cyclopentane units. In free radical substitution, the termination step between two alkyl radicals gives rise to a new C-C bond, and the number of carbon atoms in the product should be the sum of that in the alkyl radicals.

The radical formed should be 

Hence the termination step between two alkyl radicals should be:



18 3-chlorobenzoic acid can be synthesized from benzene in three steps.



3-chlorobenzoic acid

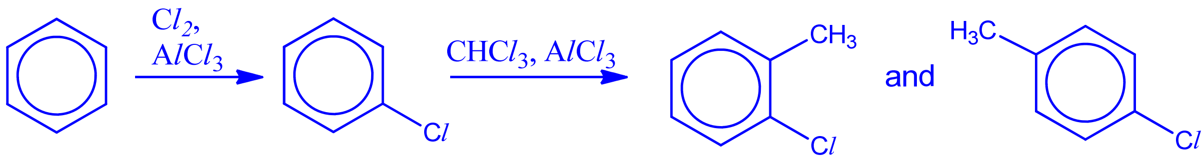
Which of the following is the best method for this synthesis?

	Step 1	Step 2	Step 3
A	Cl_2, $AlCl_3$	CH_3Cl, $AlCl_3$	$KMnO_4$, H_2SO_4
B	Cl_2, $AlCl_3$	$KMnO_4$, H_2SO_4	CH_3Cl, $AlCl_3$
C	CH_3Cl, $AlCl_3$	$KMnO_4$, H_2SO_4	Cl_2, $AlCl_3$
D	CH_3Cl, $AlCl_3$	Cl_2, $AlCl_3$	$KMnO_4$, H_2SO_4

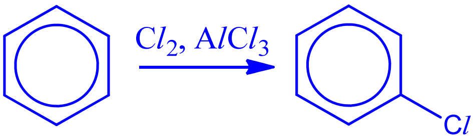
Answer: C

In this synthesis, we need to substitute $–CH_3$ (which is subsequently oxidised to $–CO_2H$) and $–Cl$ onto the benzene ring. Since both $–CH_3$ and $–Cl$ are 2,4-directing, but we want a 1,3-disubstituted product, we need to get $–CH_3$ on the ring first so that we can oxidise it to $–CO_2H$, which is 3-directing.

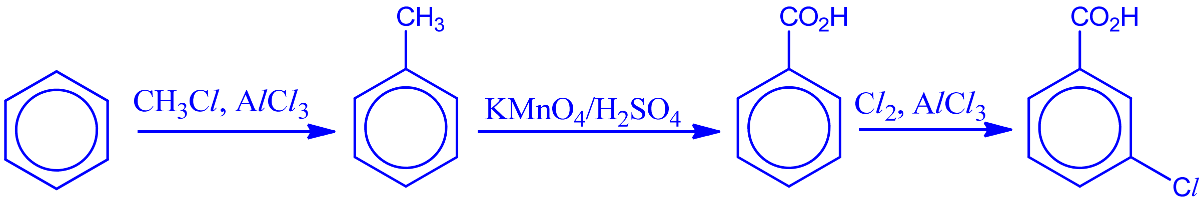
Option **A:** $–CH_3$ is substituted on 2- and 4-positions instead of the 3-position.



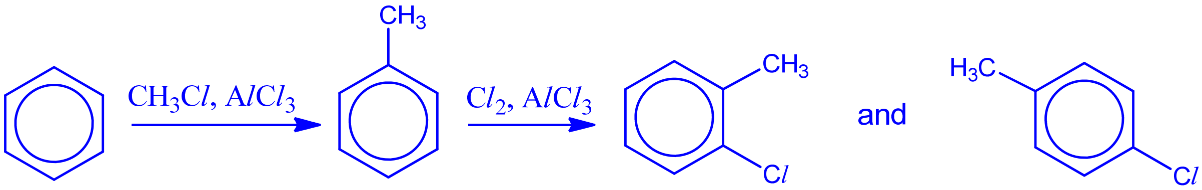
Option **B**: No alkyl side-chain for $KMnO_4$ to oxidise in Step 2.



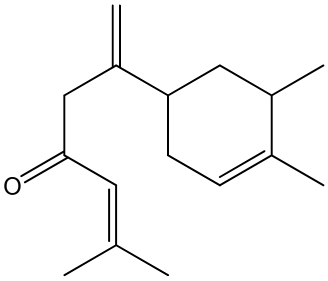
Option **C**:



Option **D**: –C*l* is substituted on 2- and 4-positions instead of the 3-position.



19 The structure of a β-atlantone derivative is shown below.



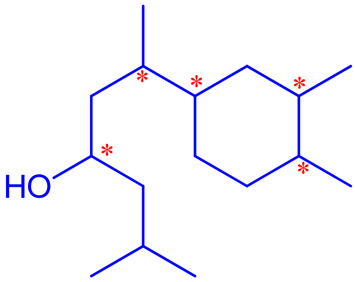
When it is completely reacted with hydrogen in the presence of platinum when heated, how many chiral centres does the product molecule possess?

A 2 **B** 3 **C** 4 **D** 5

Concept: Alkenes, Carbonyl Compounds: Reduction using H_2/Pt

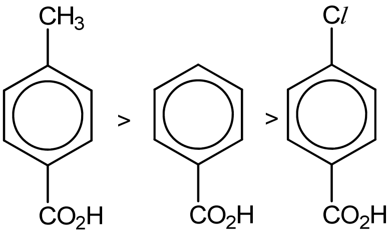
Answer: D

Reduction of C=C bonds and the ketone functional group gives the following product, which has 4 chiral centres:

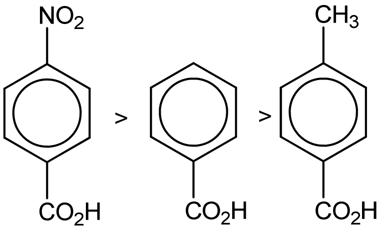


20 Which of the following correctly lists the compounds in order of decreasing acidity in aqueous solution?

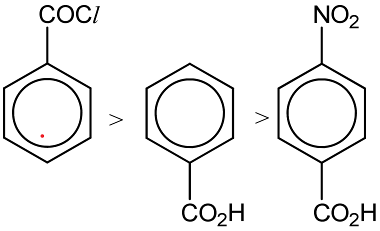
A



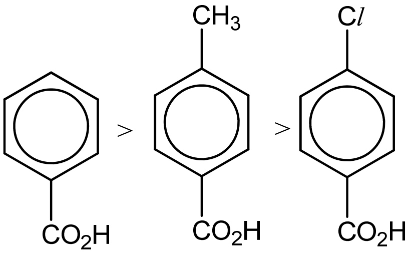
B



C



D



Answer: B

Electron-withdrawing group	$-NO_2$, $-Cl$
Electron-donating group	$-CH_3$

***Refer to Pg 17 of Data Booklet for the list of electron-donating groups (which activate ring reactivity) and electron-withdrawing groups (which deactivate ring reactivity).

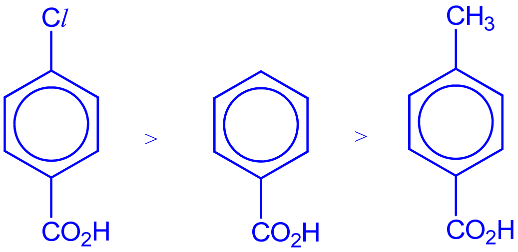
Note that

- electron-withdrawing groups increase acid strength by dispersing the negative charge on O atom and stabilizing the carboxylate ion; while
- electron-donating groups intensify the negative charge on O atom and destabilise the carboxylate ion.

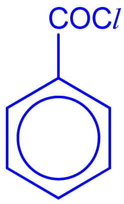
Hence option B is correct.

For the other options,

A & D The correct order should be

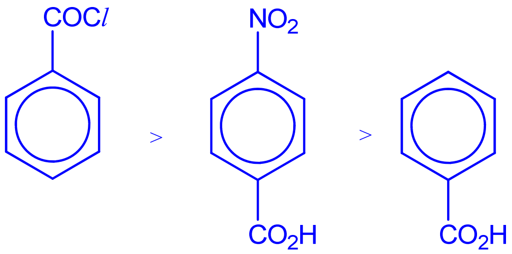


C Note that the following compound

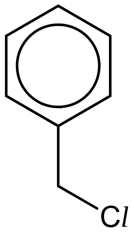


is an acyl chloride and undergoes hydrolysis readily to give HC*l* which is a strong acid, hence it is the strongest acid.

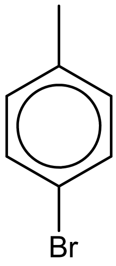
Hence, the correct order should be



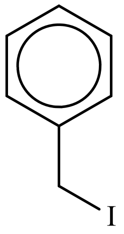
21 Equal amounts of compounds **W**, **X**, **Y** and **Z** are added separately to four test-tubes containing equal concentrations of ethanolic silver nitrate solution in a heated water bath. No precipitate forms in two of the tubes. In the other two tubes, precipitates form at different rates.



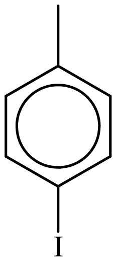
W



X



Y



Z

Which statements are correct?

1 The compounds which do not form a precipitate are **X** and **Z**.
2 The colour of the precipitate which forms the fastest is white.
3 The precipitate which forms the fastest weighs more than the other precipitate.

A 1, 2 and 3 **B** 1 and 3 only **C** 2 and 3 only **D** 1 only

Answer: B

1 In both **X** and **Z**, and halogen is directly connected to the benzene ring. This results in a stronger C−X bond, hence **X** and **Z** do not undergo nucleophilic substitution.✓

2 The C-I bond is weaker than the C−C*l* bond, hence it will break more readily. The colour of the precipitate should be yellow instead of white (which is the colour of AgC*l*), since it is AgI that forms the fastest. ×

3 Since equal amounts (i.e., no. of moles) of the compounds **W** to **Z** are used, the same no. of moles of precipitate should form for **X** and **Z**. The M_r of AgI is greater than that of AgC*l*, so the AgI precipitate should weigh more than the AgC*l* precipitate. ✓

22 The following reaction gives a mixture of organic products.

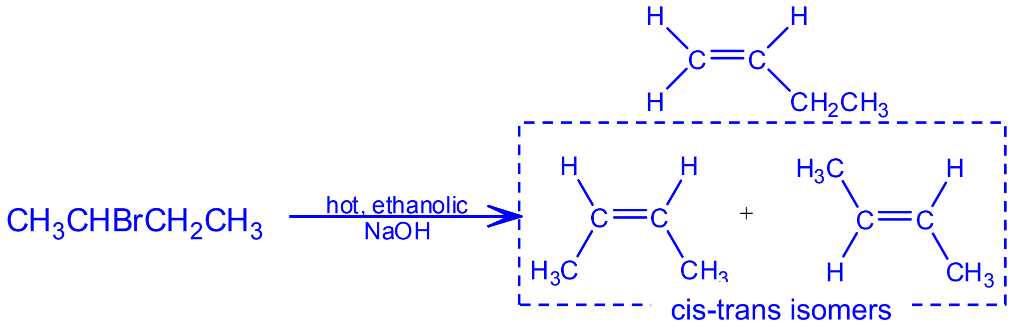
Which of the following statements are true?

1 The organic products formed are mainly alcohols.
2 The predominant type of reaction occurring is nucleophilic substitution.
3 There is a pair of cis-trans isomers among the organic products.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

Answer: D

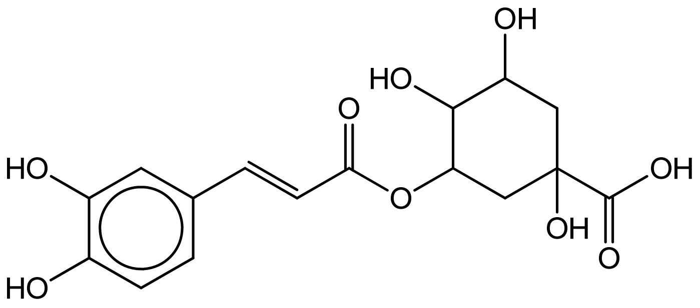
The reaction type is **elimination**. HBr can be eliminated from carbons 1 & 2, or carbons 2 & 3, to give three products, among which there is a pair of cis-trans isomers.



Do not confuse this reaction with the nucleophilic substitution of Br by OH^-, which takes place preferably under aqueous conditions instead of ethanolic conditions.

23 Chlorogenic acids account for up to 8% of the composition of unroasted coffee beans. More than 40 different varieties have been identified in green coffee beans, with 5-caffeoylquinic acid being the most prevalent.

The structure of 5-caffeoylquinic acid is shown below.



5-caffeoylquinic acid

How many moles of aqueous sodium hydroxide, sodium hydrogencarbonate and phosphorus(V) chloride will react with one mole of 5-caffeoylquinic acid at room temperature?

	NaOH(aq)	$NaHCO_3$(aq)	PCl_5(s)
A	6	3	6
B	5	1	3
C	4	3	4
D	3	1	4

Answer: D

Note:

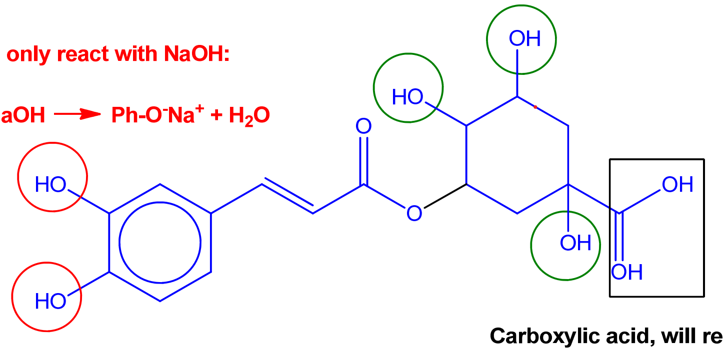
- NaOH(aq) will react with phenols and carboxylic acids only.
- $NaHCO_3$(aq) will react with carboxylic acids only.
- PCl_5(s) will react with alcohols and carboxylic acids only.

Alcohol, will only react with PCl_5

$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$

Phenol, will only react with NaOH:

$Ph\text{-}OH + NaOH \longrightarrow Ph\text{-}O^-Na^+ + H_2O$



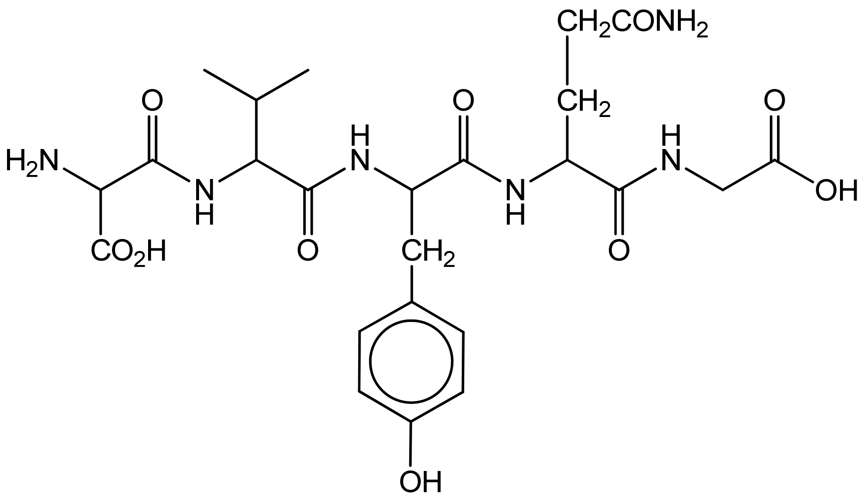
Carboxylic acid, will react with NaOH, $NaHCO_3$ and PCl_5

$RCO_2H + NaOH \longrightarrow RCO_2Na + H_2O$

$RCO_2H + NaHCO_3 \longrightarrow RCO_2Na + H_2O + CO_2$

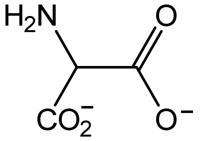
$RCO_2H + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

24 The structure of a polypeptide chain is shown below.

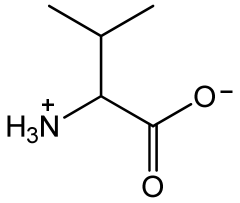


Which of the following will be formed when this polypeptide chain is heated under reflux with 6 mol dm^{-3} of NaOH(aq)?

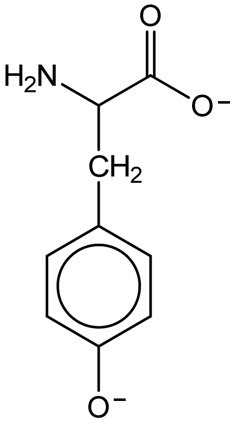
1



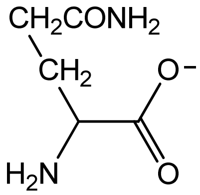
2



3



4



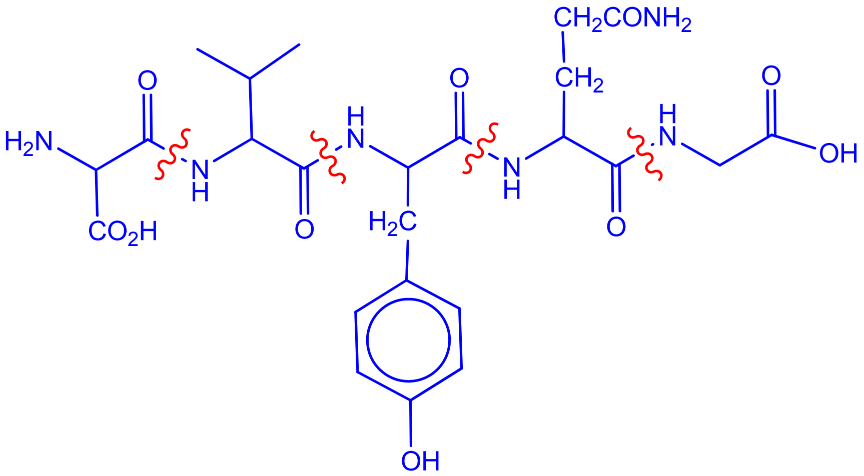
A 1 and 3 only

B 2 and 4 only

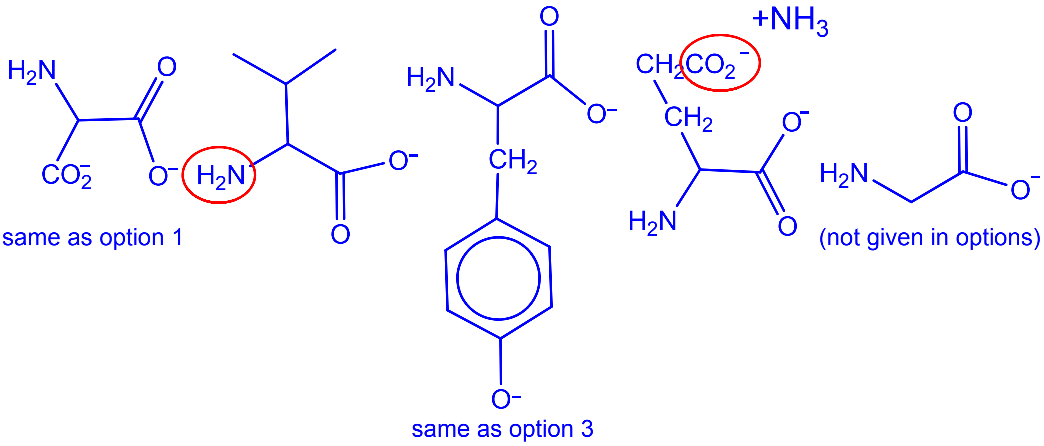
C 1, 3 and 4 only

D 1, 2, 3 and 4

Answer: A (1 and 3 only)



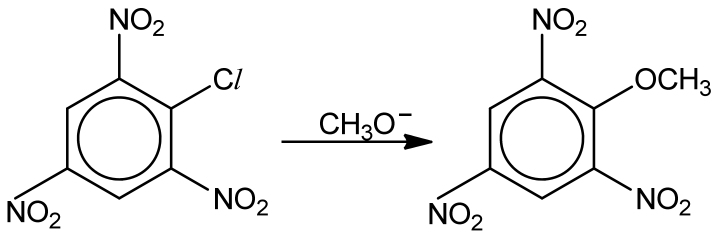
Upon hydrolysis with NaOH(aq), the correct products should be:



Option 2 is wrong as there should not be $-NH_3^+$ present when NaOH is used.

Option 4 is wrong as the amide group ($-CONH_2$) of the R-group should also be hydrolysed

25 Methoxide anion, CH_3O^-, can be generated when methanol reacts with sodium metal. The following reaction shows how methoxide anion reacts with an organic compound under suitable conditions.



Which of the following is the correct mechanism for the above reaction?

A electrophilic addition

B electrophilic substitution

C nucleophilic addition

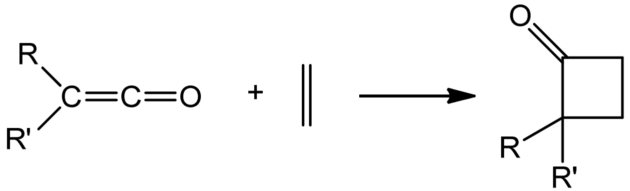
D nucleophilic substitution

Answer: D

Methoxide anion, CH_3O^-, is a **nucleophile** (lone pair of electrons to be donated) which is attracted to the **electron deficient C** of the benzene ring bonded to C*l*. (Due to the presence of 3 electron withdrawing NO_2 groups, the C–C*l* bond is highly polarised and weakened)
Since the benzene ring is restored at the end of the reaction, this reaction is a **substitution** reaction instead of an addition reaction. Hence, the correct mechanism of this reaction is a nucleophilic substitution.

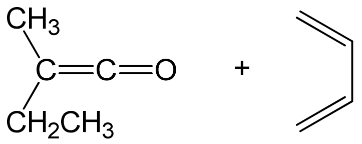
(Note that under normal conditions, C–C*l* bond of chlorobenzene does have partial double bond character and will **NOT** be hydrolysed.)

26 Ketenes contain a carbon involved in both alkene and ketone functional groups. It is a reactive compound which undergoes cycloaddition reaction readily with unsaturated compounds to form cyclic rings. One example of such a reaction is shown below.

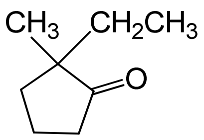


ketene

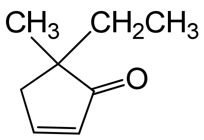
Which of the following is the correct product formed for the following cycloaddition reaction?



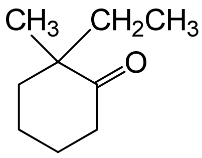
A



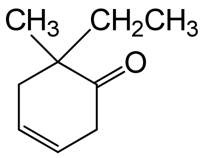
B



C



D

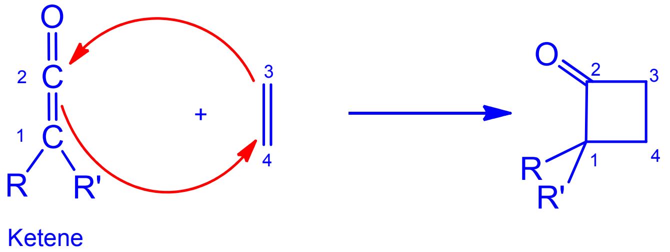


Answer: D

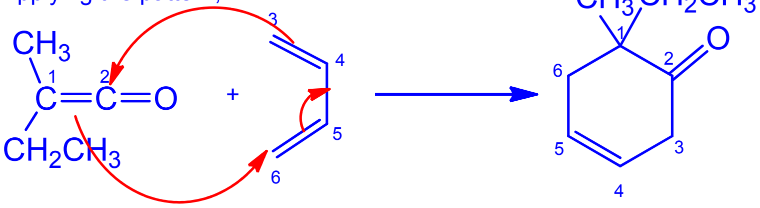
A and B cannot be the correct answer as there would be a loss of 1 C from the reactants to molecules A and B.

C is not the correct answer because there is an addition of 2 H due to a missing C=C. (by comparing the M_r of the reactants and C). In the given reaction, the number of H and C and O should still stay the same after the cycloaddition reaction.

Recognising the pattern,



Applying the pattern,



27 *Use of the Data Booklet is relevant to this question.*

When a current is passed through a solution of butanoic acid, $CH_3CH_2CH_2CO_2H$, the following reaction occurs at the cathode.

$$CH_3CH_2CH_2CO_2H + 4H^+ + 4e^- \rightarrow CH_3CH_2CH_2CH_2OH + H_2O$$

Oxygen is produced at the anode.

Which volume of oxygen, measured at room temperature and pressure, is produced when 0.015 mol of butanoic acid is electrolysed?

A 90 cm^3 **B** 180 cm^3 **C** 360 cm^3 **D** 720 cm^3

Answer: C

The half-equation for the oxidation of water to produce oxygen (under acidic conditions) is as follows:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Hence, $O_2 \equiv 4e^- \equiv CH_3CH_2CH_2CO_2H$

No. of moles of O_2 = 0.0150 mol

Volume of O_2 = 0.0150 x 24000 = 360 cm^3

28 Some standard reduction potentials are given below.

$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07 V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33 V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V

Which oxidation is **not** feasible under standard conditions?

A chloride ions by acidified manganate(VII) ions

B bromide ions by chlorine

C manganese(II) ions by acidified dichromate(VI) ions

D chromium(III) ions by chlorine

Answer: C

A chloride ions by acidified manganate(VII) ions
$E_{cell}^{\ominus} = 1.52 - 1.36 > 0$ ✓

B bromide ions by chlorine
$E_{cell}^{\ominus} = 1.36 - 1.07 > 0$ ✓

C manganese(II) ions by acidified dichromate(VI) ions
$E_{cell}^{\ominus} = 1.33 - 1.52 < 0$ ✗

D chromium(III) ions by chlorine
$E_{cell}^{\ominus} = 1.36 - 1.33 > 0$ ✓

29 A compound of chromium with the general formula $CrCl_3.6H_2O$ forms an aqueous solution. When this solution is treated with an excess of aqueous silver nitrate, only two third of the total chloride present is precipitated as $AgCl$.

Which of the following represents the structure of the chromium-containing ion present in the original compound?

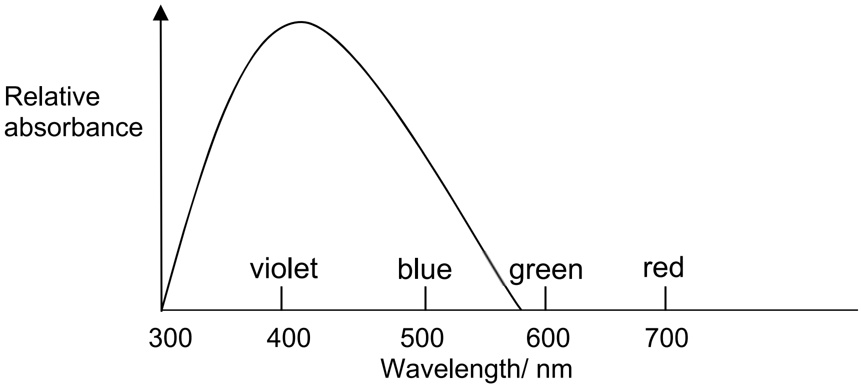
A	Cr^{3+}	**C**	$[Cr(H_2O)_5Cl]^{2+}$
B	$[Cr(H_2O)_6]^{3+}$	**D**	$[Cr(H_2O)_4Cl_2]^+$

Answer: C

Since only two third of the total chloride present is precipitated as $AgCl$, the complex of the chromium compound is $[Cr(H_2O)_5Cl]^{2+} \bullet 2Cl^-$, where 2 Cl^- are free ions and are not bonded to the central metal ion through dative bonding and thus free to react with silver ions to form $AgCl$ ppt.

30 The chromium picolinate complex is soluble in water and the visible absorption spectrum of the complex is shown below:

[A visible absorption spectrum is a graph depicting the absorption of radiation by a material over a range of visible light wavelengths.]



What is the most likely colour of the chromium picolinate complex?

A violet

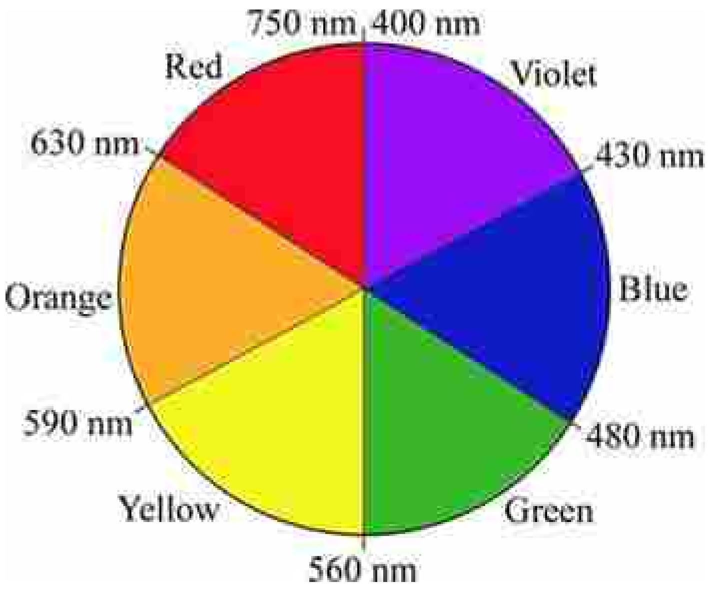
B blue

C yellow

D green

Answer: C

In general, the observed colour of an object corresponds to the wavelengths that are not absorbed by the object. The colour observed is complementary of the colour of light (wavelengths) absorbed. Since the complex absorbed light in the violet/blue region, the colour observed will be yellow/orange.



Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY **9729/02**

Paper 2 Structured Questions **Friday 17 August 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

WORKED SOLUTIONS

This document consists of **19** printed pages.

Answer **all** the questions in the spaces provided.

1 In atmospheric chemistry, NO_x is a generic term for the nitrogen oxides that are most prevalent for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as tropospheric ozone. In the atmosphere, dinitrogen pentoxide (N_2O_5) is an important reservoir of the NO_x species that are responsible for ozone depletion.

(a) In the laboratory, the kinetics involving the decomposition of N_2O_5 into NO_2 and O_2 can be investigated by dissolving it in an organic solvent such as tetrachloromethane, CCl_4. The decomposition of N_2O_5 was found to be a first-order reaction.

$$2N_2O_5 \rightarrow 4NO_2(g) + O_2(g)$$

Table 1.1 below shows the variation of $[N_2O_5]$ with time.

Time / s	$[N_2O_5]$ / mol dm^{-3}	ln $[N_2O_5]$
0	0.910	**-0.0943**
300	0.750	**-0.288**
600	0.640	**-0.446**
1200	0.440	**-0.821**
3000	0.160	**-1.83**

Table 1.1

(i) State the rate equation for the decomposition of N_2O_5.

Rate = k$[N_2O_5]$ .... [1]

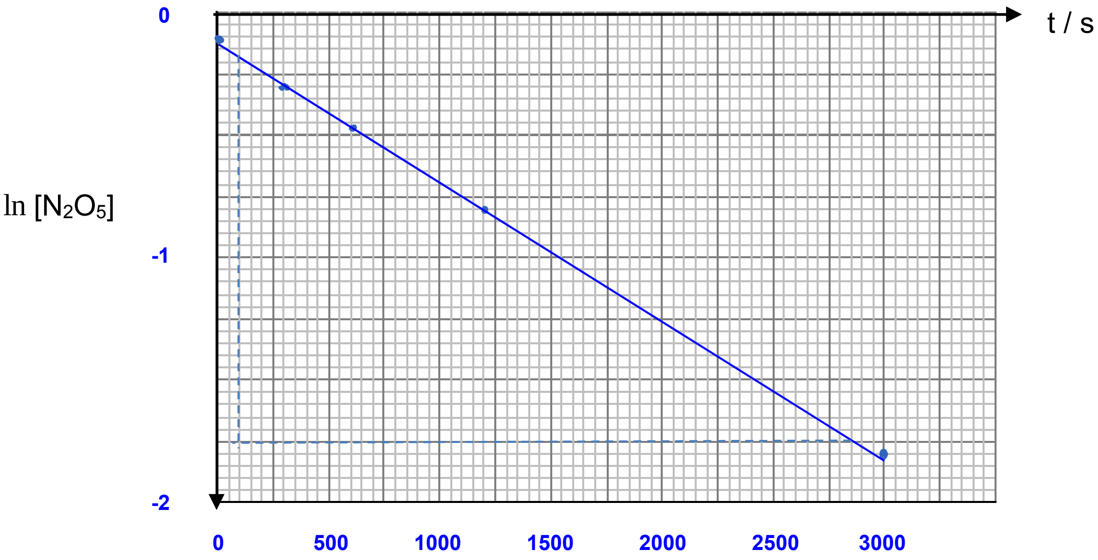
(ii) The rate equation for the decomposition of N_2O_5 can also be expressed as:

$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o$$

where $[N_2O_5]_o$ is the initial concentration of N_2O_5 and $[N_2O_5]_t$ is the concentration of N_2O_5 at time, *t*.

Using relevant data in Table 1.1, calculate the values for ln $[N_2O_5]$ and complete Table 1.1. [1]

(iii) Using the following axes and relevant data in Table 1.1, plot a graph of ln $[N_2O_5]$ against time (in second), showing how the concentration of N_2O_5 changes with time.



[2]

(iv) Using your graph, determine a value for the rate constant, k, for the decomposition of N_2O_5. State the units of k clearly. [2]

Using the points (100, -0.155) and (2850, -1.75)

k = – gradient

$$= -\left[\frac{-0.155-(-1.75)}{100-2850}\right]$$

$$= 5.80 \times 10^{-4}\ s^{-1}$$

(v) Hence determine a value for the half-life of the decomposition of N_2O_5. State the units clearly. [1]

$$t_{1/2} = \frac{\ln 2}{k}$$

$$= \frac{\ln 2}{5.80 \times 10^{-4}}$$

$$= 1195\ s$$

(vi) Outline another experiment to determine the rate constant, k, for the decomposition of N_2O_5 in tetrachloromethane.

You are provided with the same solution of N_2O_5 used in the experiment described in **(a)**.

No details regarding use of specific glassware are required.

1. Measure the volume of gases (NO_2 and O_2) produced OR the colour intensity of the brown NO_2 gas (using a colorimeter) at regular time intervals from the start of reaction

2. Plot a graph of "volume of gases produced against time" OR "colour intensity against time" and determine the half-life from the graph.

3. Use the equation $t_{1/2} = \frac{ln2}{k}$ to determine the value of k.

[2]

(b) The NO_2 produced in the decomposition reaction in **(a)** can exist in equilibrium with dinitrogen tetroxide (N_2O_4):

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

An experiment was conducted at 25 °C by varying initial concentrations of N_2O_4 and NO_2 contained in a closed reaction vessel. The initial and equilibrium concentrations of the two gases are shown in Table 1.2.

Experiment No	Initial concentration / mol dm^{-3}		Equilibrium concentration / mol dm^{-3}	
	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$
1	0.000	0.200	0.0898	0.0204
2	0.600	0.040	0.594	0.0523
3	0.500	0.030	0.491	0.0475
4	0.446	0.050	0.448	0.0457
5	0.670	0.000	0.643	0.0547

Table 1.2

(i) State *Le Chatelier's Principle*.

***Le Chatelier's Principle* states that if a *change* (e.g. change in concentration, pressure and temperature) is made to a system *in equilibrium*, the system reacts in such a way as to tend to <u>oppose the change</u>, and a *new equilibrium* is formed.**

[1]

(ii) State what will be observed when the pressure in the reaction vessel is decreased.

The brown colour of the gas (NO_2) darkens.

.... [1]

(iii) Identify the experiment that gives the initial concentration of N_2O_4 : NO_2 in the ratio 15:1.

Experiment 2

.... [1]

(iv) Based on the experiment identified in **(b)(iii)**, calculate a value for the equilibrium constant, *K*c. [1]

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{(0.0523)^2}{(0.594)}$$

$$= 4.60 \times 10^{-3} \text{ mol dm}^{-3}$$

(v) For reversible reactions involving gases, the concentrations of the gaseous reactants and products can also be expressed in terms of their partial pressures, and the value of the corresponding K_p can then be determined. K_p and K_c is related by the following expression:

$$K_p = K_c(0.0821T)^{\Delta n}$$

where Δn = moles of gaseous products – moles of gaseous reactants based on given stoichiometric equation and T is temperature in Kelvin.

Using your answer in **(b)(iv)** and the above expression, calculate a value for the K_p for the reversible reaction between N_2O_4 and NO_2.

$$K_p = K_c(0.0821T)^{\Delta n}$$

$$= (4.60\times10^{-3})(0.0821)(298)^{(2-1)}$$

$$= 0.113$$

[2]

[Total: 15]

2 **(a)** Marine organisms such as crabs use peptide signaling molecules such as glycyl-L-histidyl-L-lysine (GHK) to detect predators. In order for this peptide signaling molecule to function in water, it must exist in the form of a zwitterion.

However, due to the increase in carbon dioxide levels in the ocean, the pH of the ocean decreases as shown in Fig. 2. This affects the structure and function of the peptide signaling molecule and thus affecting the survival of these marine organisms.

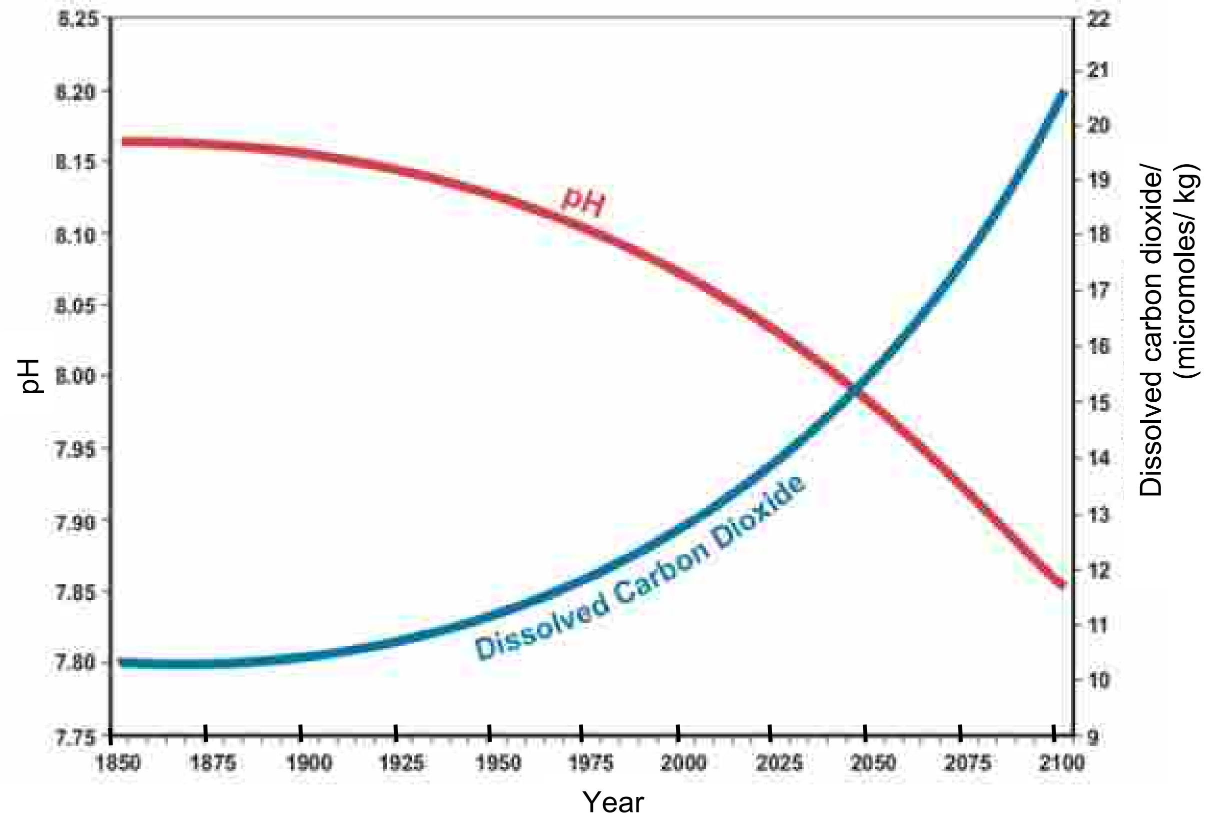


Fig. 2

(i) State what is meant by a *zwitterion*.

Zwitterion is a species where it is dipolar ion and have no nett charge. [1]

(ii) Explain briefly why GHK, as a *zwitterion*, is highly soluble in water.

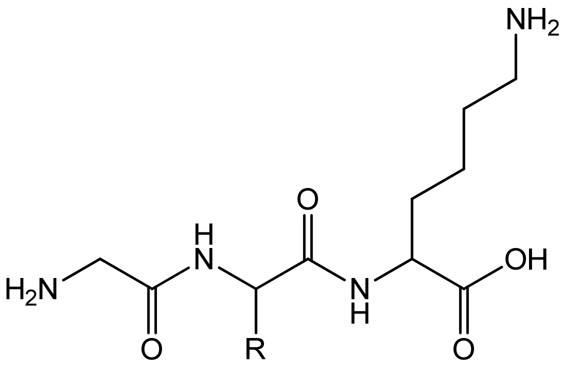
GHK as a zwitterion is able to form ion-dipole attraction with water molecules.

[1]

(iii) Write an equation showing how the pH of the ocean decreases due to rising concentration of CO_2.

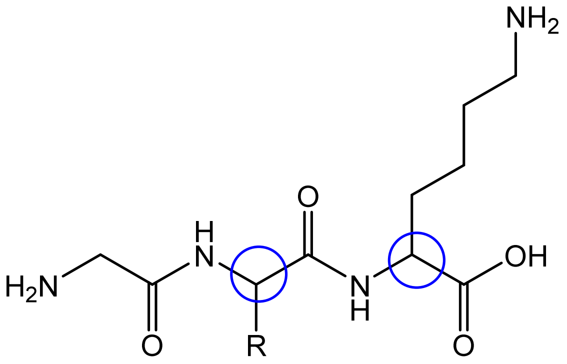
$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ [1]

The structure of GHK is shown below where R, which is the histidine side chain, need not be considered for this question.

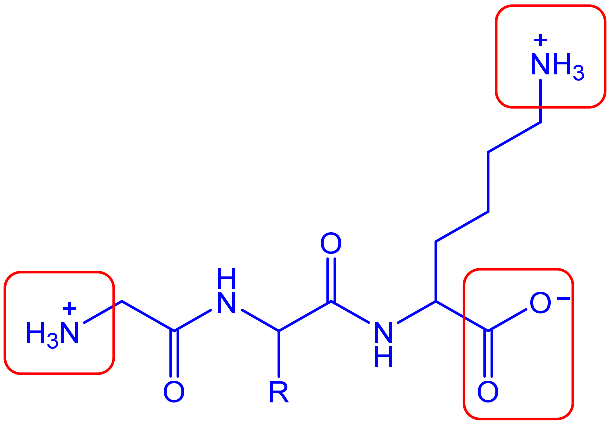


GHK

(iv) Circle any chiral carbon atom on the above structure, GHK. [1]



(v) There can be three pK_a values associated with GHK: 2.80, 7.98, 11.44. Make use of these pK_a values to suggest the major species present in solutions of GHK at pH 7.



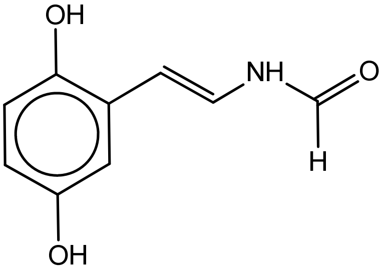
[2]

(vi) Use the graph in Fig. 2 to determine from which year onwards more than 50% of GHK in marine organisms no longer can function as a signaling molecule. Explain why this is so.

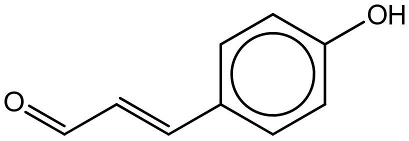
2050. For GHK no longer function as a signaling molecule, it cannot exist as a zwitterion which both the –NH_2 groups are protonated. Since the pKa value of –NH_2 is 7.98, the pH value lower than that will result in –NH_2 to be protonated .

.... [2]

(b) Bioactive molecules containing dehydrotyrosine derivatives such as erbstatin and 4-hydroxy cinnamaldehyde found in marine organisms are responsible for antibacterial properties.



erbstatin

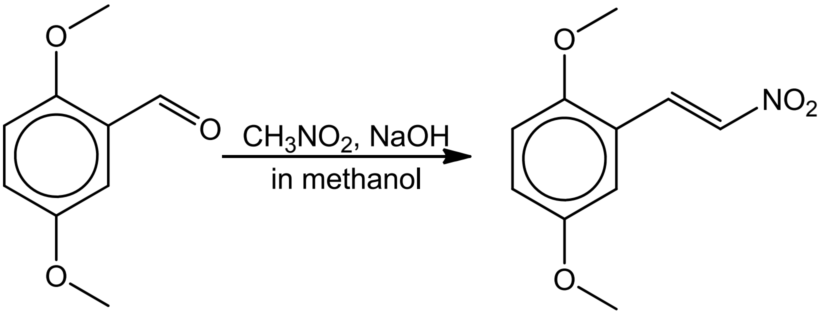


4-hydroxy cinnamaldehyde

(i) State and explain whether erbstatin or 4-hydroxy cinnamaldehyde has a higher boiling point.

Erbstatin has a higher boiling point since it can form more extensive intermolecular hydrogen bonds therefore requires more energy to overcome the intermolecular hydrogen bonds in Erbstatin compared to 4-hydroxy cinnamaldehyde. [3]

The synthesis of erbstatin involved the following step.

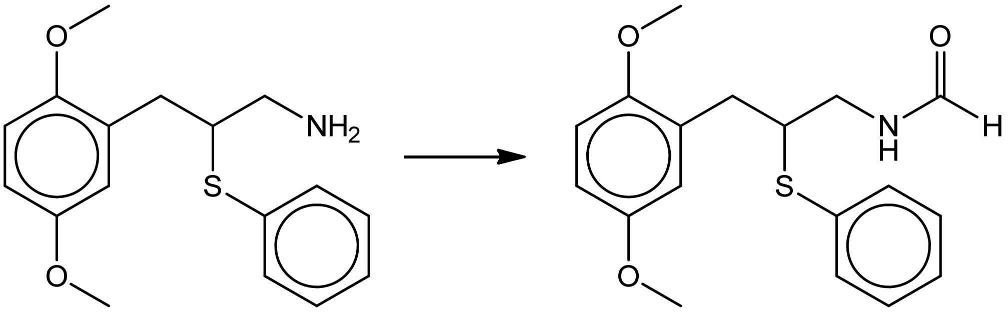


(ii) Given that NaOH is used as a base to form $^{-}CH_2NO_2$ as a nucleophile, suggest the type of reaction in the above step.

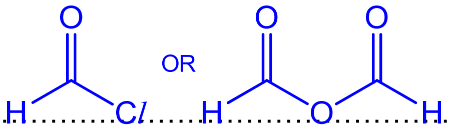
Condensation OR Addition-elimination

.... [1]

Another step in the synthesis of erbstatin is shown below.

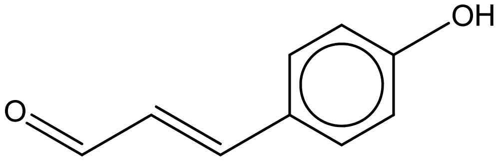


(iii) Suggest suitable reagents for the above step.

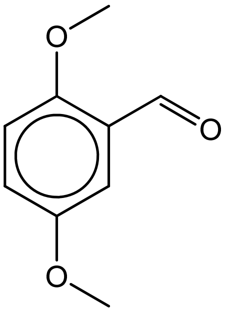


[1]

(iv) Describe a simple chemical test to distinguish between 4-hydroxy cinnamaldehyde and 2,5-dimethoxybenzaldehyde as shown below.



4-hydroxy cinnamaldehyde



2,5-dimethoxybenzaldehyde

Add neutral $FeCl_3$ to separate test tubes containing each sample.

Purple coluration is observed with erbstatin. No purple colouration observed with 2,5-dimethyoxybenzaldhyde..

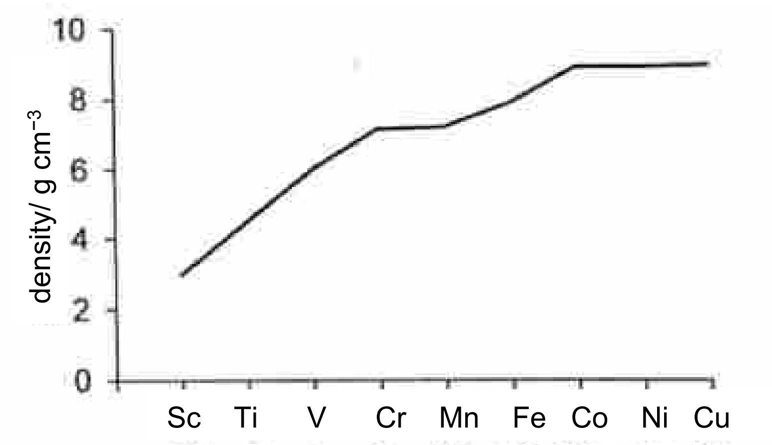
[2]

[Total: 15]

3 **(a)** d-block elements are remarkably similar to each other in physical properties. In general, they are hard, dense and good conductors of heat and electricity. Transition elements belong to d-block elements in the Periodic Table.

Although all d-block elements are metals, they do show significant physical differences when compared to s-block elements i.e., Group 1 and 2 metals.

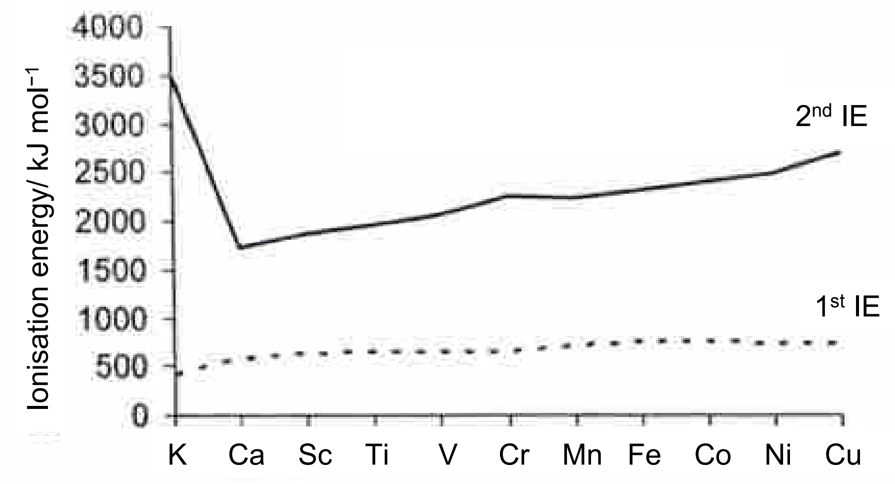
The graph below shows the densities of the elements Sc to Cu.



(i) Suggest why the densities of the elements increase from Sc to Cu.

From Sc to Cu, relative atomic mass increases and atomic radius decreases slightly(or remain invariant). The elements have a more close-packed structure and thus have a higher mass per unit volume, which is density. [2]

(ii) The graph below shows the first (dashed line) and second (solid line) ionisation energies (IE) for the element K to Cu inclusive.



Explain why the first ionisation energy remains relatively constant from Sc to Cu.

From Sc to Cu, the number of protons increases, hence the nuclear charge increases. Electrons are added to the inner 3d subshell which provides increased effective shielding between nucleus and valence 4s electron. Therefore, increase in nuclear charge almost cancel out the increase in shielding effect (effective nuclear charge increases slightly). Energy required to remove the outer 4s electrons from Sc to Cu is almost constant. [2]

(iii) Explain briefly why is the second ionisation energy of potassium so much higher than that of the other elements.

The second electron in K to be removed is from an inner 3p orbital which is more strongly attracted by the nucleus as it experiences less shielding. [1]

(b) Scandium, copper and zinc are d-block elements. However, copper is a transition element while scandium and zinc are not.

(i) Define the term *transition element*.

A transition element is a d-block element which forms one or more stable ions with partially filled d subshells. [1]

(ii) State the full electronic configuration of Sc^{3+}.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ [1]

(iii) Explain why scandium is not classified as a transition element.

Sc is not a transition element as it only forms stable Sc^{3+} ion which has empty d subshell. [1]

(c) **X** and **Y** are period 3 elements.

Element **X** forms a white oxide that is slightly soluble in cold water. Its chloride dissolves in water to form a weakly acidic solution.

Element **Y** forms two oxides. 0.03 moles of one of the two oxides produces 7.00 g of white precipitate when mixed with excess barium chloride solution. The white precipitate is insoluble in dilute strong acid. A solution is obtained when equimolar of the oxide of element **Y** is added to the oxide of element **X** with water.

Identify the elements **X**, **Y**, and the oxide of **Y**.

Explain the observations with the aid of relevant equations.

Element X: Magnesium Element Y: Sulfur

Formula of the oxide of element Y: SO_3

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$ when MgO reacts with water, sparingly soluble $Mg(OH)_2$ is formed

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$MgCl_2$ hydrolyses slightly to form a weakly acidic solution of pH 6.5

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$

Upon addition of excess barium chloride solution, $BaSO_4(s)$ is formed.

7.00 g of white ppt corresponds to the mass of 0.03 mol of $BaSO_4$.

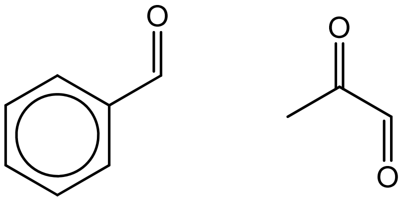
$SO_3(g) + H_2O\ (l) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$

OR $SO_4^{2-} + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

$SO_3(g) + MgO(aq) \rightarrow MgSO_4(aq)$ [7]

[Total: 15]

4 **(a)** Carbonyl compounds occur naturally, giving many signature flavours. For example, benzaldehyde in almonds and 2-oxopropanal in burnt sugar.



benzaldehyde 2-oxopropanal

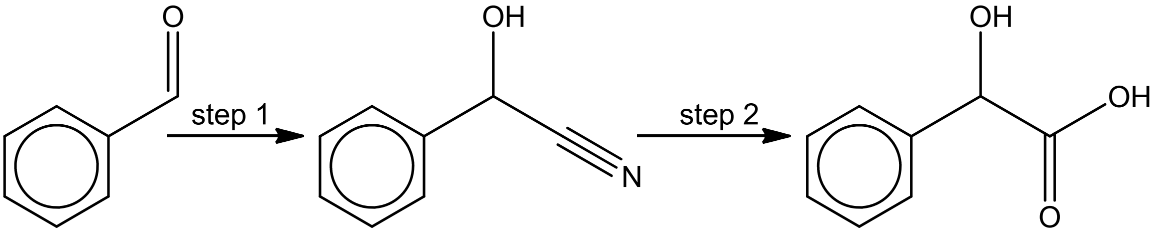
(i) Suggest a simple chemical test that could distinguish between the two compounds above. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: I_2 (aq), NaOH (aq), heat **or** Fehling's reagent/solution, heat

	Observations:	Products:
benzaldehyde	**No Yellow ppt** seen. OR **No Red ppt** seen.	No products
2-oxopropanal	**Yellow ppt** seen. OR **Red ppt** seen.	CHI_3(s) *for iodoform* Cu_2O(s) *for Fehling's Reagent used*

[3]

(ii) Benzaldehyde undergoes a possible reaction sequence as shown below to form mandelic acid, which is used as an antibacterial agent.



benzaldehyde mandelic acid

State the reagents and conditions for steps 1 and 2.

Step 1: HCN (aq), trace amount of NaOH (aq), cold 10-20 °C

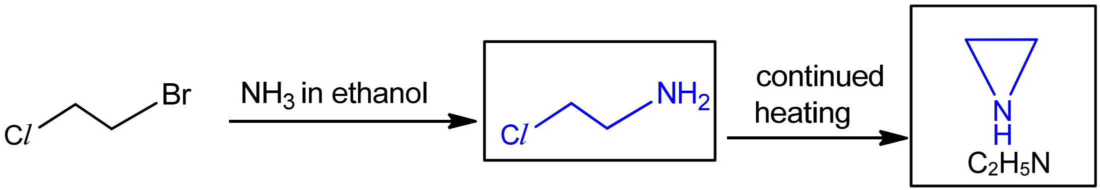
Step 2: Dilute H_2SO_4 (aq), heat under reflux [2]

(b) Another class of naturally occurring organic compounds is halogenoalkanes, e.g. bromomethane found in vegetables, chloromethane found in algae and trichloromethane found in termites.

(i) With bromomethane and chloromethane as examples, describe and explain briefly the relative reactivities of bromo- and chloro-compounds with respect to hydrolysis.

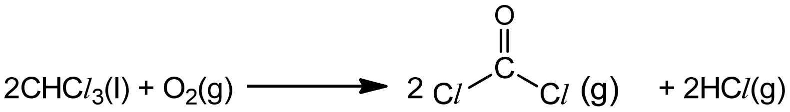
CH_3Br would be **<u>more reactive</u>** towards hydrolysis than CH_3Cl. This is because the **<u>C–Br bond is weaker</u>** than C–Cl bond and would be more easily broken during hydrolysis. [1]

(ii) This difference in reactivity can also be observed in organic reactions. Suggest the structural formulae of the compounds formed in the boxes below. The final product is a cyclic compound.



[2]

(c) Trichloromethane was previously used as an anesthetic, but chronic exposure can harm the liver where it is metabolised to toxic phosgene, $COCl_2$. This reaction can also take place slowly in the presence of oxygen and light, as represented below.



$$2CHCl_3(l) + O_2(g) \longrightarrow 2\,Cl{-}\overset{\overset{\Large O}{\|}}{C}{-}Cl\,(g) \quad + 2HCl(g)$$

(i) Construct a fully labelled energy cycle relating the reactants and products of this reaction to their gas phase atoms. Use your cycle to calculate the enthalpy change of the above reaction.

Your cycle should include relevant data from the Data Booklet together with the following data shown below:

The enthalpy change of vaporisation of $CHCl_3(l)$ is +31 kJ mol^{-1}.

$$\begin{tikzcd}
2CHCl_3(l) + O_2(g) \arrow[rr, "\Delta H_r"] \arrow[d, "2(+31)\text{ kJ mol}^{-1}"] & & 2COCl_2(g) + 2HCl(g) \arrow[ddl, "2(740 + 2(340)) + 2(431)\text{ kJ mol}^{-1}"] \\
2CHCl_3(g) + O_2(g) \arrow[dr, "2(410 + 3(340)) + 496\text{ kJ mol}^{-1}"'] & & \\
& 2C(g) + 2H(g) + 6Cl(g) + 2O(g) &
\end{tikzcd}$$

[3]

$\Delta H_r = 2(31) + 2[\underline{\mathbf{410}} + 3(\underline{\mathbf{340}})] + \underline{\mathbf{496}} - [2(\underline{\mathbf{740}}+2(\underline{\mathbf{340}})) + 2(\underline{\mathbf{431}})]$
$= \underline{-284\text{ kJ mol}^{-1}}$ (3.s.f.)

(ii) Predict, with reasons, the sign of the entropy change of the reaction in **(c)(i)**.

Entropy change of the reaction should be **positive**, as the number of **moles of gas increases** from 1 mole to 4 moles, there are more ways of arranging the particles, hence the system **increases in disorderness.** [2]

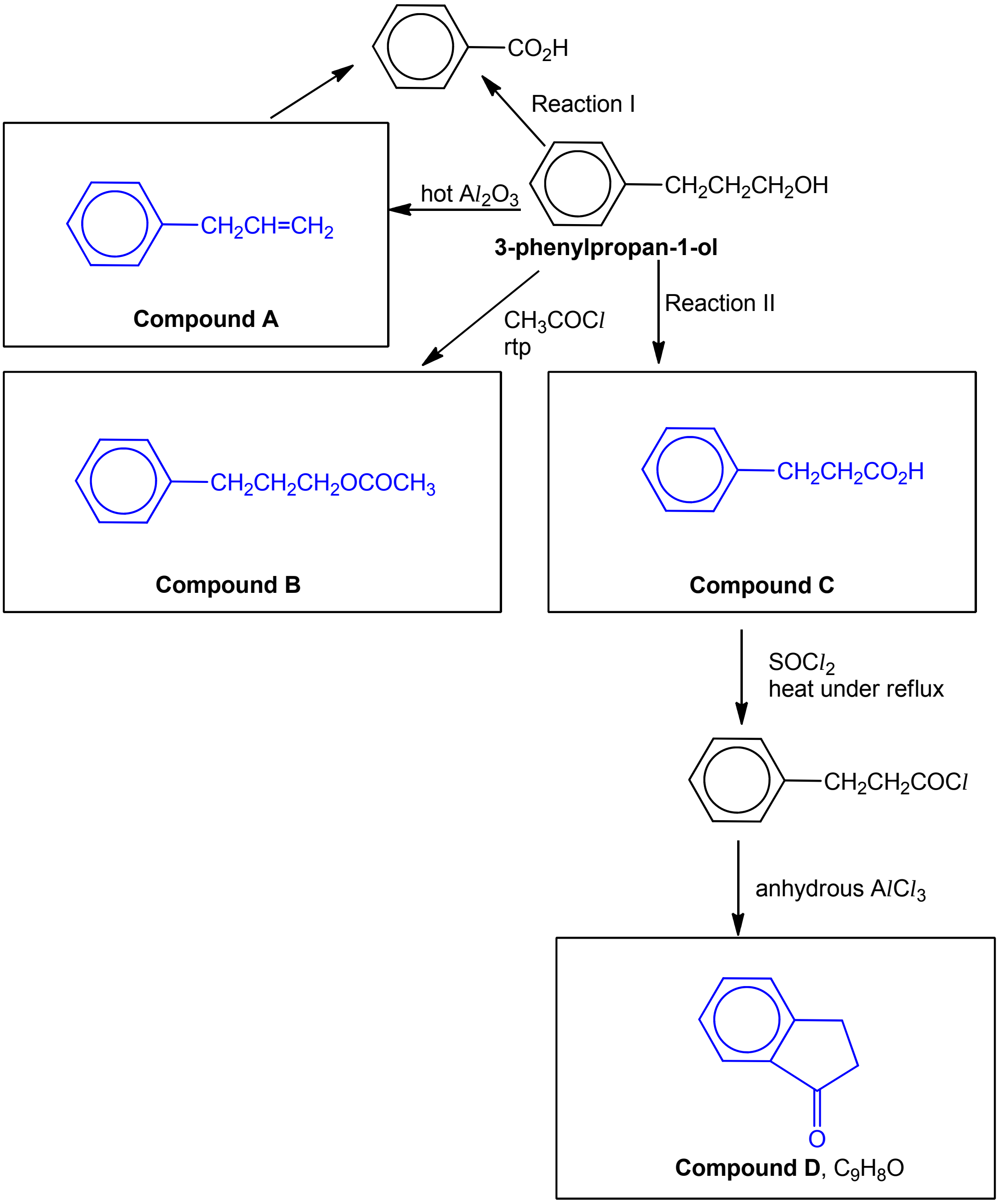
(iii) Hence, state the sign of the standard Gibbs free energy change and comment on the spontaneity of the reaction.

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be **negative**, since the enthalpy change is negative, and entropy change is positive. Thus, the reaction is always **spontaneous** at all temperature. [2]

[Total: 15]

5 **(a)** Benzene is an important precursor in the production of many chemicals. 3-phenylpropan-1-ol is an example of an organic compound which contains the benzene ring as a substituent.

(i) The following reaction scheme shows the reactions of 3-phenylpropan-1-ol. Suggest the structural formulae of compounds **A**, **B**, **C** and **D** in the boxes below.



[4]

(ii) Using the reaction scheme for the reactions of 3-phenylpropan-1-ol, state the reagents and conditions for reactions I and II. [2]

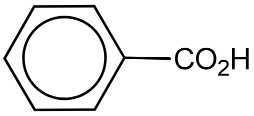
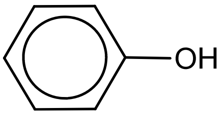
Reaction I **$KMnO_4$, dilute H_2SO_4, heat under reflux**

Reaction II **$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux**

(b) There is another form of important organic compounds which are derived from benzene. Benzene derivatives are formed when one of the hydrogens on the ring is replaced with a different functional group.

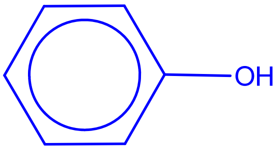
Benzoic acid and phenol are examples of such benzene derivatives which exhibit acidic character when dissolved in water.

The K_a values of benzoic acid, carbonic acid and phenol are given in the table below.

acid	structural formula	K_a / mol dm^{-3}
benzoic acid		6.3×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
phenol		1.3×10^{-10}

Both benzoic acid and phenol are reacted with sodium hydroxide to form sodium benzoate and sodium phenoxide respectively.

(i) Draw the organic product formed when CO_2 is bubbled through a solution of aqueous sodium phenoxide. [1]



(ii) However, no reaction occurs when CO_2 is bubbled through a solution of aqueous sodium benzoate. Explain why this is so. [1]

CO_2 dissolves in water to give <u>carbonic acid, H_2CO_3</u> which is a <u>weaker acid</u> ($K_a = 4.5 \times 10^{-7}$) compared to benzoic acid ($K_a = 6.3 \times 10^{-5}$) and therefore it is <u>not able</u> to <u>donate proton to benzoate ion to form benzoic acid</u>.

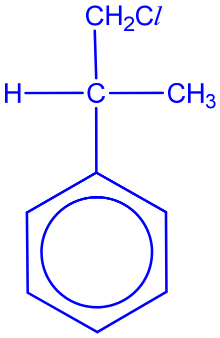
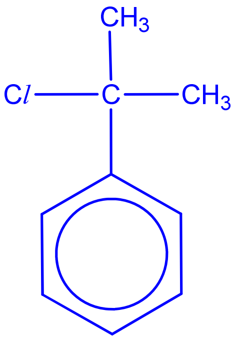
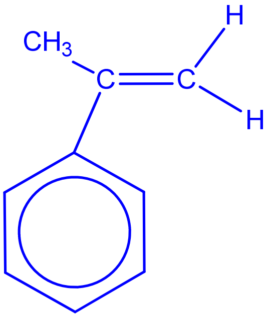
(c) Cumene, C_9H_{12}, is another benzene derivative that can be used to produce phenol and propanone.

When a sample of cumene is reacted with limited chlorine in the presence of UV light, only two monochlorinated products, **X** and **Y** are formed. Only compound **X** has a chiral carbon. Both **X** and **Y** react with reagent **W** under heat to form hydrocarbon **Z**. Hydrocarbon **Z** is able to decolourise aqueous bromine.

(i) State reagent **W**. [1]

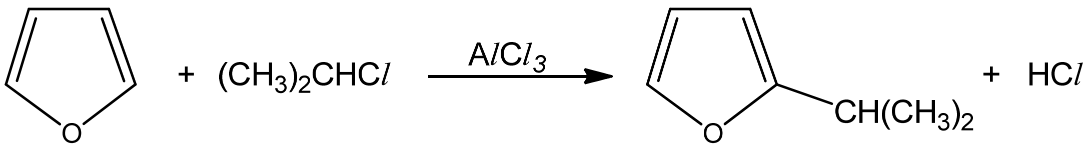
NaOH dissolved in ethanol / alcoholic NaOH/ NaOH (alc)

(ii) In the space below, give the structural formula of compound **X**, **Y** and **Z**. [3]

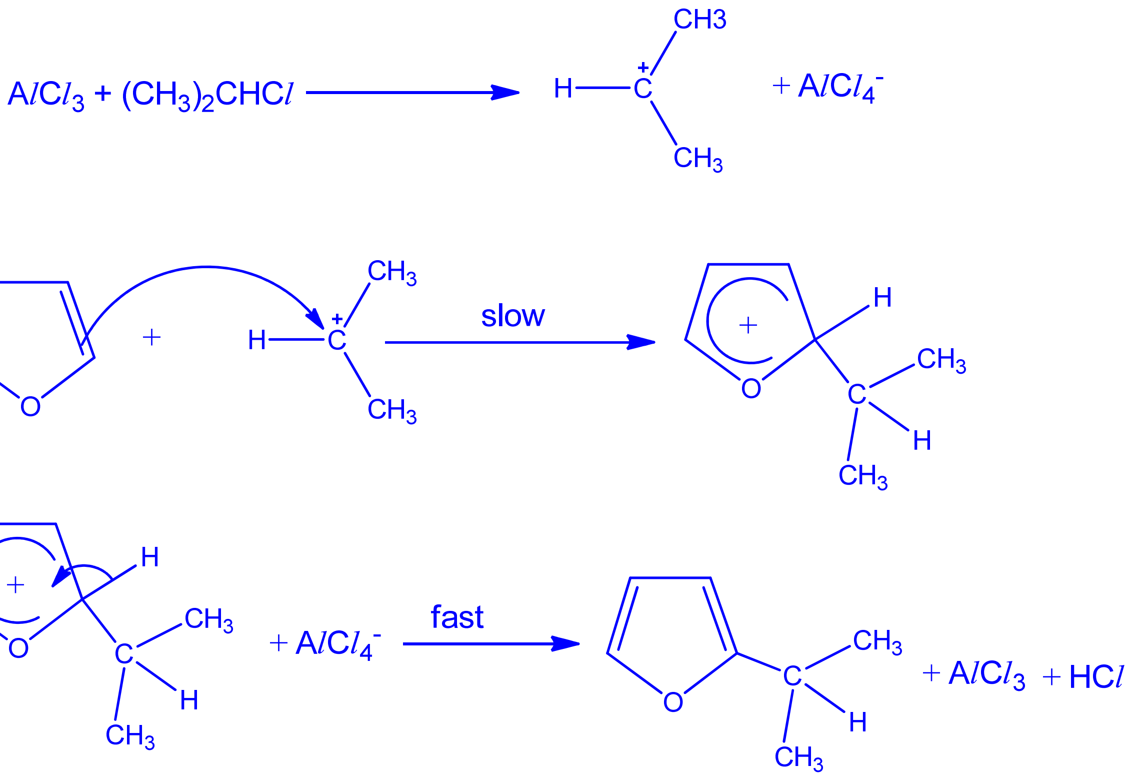
Compound X	**Compound Y**	**Compound Z**
		

(d) As an aromatic compound, benzene undergoes electrophilic substitution reactions. Like benzene, furan, a heterocyclic five-membered aromatic ring with one O atom and four carbon atoms, is also able to undergo electrophilic substitution reactions under suitable conditions.

Outline the mechanism of the reaction below, clearly showing all the steps involved.



furan



[3]

[Total: 15]

Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 24 August 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

WORKED SOLUTIONS

Section A

Answer **all** the questions in this section.

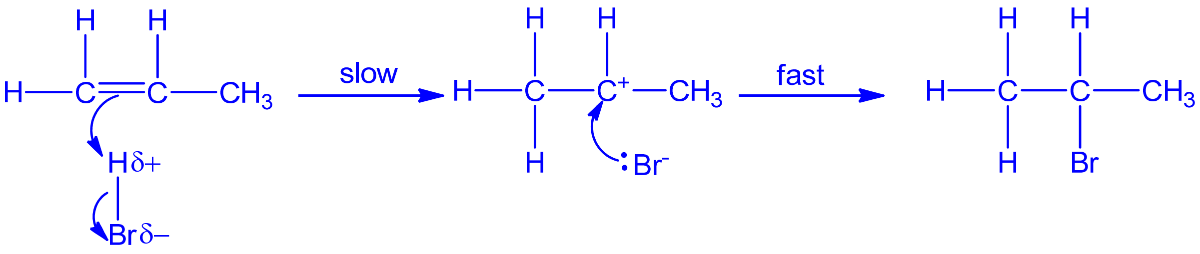
1 Propene is a colourless gas that is produced in large quantities by the petrochemical industry. It is used in the production of synthetic rubber and as a propellant in aerosols.

(a) When propene reacts with HBr, 2-bromopropane is produced as the major product.

$$CH_2{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$$

(i) Describe the mechanism of the above reaction, using curly arrows to show the movement of electrons. [4]

Electrophilic addition



Correct partial charges, lone pair of electrons, slow/fast steps

Correct curly arrows

Correct secondary carbocation intermediate

(ii) When propene reacts with BrC*l*, 1-bromo-2-chloropropane is produced as the major product.

$$CH_2{=}CHCH_3 + BrCl \rightarrow CH_2BrCHClCH_3$$

With reference to your answer in **(i)**, explain why the two reactions give major products with bromine in different positions. [2]

Br is more electronegative than H but less electronegative than C*l*, hence Br acquires a partial positive charge in BrC*l* .Thus, Br adds first to form the more stable carbocation where the positive charge is on the second carbon

(iii) The product of the reaction in **(ii)** has a chiral carbon, but it is optically inactive. Explain why this is so. [2]

There is equal chance of Cl^- attacking the trigonal planar carbon in the carbocation intermediate from either side of the plane. Thus, both enantiomers are formed in equal amounts/a racemic mixture is formed.

(b) 2-bromopropane reacts with hot aqueous sodium hydroxide, whereas 2-bromopropene does not. Suggest reasons for this difference in reactivity. [2]

In 2-bromopropene, p orbitals of Br overlap with π bond (one of the lone pairs of electrons on Br is delocalised into the C=C π bond), hence there is a partial double bond character for the C-Br bond. This makes the C-Br bond stronger and harder to break for nucleophilic substitution to occur.

The carbon of the C–Br bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks.

The electron rich C=C π bond will repel the negatively charged incoming nucleophile, hence the attack of the nucleophile will be less likely to occur.

(c) Propene can undergo mild oxidation in the presence of cold acidified potassium manganate(VII), to give $CH_2(OH)CH(OH)CH_3$.

(i) State the IUPAC name of the product of the above reaction. [1]

Propane-1,2-diol

(ii) Construct the half–equation for the oxidation of propene as described above. [1]

$CH_2{=}CHCH_3 + 2H_2O \rightarrow CH_2(OH)CH(OH)CH_3 + 2H^+ + 2e^-$

(iii) Hence, write the equation for the overall reaction, showing clearly the stoichiometry of reaction between propene and manganate(VII) ions. [1]

$5CH_2{=}CHCH_3 + 2MnO_4^- + 2H_2O + 6H^+ \rightarrow 5CH_2(OH)CH(OH)CH_3 + 2Mn^{2+}$

(d) At room temperature and pressure, 28 cm^3 of propene was bubbled into 40.0 cm^3 of 0.0200 mol dm^{-3} acidified $KMnO_4$(aq). The resulting solution was titrated against Fe^{2+}(aq) of concentration 0.0750 mol dm^{-3}.

(i) State the colour change at endpoint for this titration. [1]

Pink/red-brown to colourless/yellow

(ii) Given that 5 moles of Fe^{2+} react with 1 mole of MnO_4^-, determine the volume of Fe^{2+}(aq) needed to reach endpoint. [3]

No. of moles of propene $= \frac{28}{24000}$

$= 1.167 \times 10^{-3}$ mol

No. of moles of MnO_4^- reacted with propene $= \frac{1.167\times10^{-3}}{5} \times 2$

$= 4.667 \times 10^{-4}$ mol

No. of moles of MnO_4^- originally $= \frac{40.0}{1000} \times 0.0200$

$= 8.000 \times 10^{-4}$ mol

No. of moles of MnO_4^- left = $8.000 \times 10^{-4} - 4.667 \times 10^{-4}$

= 3.333×10^{-4} mol

No. of moles of Fe^{2+} = $3.333 \times 10^{-4} \times 5$

= 1.667×10^{-3} mol

Volume of Fe^{2+} = $\frac{1.667\times10^{-3}}{0.0750} \times 1000$

= 22.2 cm^3

(e) A mixture of propene (M_r = 42.0) and 2-bromopropane (M_r = 122.9) kept in a vessel of volume of 3.60 dm^3 maintained at 75 °C exerts a pressure of 1.66×10^5 Pa. The mole fraction of propene in the mixture is 0.28.

Find the mass of the mixture of gases. [3]

[Total: 20]

Average M_r = $0.28 \times 42.0 + (1 - 0.28) \times 122.9$

= 100.2

$pV = \frac{m}{M_r}RT$

$m = \frac{pVM_r}{RT}$

$= \frac{1.66\times10^5\times3.60\times10^{-3}\times100.2}{8.31\times(75+273)}$

= 20.7 g

2 Copper is a transition metal, and is one of the metals used to make coins, along with silver and gold. Most copper is used in electrical equipment such as wiring and motors. It also has uses in construction and industrial machinery.

(a) One of the characteristic properties of copper is its ability to form coloured aqueous complexes shown in Fig 2.1.

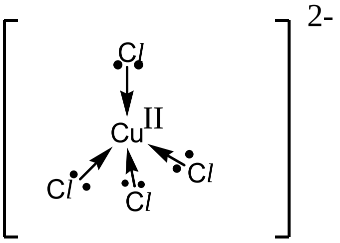
$$Cu^{2+}(aq) \xrightarrow{NH_3(aq)} \underset{\text{pale blue ppt}}{Cu(OH)_2} \xrightarrow{\text{conc HC}l} \underset{\text{yellow solution}}{\mathbf{A}} \xrightarrow{EDTA^{4-}} \underset{\text{pale blue solution}}{\mathbf{B}}$$

Fig. 2.1

(i) State the complex ion **A**. [1]

$[CuCl_4]^{2-}$

(ii) Draw the structure of complex ion **A**. [2]



(iii) EDTA^{4-} is a hexadentate ligand. Deduce the formula of the complex ion **B**. [1]

$[Cu(EDTA)]^{2-}$

(iv) Suggest why complex **B** is readily formed from complex **A**. [1]

$[Cu(EDTA)]^{2-}$ is more stable as compared to $[CuCl_4]^{2+}$, therefore Cl^- ligands will be displaced by the stronger EDTA^{4-} ligands. OR EDTA^{4-} is a stronger ligand than Cl^-.

(v) Explain why aqueous Cu^{2+} ions are blue in colour. [3]

When ligands approach/are attached/bonded to the copper ion, they will cause the incompletely/ partially-filled/3d^9 degenerate d-orbitals to split into two slightly different energy levels, d and d* [OR] two groups of non-degenerate d-orbitals with small energy gap.

When electrons from the lower lying d-orbitals absorbs energy (orange colour) in the visible light region, it will be excited to the higher energy d* orbital. This is known as d-d* electronic transition.

The complementary colours, which is not absorbed which is blue is seen/ the colour observed is complementary to the colour that is absorbed.

(vi) The numerical value of the solubility product, K_{sp} of $Cu(OH)_2$ is 2.20×10^{-20} at 25 °C. Write the expression for K_{sp} and state its units. Calculate the solubility of $Cu(OH)_2$ at 25 °C. [3]

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Cu^{2+}][OH^-]^2$

Units: $mol^3\ dm^{-9}$

Let the solubility of $Cu(OH)_2$ be x mol dm^{-3}

$K_{sp} = [Cu^{2+}][OH^-]^2 = x(2x)^2$

$2.20 \times 10^{-20} = 4x^3$

$x = 1.77 \times 10^{-7}$ mol dm^{-3}

(b) When an aqueous solution of ammonia is shaken with an organic solvent, trichloromethane, at room temperature, the following equilibrium is set up between the two immiscible liquids.

$NH_3(aq) \rightleftharpoons NH_3(organic)$ *equilibrium 1*

The equilibrium constant, K_c, for this reaction is 0.04.

Water that is contaminated with copper(II) sulfate is harmful to crops, animals and humans. Some water that has been contaminated with 0.100 mol dm^{-3} copper(II) sulfate was allowed to reach dynamic equilibrium at room temperature with an excess of ammonia and trichloromethane. The aqueous layer was found to contain 0.660 mol dm^{-3} of ammonia, some of which reacted with $Cu^{2+}(aq)$ according to the following equation

$$Cu^{2+}(aq) + nNH_3 \rightarrow [Cu(NH_3)_n]^{2+}$$

The organic layer contained 0.0104 mol dm^{-3} of ammonia.

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the forward rate of reaction is equal to the reverse rate of reaction. There is no net change in the concentrations of the reactants and the products.

(ii) Explain the relative solubility of ammonia in water and trichloromethane in terms of the intermolecular forces involved. [2]

Ammonia is able to form hydrogen bonding with water, which is much stronger than the permanent dipole-permanent dipole attractions with trichloromethane molecules. Due to the strong forces of attraction between ammonia and water molecules, ammonia is highly soluble in water.

(iii) Hence, in terms of the position of equilibrium, explain why the value of K_c for equilibrium *1* is relatively low. [1]

Therefore, the position of equilibrium lies largely to the left and K_c for this reaction is relatively low.

(iv) By calculating $[NH_3(aq)]$ present, show that the value of n in $[Cu(NH_3)_n]^{2+}$ is 4. [2]

$$0.04=\frac{[NH_3(organic)]}{[NH_3(aqueous)]}$$

$$0.04=\frac{0.0104}{[NH_3(aqueous)]}$$

$$[NH_3(aqueous)]=\frac{0.0104}{0.04}=0.26\ mol\ dm^{-3}$$

Concentration of NH_3 which reacted with $Cu^{2+}(aq)$ = 0.660 – 0.26
= 0.40 mol dm^{-3}

Mol ratio of Cu^{2+} : NH_3 = 0.100 : 0.400 = 1 : 4
n is 4.

(c) Another characteristic property of transition metal ion is its ability to catalyse reactions.

The rate of the reaction between iodide and peroxodisulfate(VI) ions

$$S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

is very slow. If a small amount of aqueous transition metal, cobalt(II) ions is added to the mixture, the rate of reaction increases.

(i) By considering relevant half equations from the *Data Booklet*, construct chemical equations to show how cobalt(II) ions behave as a catalyst in this reaction. No calculation is required. [2]

$$S_2O_8^{2-} + \underset{\text{catalyst}}{2Co^{2+}} \longrightarrow 2SO_4^{2-} + 2Co^{3+}$$

$$2Co^{3+} + 2I^- \longrightarrow I_2 + \underset{\text{catalyst regenerated}}{2Co^{2+}}$$

(ii) Suggest another transition metal ion, which will be able to catalyse this reaction. [1]

Fe^{2+}, Fe^{3+}, Mn^{3+}, Mn^{2+}, VO_2^+, VO^{2+}.

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\ominus$ = +2.01V

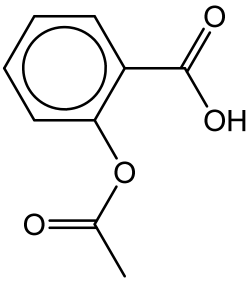
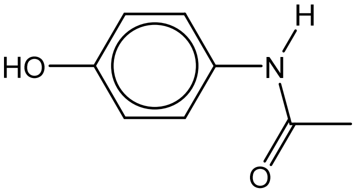
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus$ = +0.54V

(Transition metal ion redox system requires a $E^\ominus$ of between +0.54V and +2.01V.)

[Total: 20]

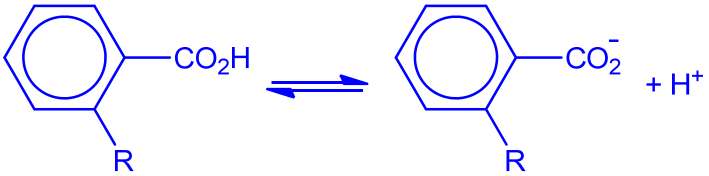
3 **(a)** Analgesics are medicines used to relieve pain. The two most common analgesics in the market are aspirin and paracetamol. Their structures and corresponding pK_a values are shown in Table 3.1.

Table 3.1

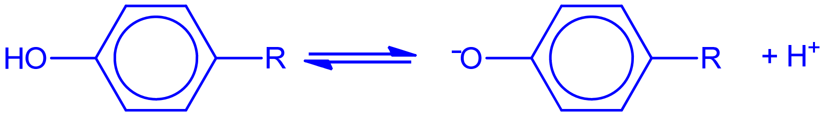
Name of analgesic	Structure	pK_a value
Aspirin		3.49
Paracetamol		10.30

(i) Explain the difference in the pK_a values between aspirin and paracetamol. [2]

Aspirin is a stronger acid than paracetamol (due to its lower pK_a value) because in the carboxylate ion of aspirin, the negative charge on oxygen atom can be delocalised to a greater extent over the C atom and both O atoms. Hence the carboxylate ion is more resonance-stabilised. Position of equilibrium lies more to the right and aspirin dissociates to a larger extent.



For the phenoxide ion of paracetamol, the negative charge is only delocalised into the benzene ring and hence is less stable. Hence position of equilibrium lies less to the right and paracetamol dissociates to a smaller extent compared to that of Aspirin.



Paracetamol can be synthesised from phenol in a 3-step process shown in Fig 3.1.

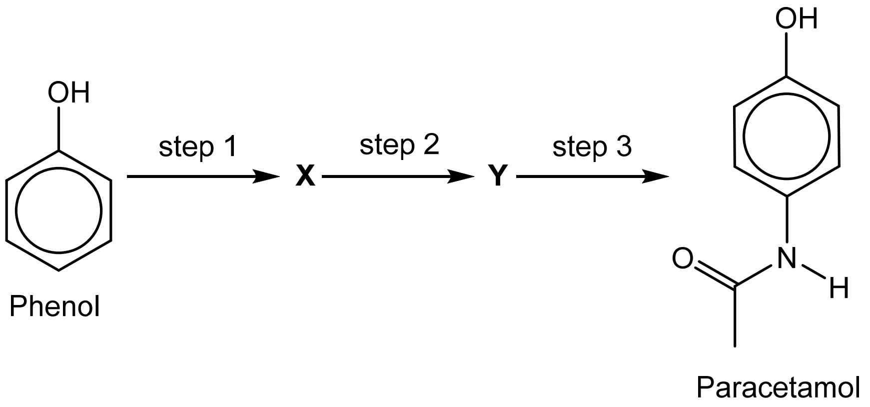
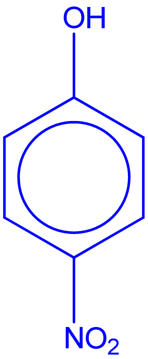
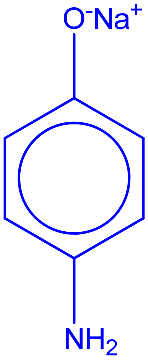


Fig. 3.1

(ii) Suggest the structures for intermediates **X** and **Y**. [2]



X



Y

(iii) Suggest the reagents and conditions required for step 1 to 3. [3]

Step 1: dilute HNO_3

Step 2: 1. Sn, conc HC*l*, heat under reflux; 2. NaOH (aq)

Step 3: CH_3COCl

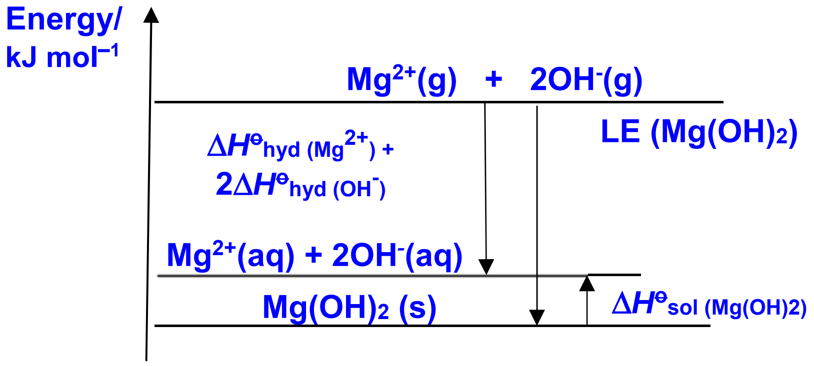
(b) The use of aspirin has been shown to increase the risk of gastrointestinal bleeding. Hence buffering agents are added to aspirin to mitigate the problem of gastrointestinal bleeding. These buffering agents work by preventing the aspirin from concentrating in the walls of the stomach. Common buffering agents used include magnesium hydroxide, $Mg(OH)_2$, and calcium carbonate, $CaCO_3$.

Some relevant standard enthalpy change of hydration values and lattice energy of $Mg(OH)_2$, are shown in Table 3.2.

Table 3.2

Enthalpy term	Value / kJ mol^{-1}
Standard enthalpy change of hydration of $Mg^{2+}(g)$	–1926
Standard enthalpy change of hydration of OH^- (g)	–460
Lattice energy of $Mg(OH)_2(s)$	–2998

Using relevant data in the table above, construct an energy level diagram to determine the standard enthalpy change of solution, $\Delta H_{sol}^\ominus$, of $Mg(OH)_2$ in water. [3]



ΔH_{sol} = – lattice energy + $\Sigma\Delta H_{hyd}$

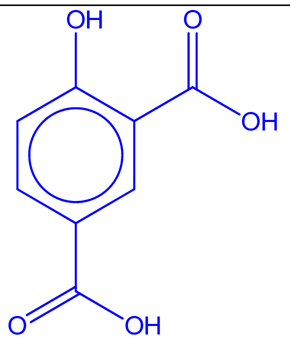
= – (-2998) + (-1926 – 2 x 460)

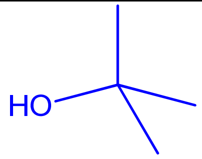
= + 152 kJ mol^{-1}

(c) Compound **A** is an unsaturated ester containing a benzene ring and has a molecular formula of $C_{16}H_{22}O_3$. **A** reacts with neutral $FeCl_3$ to give violet colouration. **A** reacts with H_2 in the presence of Ni to produce compound **B** ($C_{16}H_{24}O_3$). **B** exhibits enantiomerism whereas **A** does not.

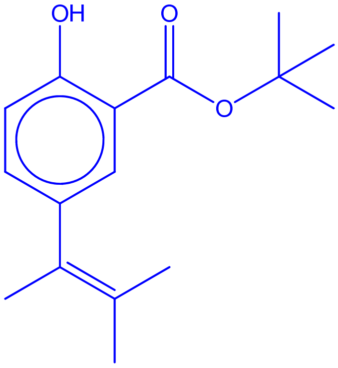
On heating with acidified $KMnO_4$, **A** gives three organic products, **C**, $C_8H_6O_5$, **D**, $C_4H_{10}O$ and propanone (CH_3COCH_3). 1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HC*l*. Effervescence is observed when a small piece of sodium metal is added to **D**.

Suggest the structures for **A** to **D** and explain the reactions described. [10]

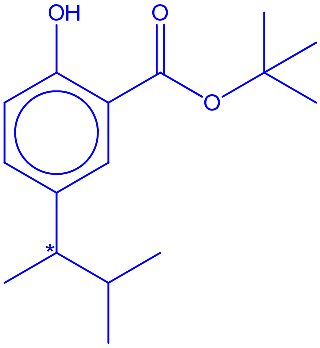
Observation/data	**Type of reaction**	**Deduction**	**Structure**
A reacts with neutral $FeCl_3$ to give violet colouration.	-	**A** is a phenol/ contains a phenolic group.	-
A reacts with H_2 in the presence of Ni to produce compound **B** ($C_{16}H_{24}O_3$).	catalytic addition/ reduction of C=C bond	**A** is likely to contain only one C=C bond since there is an addition of 2 H atoms in **B**.	-
B exhibits enantiomerism whereas **A** does not.	-	**B** contains a chiral carbon whereas **A** does not.	-
On heating with acidified $KMnO_4$, **A** gives three organic products, **C**, $C_8H_6O_5$, **D**, $C_4H_{10}O$ and propanone (CH_3COCH_3).	Acidic hydrolysis of ester, oxidative cleavage and side-chain oxidation	Hydrolysis of ester occurred to form a carboxylic acid and an alcohol. There is side chain oxidation on the benzene ring since there is loss of 1 C atom (or formation of 1 mol of CO_2).	-
1 mole of **C** reacts with excess PCl_5 to produce 2 moles of HC*l*.	Nucleophilic substitution of –OH group	**C** is likely to contain a benzene ring with 2 carboxylic acid groups and 1 phenol group.	 **C**

Effervescence is observed when a small piece sodium metal is added to **D**.	Redox reaction	**D** is likely to be <u>a tertiary alcohol</u> since it is not oxidised by acidic $KMnO_4$.	 **D**

Hence structures of **A** and **B** are



A



B

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** The decomposition of calcium and magnesium carbonates has industrial application as flame retardants due to the endothermic nature of these reactions.

(i) Write an equation showing the thermal decomposition of calcium carbonate. [1]

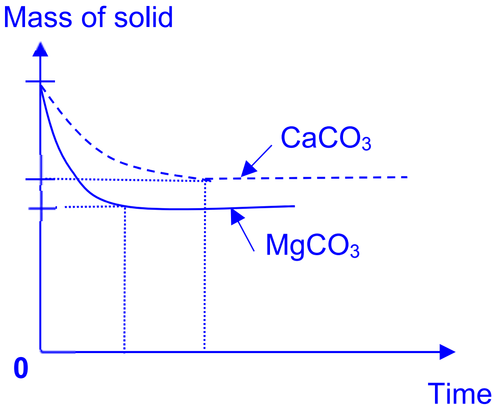
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(ii) Compare and explain the decomposition temperature of calcium and magnesium carbonates. [3]

$CaCO_3$ decomposes at a higher temperature as compared to $MgCO_3$. This is because Ca^{2+} has a larger ionic radius than Mg^{2+}, and a lower charge density. Thus Ca^{2+} polarises the carbonate ion to a lesser extent hence the C-O bonds are stronger which require higher temperature to break.

(iii) Separate samples of calcium carbonate and magnesium carbonate of the same mass, were decomposed completely under constant heating and the variation of the masses of the two samples were measured.

Sketch a graph of the mass of solid against time for the two separate samples, indicating clearly the time when decomposition was complete and the final mass for each sample. No calculations are required. [2]



(iv) Besides absorption of heat to slow down the spread of a flame, suggest another reason why $CaCO_3$ acts as a flame retardant. [1]

CO_2 released can displace the oxygen required for a combustion.

(b) One way to study reaction mechanisms is to deduce the rate equation from kinetics experiments, such as that for the redox reaction between manganate (VII) ions and ethanedioate ions.

$$2\,MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

A study of the kinetics of this reaction was carried with a suitable catalyst and with $[C_2O_4^{2-}]$ at 2.00 mol dm^{-3} and data collected are shown in Table 4.1

Table 4.1

time / min	$[MnO_4^-]$ / mol dm^{-3}
0	0.0200
3	0.0160
6	0.0128
9	0.0104
12	0.0084
15	0.0068
18	0.0056

(i) Plot the data on suitable axes, using the graph paper provided. [2]

(ii) Use your graph to determine the order of reaction with respect to $[MnO_4^-]$, showing your working clearly including construction lines on your graph. [2]

(iii) Given that the reaction is first order with respect to $[C_2O_4^{2-}]$, give the rate equation for the reaction. [1]

(iv) Determine the initial rate from the graph and use it, together with your rate equation, to calculate the rate constant for the reaction, stating its units. [2]

(v) Without the initial addition of the catalyst, the reaction is initially slow then speeds up due to autocatalyst, Mn^{2+}, produced, and finally slows down due to low concentration of reactants remaining.

Sketch a graph $[MnO_4^-]$ against time if the experiment was repeated without the initial addition of catalyst. [1]

(ii) Using half-lives,
1st half-life = 2nd half-life = 9.6 min

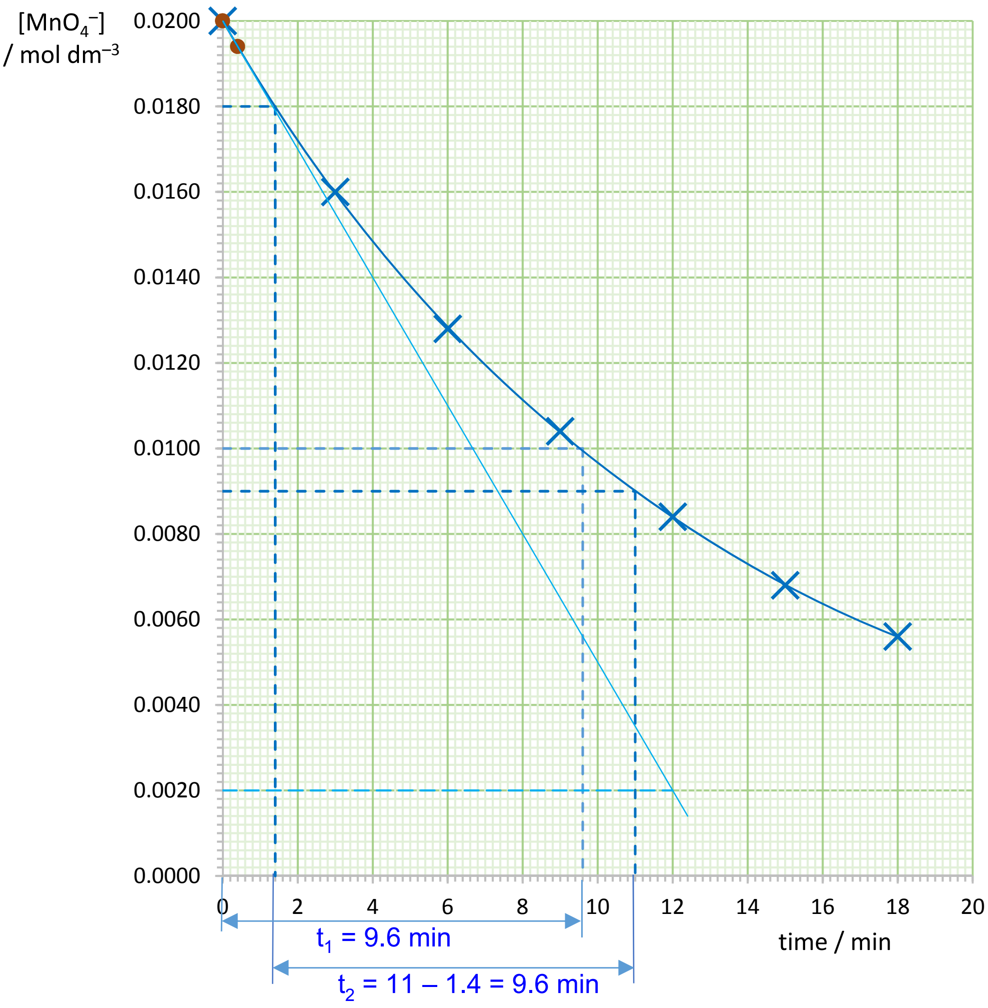
Since both half-lives are constant, the order of reaction with respect to $[MnO_4^-]$ is 1.

(iii) rate = k $[C_2O_4^{2-}]$ $[MnO_4^-]$

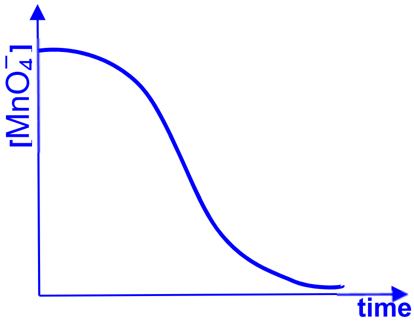
(iv) rate = $-\dfrac{0.0200-0.0020}{0-12}$

= 0.00150 mol dm^{-3} min^{-1}

k = $\dfrac{\text{rate}}{[C_2O_4^{2-}][MnO_4^-]} = \dfrac{0.00150}{2.00\ (0.0200)}$ **= 0.0375 mol^{-1} dm^{3} min^{-1}**


$[MnO_4^-]$ / mol dm^{-3}
0.0200
0.0180
0.0160
0.0140
0.0120
0.0100
0.0080
0.0060
0.0040
0.0020
0.0000
0
2
4
6
8
10
12
14
16
18
20
time / min
t_1 = 9.6 min
t_2 = 11 – 1.4 = 9.6 min

(v)


$[MnO_4^-]$
time

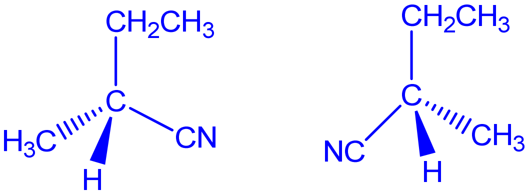
(c) Another way to study reaction mechanisms is to make deductions from the ease of obtaining the products as well as the identity of products formed.

2-bromobutane undergo nucleophilic substitution with nitrile, CN^-, relatively faster, as compared to the reaction of 2-chlorobutane with nitrile, CN^-.

(i) Under suitable conditions, an initially optically pure (only one enantiomer) sample of 2-bromobutane can undergo reaction with CN^-, and produce a mixture which is almost optically inactive.

Name the mechanism that has taken place for this, and give the structures of the products formed. [2]

Mechanism: Nucleophilic substitution reaction (S_N1)



(ii) A suitable condition for the reaction in **(i)** can be the use of neutral **polar** solvent (e.g. propanone) instead of non-polar solvents. Suggest why this is the case in consideration of the mechanism stating clearly the interactions involved. [1]

Polar solvents can help to <u>stabilise the carbocation</u> formed, due to the <u>ion-dipole interactions</u> between the carbocation and polar solvent molecules, which allows the reaction to proceed via S_N1 mechanism.

(iii) Explain why 2-chlorobutane reacts more slowly with nucleophiles, relating to the steps in the mechanism in **(i)**. Quote relevant values from the *Data Booklet* to substantiate your answer. [2]

BE (C–C*l*) = 340 kJ mol^{-1}; BE (C–Br) = 280 kJ mol^{-1}

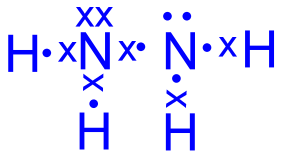
The C–C*l* bond is <u>stronger</u> than C–Br bond, and the breaking of this bond is involved in the <u>slow or rate-determining step (*required if S_N1 given in (i)*)</u>, hence the reaction is slower with 2-chlorobutane

[Total: 20]

5 (a) The decomposition of hydrazine, N_2H_4, can be used to produce H_2 gas as shown in the following reaction.

$$N_2H_4 \rightarrow 2H_2 + N_2$$

(i) Draw a dot-and-cross diagram showing the bonding in N_2H_4. [1]



(ii) Use your diagram to suggest the shape of N_2H_4 about nitrogen atom. [1]
Trigonal pyramidal

(iii) Use your diagram to suggest the bond angle about N atom in N_2H_4. [1]
107°

(i) The boiling points of hydrazine, nitrogen and ammonia are shown in Table 5.1

Table 5.1

compound	boiling point/ °C
N_2H_4	114
NH_3	–33
N_2	–196

Suggest an explanation for the difference in boiling points of these three compounds. [4]

All three compounds have simple molecular structures.

The hydrogen bonding between NH_3 molecules is stronger than the instantaneous dipole-induced dipole (id-id) attraction between N_2 molecules. Greater amount of energy required to overcome the intermolecular H-bonding in NH_3 than the intermolecular id-id in N_2. Thus, boiling point of NH_3 is higher.

The hydrogen bonding between hydrazine molecules is more extensive (2 hydrogen bonds per molecule) than between NH_3 molecules (1 hydrogen bond per molecule). Greater amount of energy required to overcome the more extensive intermolecular Hydrogen bonding in hydrazine molecules than in NH_3. Thus, boiling point of hydrazine is higher.

(b) Hydrazine can be used in a fuel cell to generate electricity. At the anode, nitrogen gas is produced from hydrazine in alkaline medium. At the cathode, oxygen gas is being supplied into water.

(i) Construct half equations for the anode and cathode reactions. [2]

Anode: $N_2H_4 + 4OH^- \rightarrow 4H_2O + N_2 + 4e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(ii) Hence, write the overall equation. [1]

$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$

(iii) The cell is capable of producing an e.m.f. of 1.56 V under standard conditions. By using suitable data from the *Data Booklet*, suggest a value of the $E^\ominus$ of the anode. [1]

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxi}$

$1.56 = +0.40 - E^\ominus_{oxi}$

$E^\ominus_{oxi} = -1.16$ V

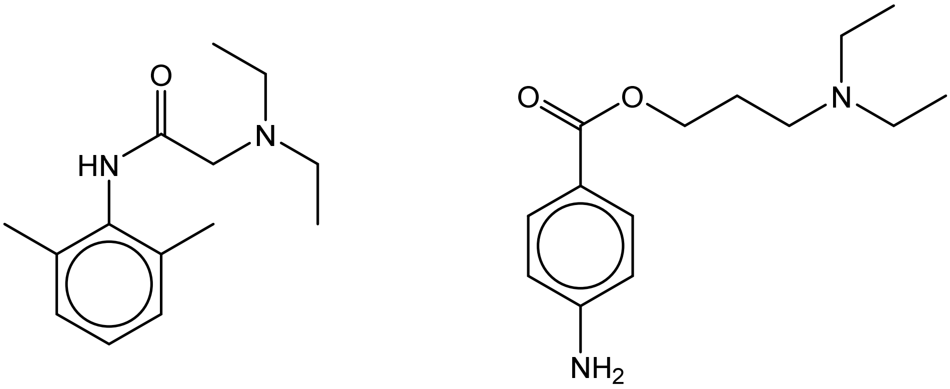
(iv) Calculate ΔG for the reaction. [1]

$\Delta G = -nFE^\ominus_{cell}$
$= -\frac{4 \times 96500 \times 1.56}{1000}$
$= -602$ kJ mol^{-1}

(v) State one possible advantage of using fuel cell compared to burning hydrocarbons in car engines. [1]

It is pollution free. (only harmless/inert gases are produced, in this case, H_2O and N_2)
It has a high power to mass ratio.
It is highly efficient.

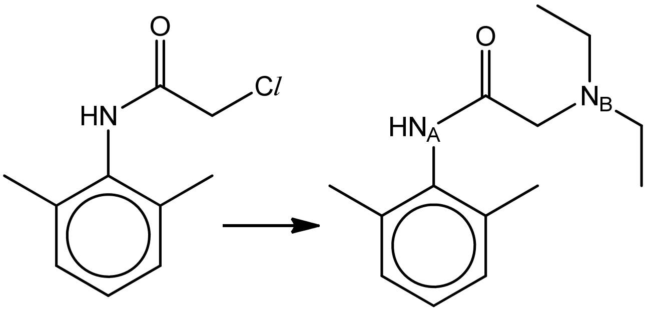
(c) Local anesthesia is used in surgeries where it is applied to numb the feelings of a specific part of a body. Lidocaine and procaine are examples of local anesthesia shown in Fig 5.1



lidocaine procaine

Fig. 5.1

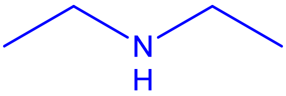
The final step of the synthesis of lidocaine is shown in Fig 5.2.



lidocaine

Fig. 5.2

(i) Suggest a reagent for the above reaction. [1]

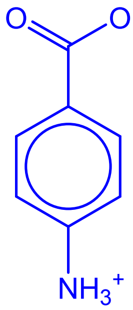


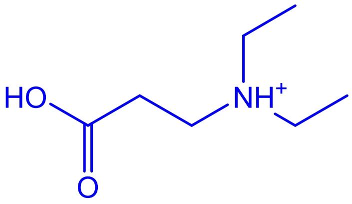
(ii) Suggest how the basicity of N_A might compare to that of N_B. Give reasons for your answers. [2]

N_A is <u>less basic</u> than N_B due to
the <u>lone pair of electrons on nitrogen atom</u> in the amide bond is being <u>delocalised into the C=O group</u>, making it less available to accept a proton.

(iii) A possible single chemical test to distinguish procaine and lidocaine involves the use of acidified potassium dichromate. Explain the chemistry involved, including any observation. Draw the structures of the products for the positive test. [3]

Hydrolysis of ester or amide bond, followed by oxidation of alcohol formed of procaine.
Orange potassium dichromate turns green with procaine.





(iv) Suggest another reagent that can also be used to distinguish between lidocaine and procaine. [1]

Aqueous bromine/ bromine in hexane

[Total: 20]

Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

Paper 4 Practical

9729/04

Thursday 16 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper

WORKED SOLUTIONS

This document consists of **14** printed pages.

[Turn over

1 **Z** is an oxidising agent. You are required to use a solution of iodine in potassium iodide to determine the mass of **Z** needed to liberate 1 mole of iodine from potassium iodide.

FA3 is an aqueous solution of iodine, I_2, in potassium iodide, KI.
FA4 is a 0.100 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3.5H_2O$.
FA5 is an aqueous solution containing 2.00 g dm^{-3} **Z**, an oxidising agent.

You are to follow the following procedure and record your results as instructed.

Titration 1

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask.
2 Titrate the iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette until the solution becomes colourless.
3 Repeat the titration as many times as you think necessary to obtain accurate results.
4 Record your results of titration in a suitable tabulated form below.

Titration of iodine in **FA3** with **FA4**

	Rough	Accurate		
Final burette reading /cm^3	**19.90**	**39.60**	**19.70**	
Initial burette reading /cm^3	**0.00**	**19.90**	**0.00**	
Volume of **FA4** used /cm^3	**19.90**	**19.70**	**19.70**	
		√	√	

Summary

25.0 cm^3 of **FA3** required **19.70** cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[5]

At least 2 sets of burette readings taken.
Burette readings recorded to 2 d.p.
Precision of V_{FA4} ± 0.10 cm^3 and correct average of V_{FA4} taken.

(a) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with 25.0 cm^3 of **FA3**.

Amount of $Na_2S_2O_3$ = $(\frac{19.70}{1000} \times 0.100)$ mol
= 1.97×10^{-3} mol
Moles of $Na_2S_2O_3$ = 1.97×10^{-3}

[1]

(b) Calculate how many moles of I_2 present in 25.0 cm^3 of **FA3** using the following equation for the reaction between iodine and thiosulfate ions.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Amount of I_2 = $(\frac{1}{2} \times 1.97 \times 10^{-3})$ mol
= 9.85×10^{-4} mol

Moles of I_2 = 1.97×10^{-3}

[1]

Titration 2

1 By using a pipette, transfer 25.0 cm^3 of **FA3,** an aqueous solution of iodine in potassium iodide, into a conical flask and then using a second pipette, add 25.0 cm^3 of **FA5**, an aqueous solution containing 2.00 g dm^{-3} of the oxidising agent, **Z**.

2 Titrate the total iodine present with **FA4**, 0.100 mol dm^{-3} aqueous sodium thiosulfate, from a burette as before until the solution becomes colourless.

3 Repeat the titration as many times as you think necessary to obtain accurate results.

4 Record your results of titration in a suitable tabulated form below.

Titration of total iodine now in **FA3** with **FA4**

	Rough	Accurate		
Final burette reading /cm^3	**29.70**	**29.50**	**29.50**	
Initial burette reading /cm^3	**0.00**	**0.00**	**0.00**	
Volume of **FA4** used /cm^3	**29.70**	**29.50**	**29.50**	
		√	√	

Summary

25.0 cm^3 of **FA3** to which 25.0 cm^3 of **FA5** had been added required **29.50** cm^3 of **FA4** for titration.

Show which results you used to obtain this value of the volume of **FA4** by placing a tick (√) under the readings used.

[3]

Precision of V_{FA4} ± 0.10 cm^3 and correct average of V_{FA4} taken.
Accuracy of titration results.

(c) Calculate how many moles of sodium thiosulfate were contained in the volume of **FA4** found necessary to react with the total iodine in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

Amount of $Na_2S_2O_3$ = ($\frac{29.50}{1000}$ x 0.100) mol
= 2.95 x 10^{-3} mol

Moles of $Na_2S_2O_3$ = 2.95 x 10^{-3}

[1]

(d) Calculate how many moles of I_2 present in the flask after 25.0 cm^3 of **FA3** and 25.0 cm^3 of **FA5** had been mixed.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq$$

Amount of I_2 = ($\frac{1}{2}$ x 2.95 x 10^{-3}) mol
= 1.475 x 10^{-3} mol

Moles of I_2 = 1.475 x 10^{-3}

[1]

(e) Calculate how many moles of I_2 were liberated from potassium iodide in the flask by 25.0 cm^3 of **FA5**.

[Turn over

Amount of I_2 liberated = $(1.475 \times 10^{-3} - 9.85 \times 10^{-4})$ mol
= 4.90×10^{-4} mol

Moles of I_2 = 4.90×10^{-3}
[2]

(f) Calculate the mass of **Z** present in 25.0 cm^3 of **FA5**.

Mass of Z = $(\frac{25.0}{1000} \times 2.00)$ g
= 0.0500 g

Mass of Z = 0.0500 g
[1]

(g) Hence, from **(e)** and **(f)**, calculate the mass of **Z** needed to liberate 1 mole of I_2.

Mass of Z needed to liberate 1 mol of I_2 = $(\frac{0.0500}{4.90 \times 10^{-4}})$ g
= 102 g

Mass of Z = 102 g
[2]

[Total: 17]

2 You are required to determine the basicity of an acid by carrying out some experiments with aqueous sodium hydroxide.

FA1 is a 1.00 mol dm^{-3} aqueous sodium hydroxide, NaOH.
FA2 is a 1.00 mol dm^{-3} aqueous acid which is either monobasic with the formula **HA**, or dibasic with the formula **H_2A**.

By using the results of the following experiments, you are to going to determine the basicity of **FA2**.

You are to follow the following procedure and record your results as instructed.

Experiment 1

1 By using a measuring cylinder, pour 25 cm^3 of **FA1** into the Styrofoam cup provided and record the steady temperature. Rinse the thermometer with deionised water.
2 Use another 50 cm^3 measuring cylinder to measure 25 cm^3 of **FA2** and record its temperature.
3 Carefully add **FA2** to **FA1**, stir with the thermometer and record the highest temperature reached.
4 Record your results in the table provided below.

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial temperature of **FA1** /°C	**31.0**	**31.0**	**31.0**
Initial temperature of **FA2** /°C	**31.0**	**31.0**	**31.0**
Highest temperature /°C	**37.9**	**35.6**	**40.1**
Mean initial temperature /°C	**31.0**	**31.0**	**31.0**
Temperature rise, ΔT /°C	**6.9**	**4.6**	**9.1**

Experiment 2
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 25 cm^3 of **FA1** and 50 cm^3 of **FA2**. Record your results in the table above.

Experiment 3
Thoroughly rinse out the Styrofoam cup with deionised water and repeat the experiment using 50 cm^3 of **FA1** and 25 cm^3 of **FA2**. Record your results in the table above.

(a) Complete the table of results by calculating the mean initial temperature of **FA1** and **FA2** for each of the three experiments. When calculating mean initial temperatures for **Experiments 2** and **3**, ignore the fact that the volumes mixed are unequal.

Fill in the corresponding rises in temperatures, ΔT in the table provided above.

[5]

Initial temperatures of FA1, FA2 & highest temperatures taken and recorded to 1 decimal place.
Correct mean initial temperatures recorded.
Correct ΔT recorded.

[Turn over

(b) Use your results to deduce the basicity of the acid.

From Expts 2 and 3 (Total volume of the reaction mixture is the same, 75 cm^3).

Expt 2: $NaOH(aq) + HA(aq) \longrightarrow NaA(aq) + H_2O(l)$
0.0250 0.0250 **0.0250 mol**

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0250 0.0125 **0.0250 mol**

Expt 3: $NaOH(aq) + HA(aq) \longrightarrow NaA(aq) + H_2O(l)$
0.0250 0.0250 **0.0250 mol**

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0500 0.0250 **0.0500 mol**

Since the rise in temperature, ΔT, is greater in Expt 3 as compared to that of Expt 2 (almost twice), FA2 is a dibasic acid, H_2A.

If the acid is monobasic, then the rise in temperature, ΔT, in Expts 2 and 3 should be the same.

[2]

(c) Write a full equation for the reaction between **FA1** and **FA2**. Do not omit spectator ions.

$$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$$

state symbols not required

[1]

(d) Calculate the amount of heat evolved in **Experiment 1**.
Assume 4.3 J are required to raise the temperature of 1 cm^3 of solution by 1.0 ^{o}C.

Heat evolved = (50 x 4.3 x 6.9) J
= 1483.5 J

Heat evolved = 1483.5 J

[1]

(e) Using your answers to **(c)** and **(d)**, calculate the enthalpy of neutralisation, ΔH_n, per mole of water formed.

$2NaOH(aq) + H_2A(aq) \longrightarrow Na_2A(aq) + 2H_2O(l)$
0.0250 0.0125 0.0250 mol

$$\Delta H_n = -\left(\frac{1483.5}{0.0250}\right) \text{ J mol}^{-1}$$

$$= -59.3 \text{ kJ mol}^{-1}$$

ΔH_n = - 59.3 kJ mol^{-1}

[1]

Assessment of Planning Skills

You are provided with 150 cm^3 of each of three solutions, **FA6**, **FA7** and **FA8**. You are to identify which of these solutions correspond to the following solutions:

1 mol dm^{-3} sodium hydroxide, NaOH
2 mol dm^{-3} hydrochloric acid, HCl
1 mol dm^{-3} hydrochloric acid, HCl

You are also provided with the following apparatus:

A thermometer
A Styrofoam cup
2 measuring cylinders

You are to plan a simple experiment which will allow an identification of the three solutions to be made, using only the apparatus and materials listed above and deionised water. (Note that you are **not** provided with any pH indicator).

You are **not** required to carry out the plan but you have to present your results in an appropriate manner based on your plan so that the identification can be made.

PLAN

1 **Using a measuring cylinder, pour 30 cm^3 of FA6 into the Styrofoam cup provided and record its temperature using the thermometer. Rinse the thermometer with deionised water.**

2 **Using another measuring cylinder to measure 30 cm^3 of FA7 and add it to FA6 in the Styrofoam cup. Stir, using the thermometer and record the highest temperature rise.**

3 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 30 cm^3 of FA8.**

4 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA7 and 30 cm^3 of FA8.**
(Refer to table 1 in results. The base, NaOH can be identified.)

5 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 15 cm^3 of FA7.**

6 **Thoroughly rinse out the Styrofoam cup with deionised water and repeat the Expt using 30 cm^3 of FA6 and 15 cm^3 of FA8.**
(Refer to table 2 in results. The acid, HC*l* of higher concentration can be identified.)

(Note: Specific volumes must be mentioned and the permutations of the respective solutions must be evident enough to allow identification possible. However, the total volume used for each of the three solutions used cannot exceed 150 cm^3 given.)

[5]

[Turn over

RESULTS

Table 1

V_{FA6} /cm^3	30	30	-
V_{FA7} /cm^3	30	-	30
V_{FA8} /cm^3	-	30	30
ΔT /^{o}C	T1	T1	No change

FA7 + FA8, no change in temperature, so they do not react with each other. So, FA7 and FA8 are both acids.

Therefore, FA6 is NaOH.

Table 2

V_{FA6} /cm^3 (base)	30	30
V_{FA7} /cm^3	15	-
V_{FA8} /cm^3	-	15
ΔT /^{o}C	T1	T2

Assume that T1 > T2.

Since the rise in temperature is higher for reaction between FA7 and the base, therefore FA7 is HC*l* of higher concentration (2 mol dm^{-3}).

$$\begin{array}{lclcll} \text{FA6} & & \text{FA7} & & & \\ \text{NaOH(aq)} & + & \text{HC}l\text{(aq)} & \longrightarrow & \text{NaC}l\text{(aq)} & + \ \text{H}_2\text{O}(l) \\ 0.0300 & & 0.0300 & & & \ \ 0.0300 \text{ mol} \end{array}$$

$$\begin{array}{lclcll} \text{FA6} & & \text{FA8} & & & \\ \text{NaOH(aq)} & + & \text{HC}l\text{(aq)} & \longrightarrow & \text{NaC}l\text{(aq)} & + \ \text{H}_2\text{O}(l) \\ 0.0150 & & 0.0150 & & & \ \ 0.0150 \text{ mol} \end{array}$$

[3]

[Total: 18]

3 You are to determine the identity of **FA9**.

Carry out the following experiments on the solid **FA9** which contains the **sodium cation** and **one anion** from the following list: CO_3^{2-}, Cl^-, Br^-, I^-, NO_3^-, NO_2^-, SO_4^{2-} and SO_3^{2-}.

In all tests, reagents should be added gradually until no further change is observed, with shaking after each addition.

Record your observations you make from them in the spaces provided.

Your answer should include
(i) details of colour change and precipitated formed, if any;
(ii) the identity of gases evolved, if any, and details of the test used to identify the gas.

You should indicate clearly at what stage in a test a change occurs.

No additional or confirmatory tests for ions present should be attempted.

Test	**Observation** [9]
(a) Place one third of the solid **FA9** in a test-tube and heat strongly until the solid melts and a gas is given off.	**FA9 melts to give a yellow liquid which then resolidifies to a give a white solid. Effervescence observed.**
Identify the gas evolved.	**Gas evolved rekindles/relights a glowing splint. O_2 liberated.**
Continue the strong heating for 2-3 minutes then leave the tube to cool and retain the residue for test (d).	**White residue.**
Melt a second sample of **FA9** and heat for 2-3 minutes. Leave this to cool and retain for test (h).	
(b) Using a dropper, place 1 cm depth of aqueous of sodium hydroxide into a test-tube and tip into it the remaining solid **FA9**.	**FA9 dissolves / no ppt.**
Warm gently and retain for test (c).	**Damp red litmus, no change. No NH_3 gas liberated.**
(c) Cool the test-tube and solution from (b).	
Add a half spatula full of aluminium powder and warm gently.	**Gas liberated turns damp red litmus blue. NH_3 gas evolved.**

[Turn over

Test	Observation
(d) Dissolve the residue from (a) in deionised water about 3 cm depth and divide the solution into three parts. Use these tests for (e) to (g).	[redacted]
(e) To one part of the solution from (d), add aqueous potassium iodide followed dilute sulfuric acid.	**Brown solution / iodine liberated.**
(f) To the second part of the solution from (d), add aqueous potassium manganate(VII) followed by dilute sulfuric acid.	**Purple acidified $KMnO_4$ is decolourised.**
(g) To the third part of the solution from (d), add aqueous sodium hydroxide and a half spatula full of aluminium powder. Warm gently.	 **Gas liberated turns damp red litmus blue. NH_3 gas evolved.**
(h) Take the second sample of solid, heated **FA9** that you prepared in (a). Add to dilute sulfuric acid and warm gently.	 **Brown fumes liberated.**

[9]

What anion is present in **FA9** before it is heated? **NO_3^-**

What anion is present in **FA9** after it is heated? **NO_2^-**

In test (e), the anion is behaving as **an oxidising agent**.

In test (f), the anion is behaving as **a reducing agent**.

[4]

Hence, write a balanced chemical equation for the thermal decomposition of **FA9**.

$$NaNO_3(s) \longrightarrow NaNO_2(s) + \frac{1}{2} O_2(g)$$

[1]

Assessment of Planning Skills

Each of the solutions **FA10**, **FA11** and **FA12** contains one of the cations Al^{3+}, Mg^{2+} and Zn^{2+} ions but not in that order.

You are provided with a set of test-tubes and the following reagents:

Aqueous ammonia, NH_3
Dilute hydrochloric acid, HCl
Aqueous sodium carbonate, Na_2CO_3
Aqueous sodium hydroxide, NaOH

You are required to devise and perform an experiment which will enable you to identify the cation present in each of the solutions **FA10**, **FA11** and **FA12**. You may only use any of the reagents provided above and **no** other reagent. **You should aim to use the minimum number of reactions**, where possible.

This space below is for you to plan your steps which should then be recorded, together with the observations you make in the table in the next page.

PLAN

1 **Add aqueous ammonia, NH_3 till excess to separate samples of the 3 solutions. If a white ppt is obtained and dissolves in excess NH_3, suggests the presence of Zn^{2+}.**

2 **Add aqueous sodium hydroxide, NaOH till excess to separate samples of the remaining 2 solutions.**

If a white ppt is obtained and dissolves in excess NaOH, suggests the presence of Al^{3+}, if insoluble in excess NaOH, Mg^{2+}.

[2]

In the table below, record all of your observations, and the identity of a cation as soon as this is established.

Reagent added	Observations and identities of cations		
	FA10	**FA11**	**FA12**
NH_3(aq)	**White ppt soluble in excess.** **Zn^{2+}**	**-**	**-**
NaOH(aq)	**-**	**White ppt soluble in excess.** **Al^{3+}**	**White ppt insoluble in excess.** **Mg^{2+}**

[3]

[Turn over

Deduction

Solution **FA10** contains the cation **Zn^{2+}**

Solution **FA11** contains the cation **Al^{3+}**

Solution **FA12** contains the cation **Mg^{2+}**

[1]

[Total: 20]

Qualitative Analysis Notes

[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn over

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

24 September 2018

1 hour

Additional Materials:	Data Booklet Optical Mark Sheet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this question paper and the OTAS Mark Sheet.

2 There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Mark Sheet.

3 Each correct answer will score one mark. A mark will not be deducted for wrong answer.

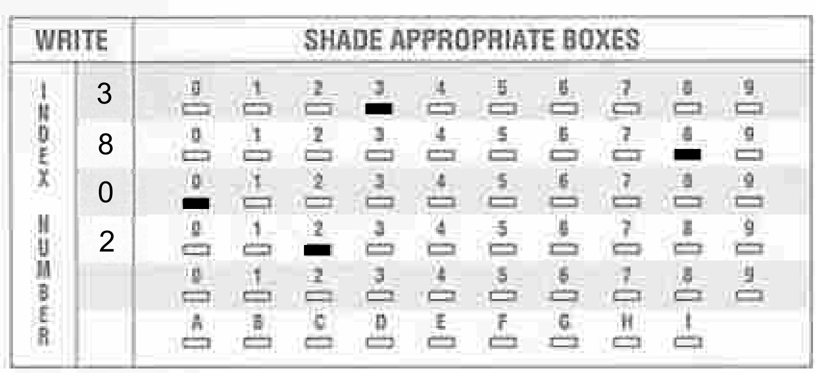
4 Any rough working should be done in this booklet.

5 The use of an approved scientific calculator is expected, where appropriate.

6 On the OTAS Mark Sheet, please shade the code as “Class/Index number”.

For illustration only:

A student from class 6C38, with index number 02, should shade “3802”.



This question paper consists of **15** printed pages and **1** blank page.

1 Which option contains one mole of the stated particles?
[D = $^{2}_{1}H$]

A carbonate ions in 60 g of sodium carbonate

B neutrons in 1.8 g of heavy water, D_2O

C electrons in 0.1 mol of OH^- ions

D oxygen atoms in 11.35 dm^3 of O_3, under s.t.p.

2 NF_3 can be obtained from the reaction between ammonia and fluorine gas.

$$4NH_3 + 3F_2 \rightarrow NF_3 + 3NH_4F$$

Which statement about the reaction is correct?

A NH_3 undergoes disproportionation.

B The oxidation number of nitrogen in NF_3 is +3.

C NH_3 is a stronger oxidising agent than F_2.

D One mole of F_2 loses two moles of electrons.

3 *Use of the Data Booklet is relevant to this question.*

Which statement regarding $^{26}Mg^{2+}$ and $^{27}Al^{3+}$ ions is true?

1 $^{26}Mg^{2+}$ has more protons than $^{27}Al^{3+}$.

2 Both ions have more neutrons than protons in their nuclei.

3 Both ions have outer electronic configuration $2s^22p^6$.

4 Both ions have the same number of neutrons.

A 1 and 2 only

B 1 and 3 only

C 3 and 4 only

D 2, 3 and 4 only

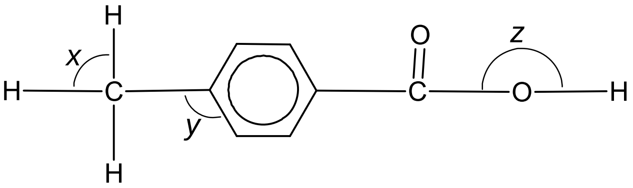
4 Two ideal gases **X** and **Y** were placed separately into two bulbs of the same volume and pressure. The density of gas **X** is three times that of gas **Y** and the molecular mass of gas **X** is twice that of gas **Y**.

What is the ratio of the temperature (in Kelvin) of gas **X** to that of gas **Y** in the two separate bulbs?

A 1 : 3 **B** 1 : 6

C 2 : 3 **D** 3 : 2

5 A compound has the structure shown.



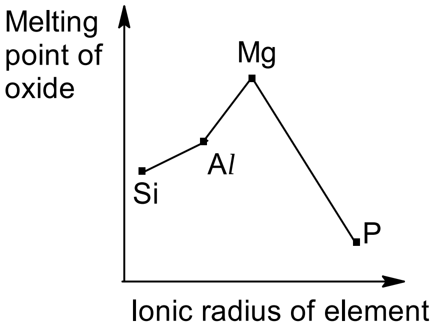
What are the values of the bond angles *x*, *y* and *z*?

	x	*y*	*z*
A	90°	109.5°	104.5°
B	90°	120°	180°
C	109.5°	109.5°	180°
D	109.5°	120°	104.5°

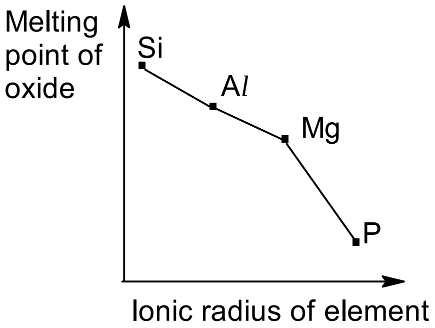
6 *Use of the Data Booklet is relevant to this question.*

Which graph shows the correct trend when the melting point of the oxide of each of the elements Mg, A*l*, Si and P is plotted against its ionic radius?

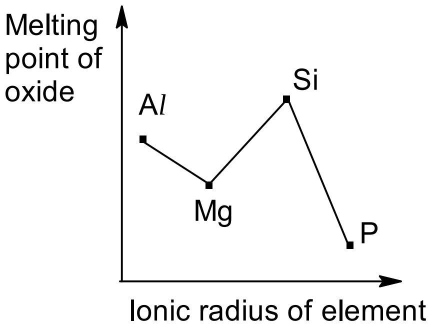
A



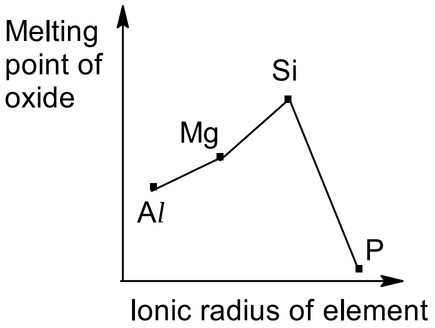
B



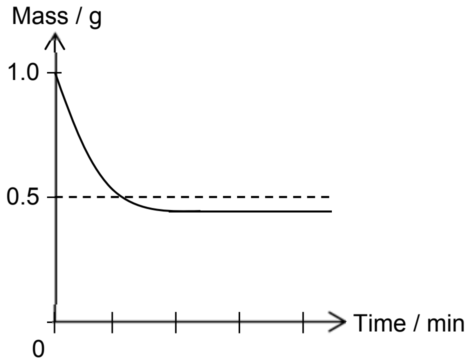
C



D

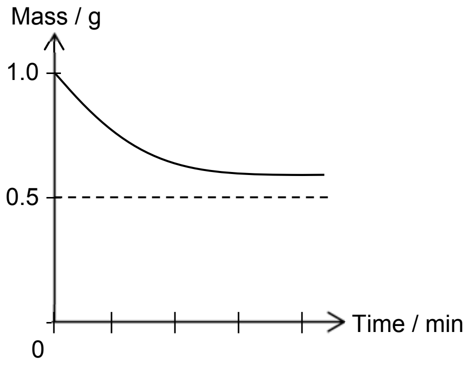


7 The graph represents the change in mass that occurs when 1.0 g of powdered magnesium carbonate, $MgCO_3$, is heated at a temperature, T.

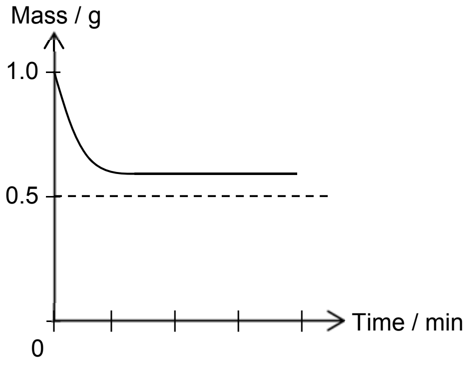


Which graph would be obtained by heating 1.0 g of powdered calcium carbonate, $CaCO_3$, at the same temperature, T?

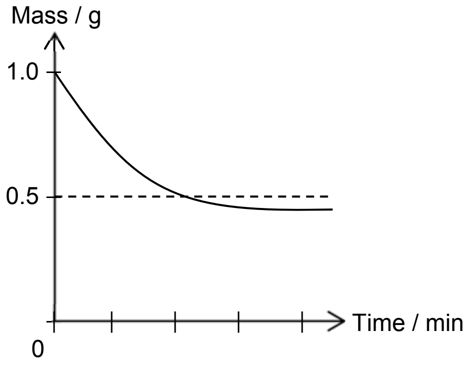
A



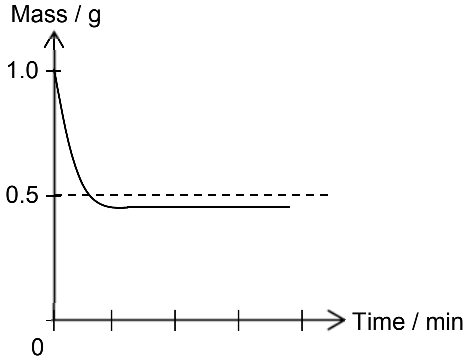
B



C



D



8 **X_2**, **Y_2** and **Z_2** are Cl_2, Br_2 and I_2 but are not necessarily in the given order.

The table below recorded observations when these halogens are separately added to aqueous solutions containing the halide ions followed by the addition of an organic solvent, CCl_4.

Experiment	Reactants	Observation after shaking with CCl_4
1	$\mathbf{X_2}$ (aq) + $\mathbf{Y}^-$ (aq)	Violet organic layer seen.
2	$\mathbf{Y_2}$ (aq) + $\mathbf{X}^-$ (aq)	*(Observations not recorded)*
3	$\mathbf{Z_2}$ (aq) + $\mathbf{X}^-$ (aq)	Orange-red organic layer seen.
4	$\mathbf{Z_2}$ (aq) + $\mathbf{Y}^-$ (aq)	Violet organic layer seen.

Which statement could be deduced from the above experiments, given **X_2** (aq) is an orange solution?

A The colour of the organic layer in Experiments 2 and 4 is the same.

B Identity of **Z_2** is Br_2.

C There is no redox reaction occurring in Experiment 3.

D **X_2** is a stronger oxidising agent than **Z_2**.

9 For which process is the enthalpy change always negative?

A Dissolving an ionic solid in water.

B Reaction between an acid and a base.

C Forming gaseous atoms from a diatomic molecule.

D Synthesising a compound from its elements.

10 A rock sample was found to contain isotopes **T** and **U** which are radioactive. Initially, the ratio of the number of atoms of **T** to **U** in the rock sample is 1 : 16. The decay of isotopes **T** and **U** was found to follow first order kinetics. The half–life of **T** is 12 days while that of **U** is 3 days.

How long, in days, will it take for a rock sample to contain a molar ratio of **T** to **U** of 4 : 1?

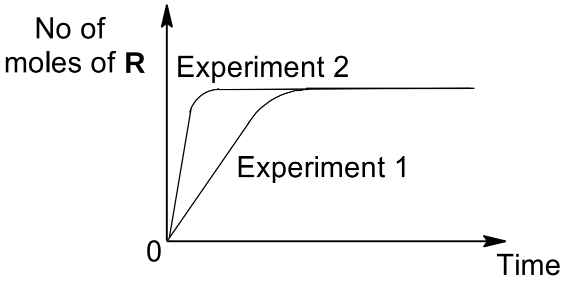
A 6 **B** 12

C 18 **D** 24

11 The stoichiometry of a reaction is shown by the equation below.

$$\mathbf{L}(g) + \mathbf{M}(g) \rightleftharpoons \mathbf{Q}(g) + \mathbf{R}(g) \qquad \Delta H = -20 \text{ kJ mol}^{-1}$$

Two experiments were carried out in enclosed vessels which the rate of production of **R** was measured. The results are shown in the diagram below.



Which changes in the conditions might explain the results shown?

1 Temperature of the vessel is higher in Experiment 2.
2 A smaller vessel is used in Experiment 2.
3 A catalyst is used in Experiment 2.

A 1, 2 and 3
B 1 and 2 only
C 2 and 3 only
D 1 only

12 In which reaction is the first reactant **not** acting as a Bronsted-Lowry base?

A $\underline{NH_3} + CH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$
B $\underline{OH^-} + HSO_4^- \rightarrow H_2O + SO_4^{2-}$
C $\underline{CH_3OH} + HClO_4 \rightarrow CH_3OH_2^+ + ClO_4^-$
D $\underline{HNO_3} + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$

13 The solubility products of calcium fluoride and calcium carbonate are 4.0×10^{-11} mol^3 dm^{-9} and 8.7×10^{-9} mol^2 dm^{-6} at 25 °C respectively.

Which statement is correct?

1 When calcium nitrate is added into a 1 dm^3 solution containing 0.01 mol of fluoride and 0.01 mol of carbonate ions in order to separate fluoride and carbonate ions, calcium fluoride is collected as the filtrate upon filtration.

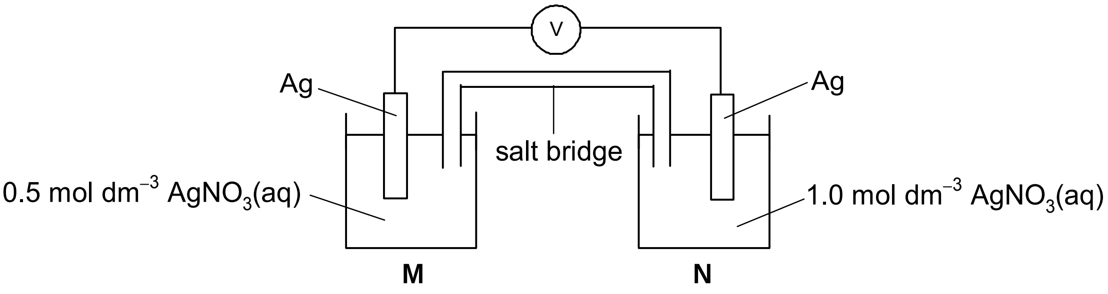
2 Calcium fluoride has a lower molar solubility than calcium carbonate.

3 Addition of sodium fluoride to a saturated solution containing calcium fluoride does not change the solubility product of calcium fluoride.

A 1, 2 and 3 only **B** 2 and 3 only

C 1 and 3 only **D** 3 only

14 A concentration cell set up is shown below. The net effect of a concentration cell is the same as mixing the two solutions of different concentrations until concentration equilibrium is established.



Which statement is true?

A The E_{cell} value decreases when small amount of NH_3 (aq) is added to the half-cell **M**.

B The E_{cell} value increases when small amount of KC*l* (s) is added to the half-cell **N**.

C The electrons flow from half-cell **N** to **M**.

D **M** is the oxidation half-cell.

15 A current of 5 amperes was passed for 5 seconds through a molten salt containing X^{3+} ions. The mass of X deposited was 5 g. If M is the relative molecular mass of X and e is the electronic charge, then an expression of Avogadro Constant is given by

A $\frac{5M}{3e}$ **B** $\frac{125}{3Me}$

C $\frac{3e}{5M}$ **D** $\frac{3Me}{125}$

16 The table shows the electronic configuration of three d–block elements in the Periodic Table.

Element	**Electronic configuration**
X	[Ar]$3d^7 4s^2$
Y	[Ar]$3d^8 4s^2$
Z	[Ar]$3d^{10} 4s^1$

Which statement is correct?

1 The electronic configuration of central metal ion for [**Y**$(CN)_6]^{4-}$ is [Ar]$3d^7$.

2 Upon reduction from **Z**Cl_2(aq) to [**Z**$Cl_2]^-$(aq), a colourless solution will be formed.

3 The $E^\ominus$ value of $\mathbf{X}^{3+}/\mathbf{X}^{2+}$ is likely to be less positive than that of $\mathbf{Z}^{3+}/\mathbf{Z}^{2+}$.

4 **X** is likely to form an oxoanion of formula $\mathbf{X}O_4^{2-}$.

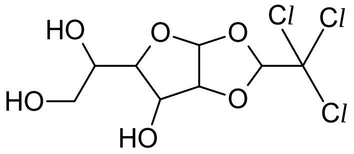
A 1, 2 and 4 only

B 2 and 3 only

C 1 and 4 only

D 3 and 4 only

17 Chloralose is a drug that is commonly used in neuroscience and veterninary medicine as an anesthetic.



chloralose

How many stereoisomers does chloralose have?

A 16

B 32

C 64

D 128

18 2,2–dimethylpropane reacts with chlorine gas in the presence of ultraviolet light to give a mixture of products.

Which statement regarding this reaction is correct?

A Only one mono-substituted product is formed.

B Only the propagation step involves C–C*l* bond formation.

C Both propagation and termination steps produce hydrogen chloride.

D Only the initiation step of the mechanism involves homolytic fission.

19 Compound **Z** can be obtained by a two-step process involving intermediate **X**.

$$HOOCCH{=}CHCOOH \xrightarrow{\textbf{step 1}} \textbf{X} \xrightarrow{\textbf{step 2}} \underset{\textbf{Z}}{HOOCCOCH_2COOH}$$

What is the identity of intermediate **X**?

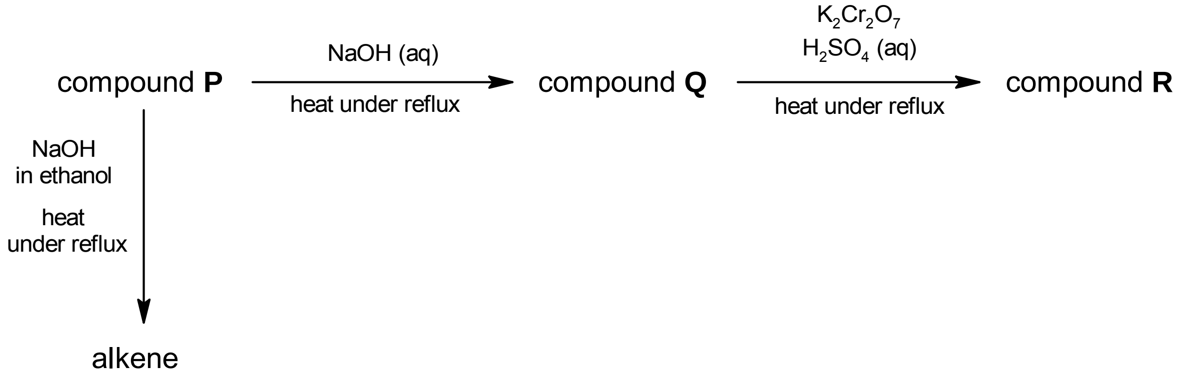
A $HOOCCH_2CH_2COOH$

B $HOOCCHBrCH_2COOH$

C $HOOCCH(OH)CH_2COOH$

D $HOOCCH(OH)CH_2OH$

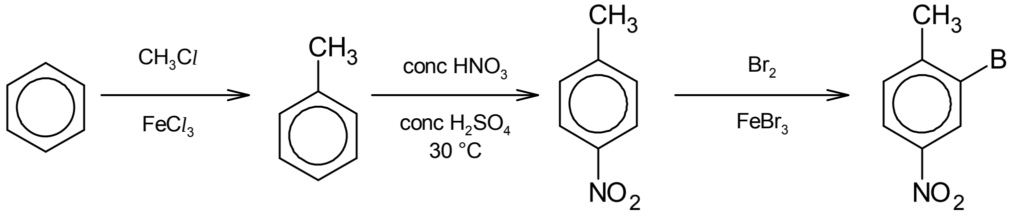
20 The flow chart below shows a series of reactions.

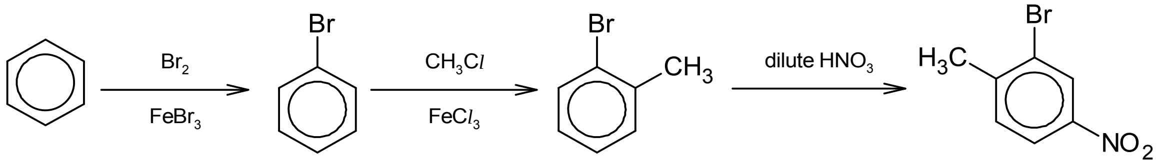


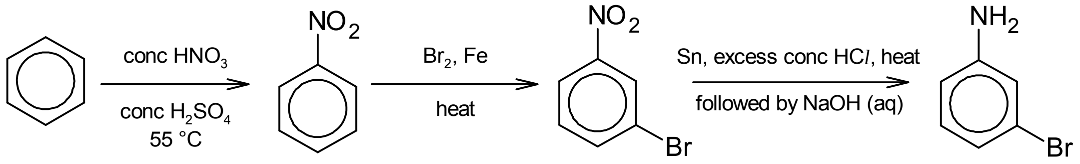
Which class of compound are **P**, **Q** and **R**?

	P	**Q**	**R**
A	halogenoalkane	primary alcohol	carboxylic acid
B	halogenoalkane	primary alcohol	aldehyde
C	primary alcohol	aldehyde	carboxylic acid
D	primary alcohol	halogenoalkane	aldehyde

21 Which of the following synthetic routes is correct?

1


2


3


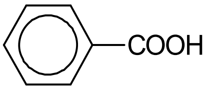
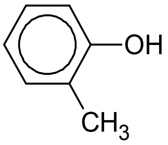
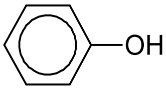
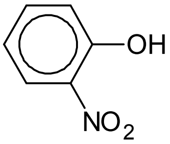
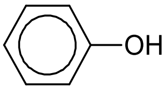
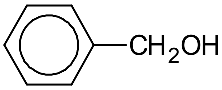
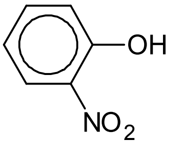
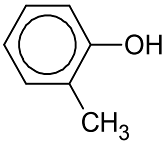
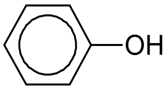
A 1 only

B 1 and 2 only

C 2 and 3 only

D 1 and 3 only

22 Which row shows the given molecules arranged in order of increasing pK_a values?

	smallest pK_a value	→	largest pK_a value
A			
B			
C	CF_3CH_2OH	$HCOOH$	CH_3OH
D			

23 Which reagent is able to distinguish between the two compounds below?

$CH_3CH(OH)CH(OH)CH_3$ $HOCH_2CH_2OCOCH_3$

A Hot alkaline I_2(aq) **B** Hot acidified $K_2Cr_2O_7$(aq)

C 2,4-DNPH **D** Neutral aqueous $FeCl_3$

24 Which products are formed when butanal reacts with Fehling's solution?

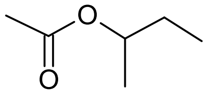
A Cu_2O and $CH_3CH_2COO^-$

B Cu_2O and $CH_3CH_2CH_2CH_2OH$

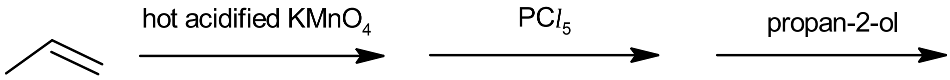
C Cu_2O and $CH_3CH_2CH_2COO^-$

D CuO and $CH_3CH_2CH_2COO^-$

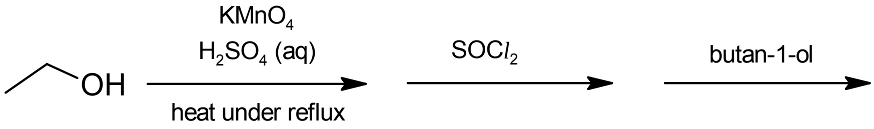
25 Which synthetic route will give the following ester as the product?



A



B

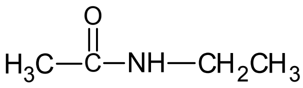


C

D

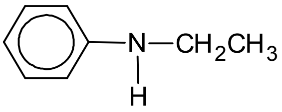
$$CH_3Br \xrightarrow[\text{heat under reflux}]{\text{KCN in ethanol}} \xrightarrow[\text{heat under reflux}]{H_2SO_4\text{ (aq)}} \xrightarrow[\text{heat under reflux}]{\substack{\text{butan-2-ol} \\ \text{conc } H_2SO_4}}$$

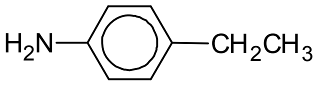
26 Which compound has the lowest pK_b value?

A 

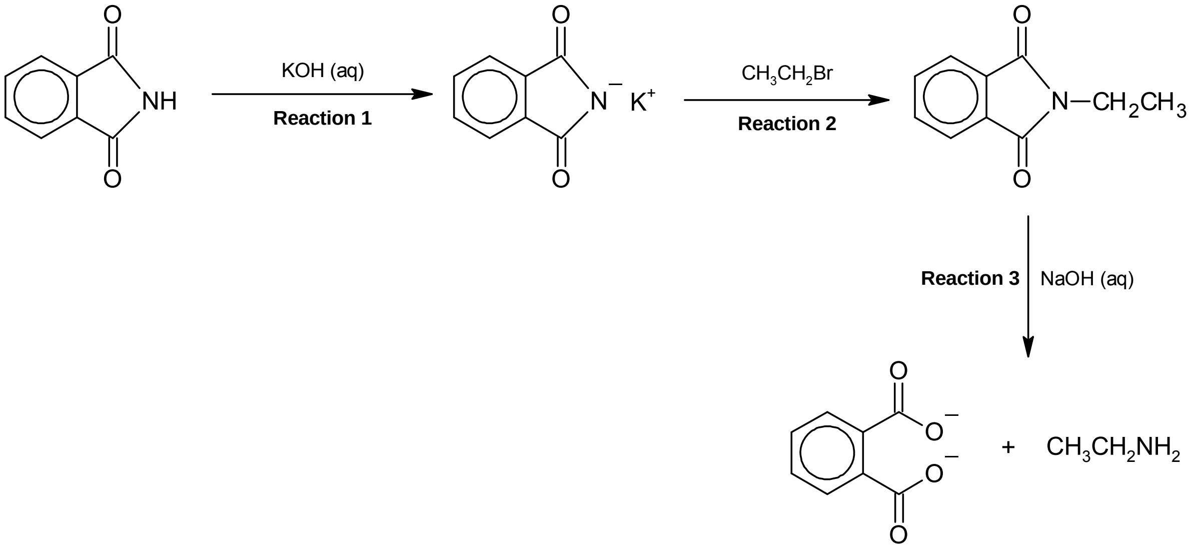
$H_3C-\overset{\overset{O}{\parallel}}{C}-NH-CH_2CH_3$

B $(CH_3CH_2)_2NH$

C 

D 

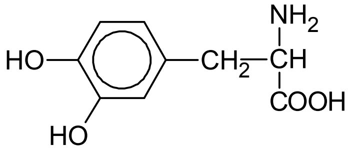
27 The diagram below shows a sequence of reactions.



How can the three reactions be classified?

	Reaction 1	**Reaction 2**	**Reaction 3**
A	hydrolysis	substitution	acid–base
B	hydrolysis	addition	acid–base
C	acid–base	substitution	hydrolysis
D	acid–base	addition	hydrolysis

28 The molecule shown is used in the treatment of Parkinson's disease.



Which statement about the molecule is correct?

1 It is likely to be soluble in water due to zwitterion formation.

2 Two Br atoms will be incorporated when aqueous bromine is added.

3 One mole of molecule reacts with three moles of sodium carbonate to form a salt.

A	1 only	**B**	1 and 2 only
C	1 and 3 only	**D**	1, 2 and 3 only

29 Nucleophilic substitution of 2–chloro–2–methylpropane follows an S_N1 mechanism.

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

S_N1 reactions take place more rapidly in polar solvents.

Which solvent should be used?

1 water

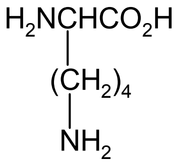
2 hexane

3 ethanol

4 tetrachloromethane

A	1 and 2 only	**B**	1 and 3 only
C	1, 2 and 4 only	**D**	1, 3 and 4 only

30 Lysine is an amino acid.

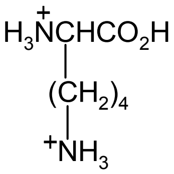


$$\begin{array}{c} H_2NCHCO_2H \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

lysine

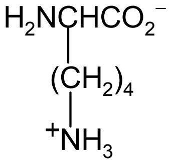
Which structure is predominant when lysine is in aqueous solution at pH 5?

A



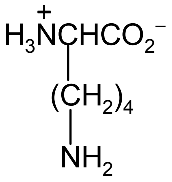
$$\begin{array}{c} H_3\overset{+}{N}CHCO_2H \\ | \\ (CH_2)_4 \\ | \\ {}^{+}NH_3 \end{array}$$

B



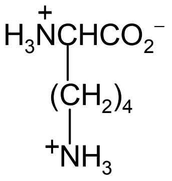
$$\begin{array}{c} H_2NCHCO_2^{-} \\ | \\ (CH_2)_4 \\ | \\ {}^{+}NH_3 \end{array}$$

C



$$\begin{array}{c} H_3\overset{+}{N}CHCO_2^{-} \\ | \\ (CH_2)_4 \\ | \\ NH_2 \end{array}$$

D



$$\begin{array}{c} H_3\overset{+}{N}CHCO_2^{-} \\ | \\ (CH_2)_4 \\ | \\ {}^{+}NH_3 \end{array}$$

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2018 DHS YEAR 6 H2 CHEMISTRY (9729) Preliminary Examination
Paper 1 MCQ – Answers

1	2	3	4	5	6	7	8	9	10
C	**B**	**D**	**C**	**D**	**A**	**A**	**A**	**B**	**D**

11	12	13	14	15	16	17	18	19	20
C	**A**	**D**	**D**	**A**	**B**	**C**	**A**	**C**	**A**

21	22	23	24	25	26	27	28	29	30
D	**B**	**A**	**C**	**D**	**B**	**C**	**A**	**B**	**D**

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write in dark blue or black pen.

3 You may use an HB pencil for any diagrams or graphs.

4 Do not use staples, paper clips, glue or correction fluid.

5 Answer **all** questions in the spaces provided on the Question Paper.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

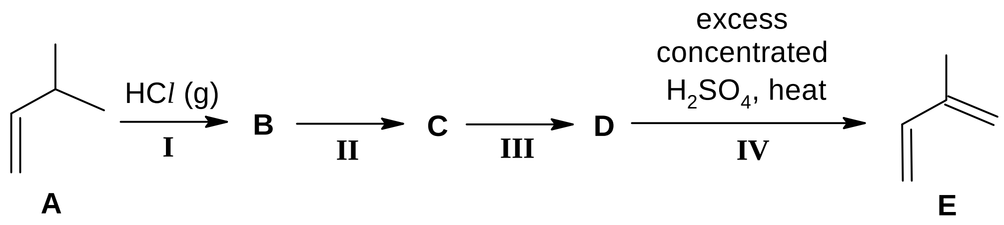
For Examiner's Use	
Question No.	**Marks**
1	**13**
2	**12**
3	**25**
4	**10**
5	**15**
Total	**75**

This question paper consists of **21** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

(a) **E** can be synthesised from 3–methylbut–1–ene, **A**, in a 4–step process as follows.



(i) **B** is a major product of step **I**.

Draw the structures of compounds **B**, **C** and **D**.

B **C** **D**

[3]

(ii) Suggest the reagents and conditions for steps **II** and **III**.

step **II** : ……………………………………………………………………………….[1]

step **III** : …………………………………………………………………………….[1]

(iii) Predict, with reasoning, whether the mixture of products formed in step **I** is optically active.

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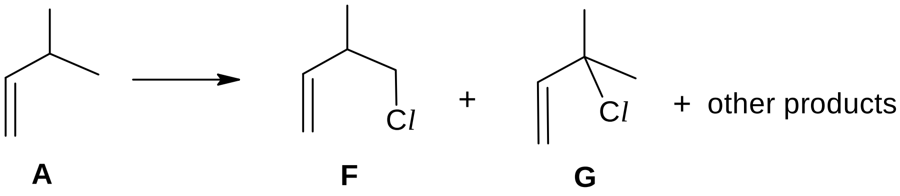
(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



(i) State the reagents and conditions used to form **F** and **G** from **A**.

…………………………………………………………………………………………[1]

(ii) Predict the ratio in which **F** and **G** will be formed.

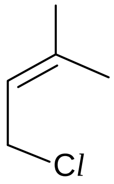
…………………………………………………………………………………………[1]

(iii) **Z** was one of the other products formed in the reaction in **(b)**. It was suggested that the radical, •**G**, is involved in the formation of **Z**.

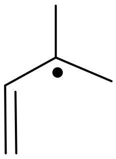
The mechanism of •**G** converting to **Z** is thought to involve 2 steps.

1. Delocalisation of unpaired electron forming •**Z**.
2. •**Z** reacts with Cl_2 to form **Z** and a radical.

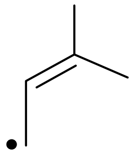
The structures of **Z**, •**G** and •**Z** are as follows.



Z



•G



•Z

Use the information above to draw out the mechanism for the conversion of •**G** to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). Use curly half-arrows to indicate the movement of unpaired electrons.

[2]

(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

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[Total: 13]

2 **(a)** Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (**J** to **R**) in Periods 2 and 3 of the Periodic Table.

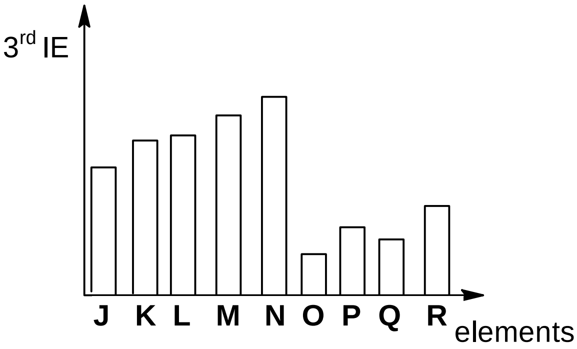

Fig 2.1

(i) Write an equation for the third ionisation energy of element **J**.

…………………………………………………………………………………….[1]

(ii) Identify element **N**.

…………………………………………………………………………………….[1]

(iii) Using your answers in **(a)(i)**, **(a)(ii)** and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3rd IE of **N** compared to **O**.

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2. The lower 3rd IE of **Q** than **P**.

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…………………………………………………………………………………….[2]

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.

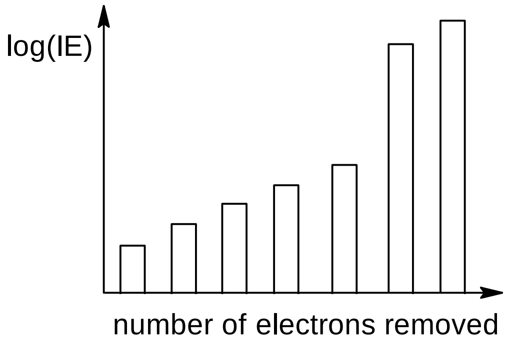

Fig 2.2

(i) Explain the general trend shown in Fig 2.2.

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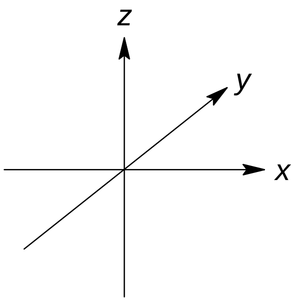
……………………………………………………………………………………………[2]

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.



[1]

(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2.

……………………………………………………………………………………………[1]

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

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……………………………………………………………………………………………[2]

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) **(i)** State what is meant by the terms:

- *Complex*

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

- *Ligand*

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

(ii) Two of the complexes formed by copper are $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$ and $CuCl_4^{2-}$. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$	$CuCl_4^{2-}$
Shape:	Shape:

[3]

(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

…………………………………………………………………………………………[1]

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.

isomer 1	isomer 2

[3]

By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: ……………………………………………………………….[1]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic configuration of these species.

Cu: [Ar]……………………[1]

Cu(I): [Ar]……………………[1]

(ii) Explain why the following statements are true.

- Copper metal is a better electrical conductor than calcium metal.
- Copper(II) salts are generally coloured.

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……………………………………………………………………………….[3]

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the $\Delta H_f^\ominus$ values for some compounds.

Compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
Cu_2O (s)	–168.6
CuO (s)	–157.3
$Cu(NO_3)_2$ (s)	–302.9
NO_2 (g)	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable $\Delta H_f^\ominus$ values from the table to calculate the $\Delta H_r^\ominus$ for this reaction.

$$Cu(NO_3)_2\text{ (s)} \rightarrow CuO\text{ (s)} + 2NO_2\text{ (g)} + \tfrac{1}{2}O_2\text{(g)}$$

[1]

(ii) Copper(I) oxide can be produced from copper(II) oxide.

$$2CuO\text{ (s)} \rightleftharpoons Cu_2O\text{ (s)} + \tfrac{1}{2}O_2\text{(g)} \qquad \text{reaction 1}$$

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

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……………………………………………………………………………………[2]

(iii) For reaction 1, $\Delta S^\ominus$ = +93.6 J K^{-1} mol^{-1}. Use this value and your answer in **(c)(ii)** to calculate $\Delta G^\ominus$.

[1]

(iv) Write the expression of the equilibrium constant, K_c, for reaction 1. State the units.

[2]

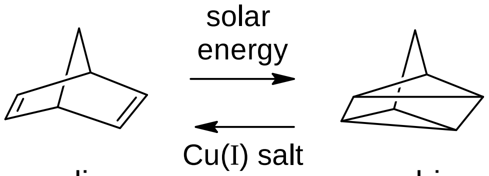
(v) For any reaction, $\Delta G^\ominus$ and the equilibrium constant, K_c, are related according to the equation,

$$\Delta G^\ominus = -2.303RT \log K_c$$

Use this equation to calculate a value of K_c for reaction 1.

[1]

(d) In 1977, Kutal *et al*. conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



norbornadiene quadricyclene

In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

…………………………………………………………………………………………[1]

(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

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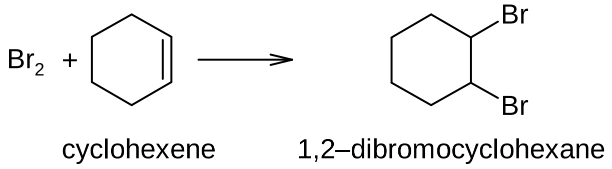
…………………………………………………………………………………………[2]

[Total: 25]

4 **(a)** Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



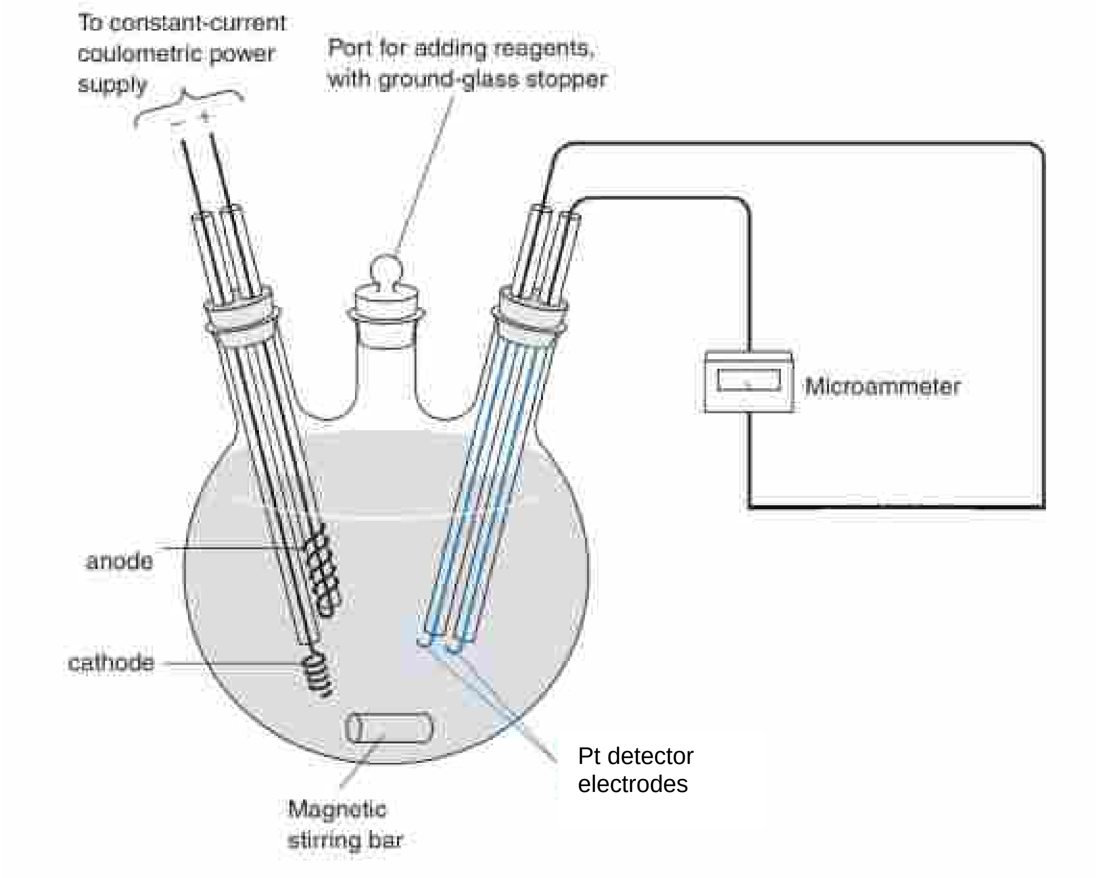
An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^- dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left–hand and right–hand sides respectively.



Br_2 generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

(i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell.

……………………………………………………………………………………….[1]

(ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

$$\text{Detector anode: } 2Br^- \rightarrow Br_2 + 2e^-$$

$$\text{Detector cathode: } Br_2 + 2e^- \rightarrow 2Br^-$$

Suggest why there is no current detected before equivalence point is reached.

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……………………………………………………………………………………………[1]

In an experiment, 2 cm^3 of 0.600×10^{-3} g cm^{-3} cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used.

[1]

(iv) The experiment was carried out with a constant current of 5×10^{-3} A for the electrolytic cell. Determine the time taken for complete titration.

[2]

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$$E = 0.32 + 0.029 \log_{10} [I_2]\text{, where } [I_2] \text{ is expressed in mol dm}^{-3}.$$

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

[1]

(ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

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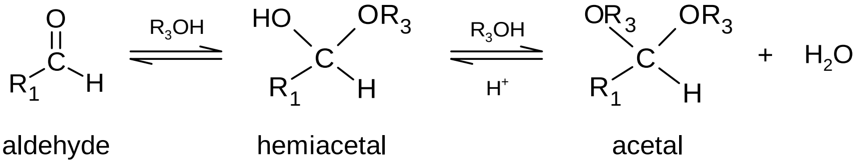
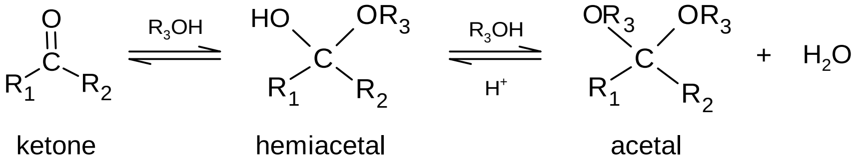
…………………………………………………………………………………………………[2]

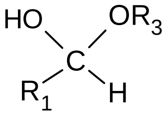
[Total: 10]

5 **(a)** Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



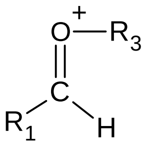


The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



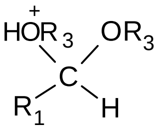
hemiacetal

1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

3. Nucleophilic attack of alcohol, R_3OH, on the oxonium ion to give



4. Loss of a proton to give the acetal.

(i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

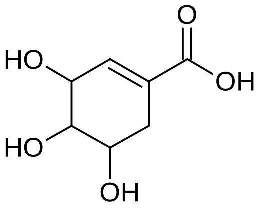
(ii) State the purpose of removing water from the reaction mixture.

……………………………………………………………………………………….

……………………………………………………………………………………….

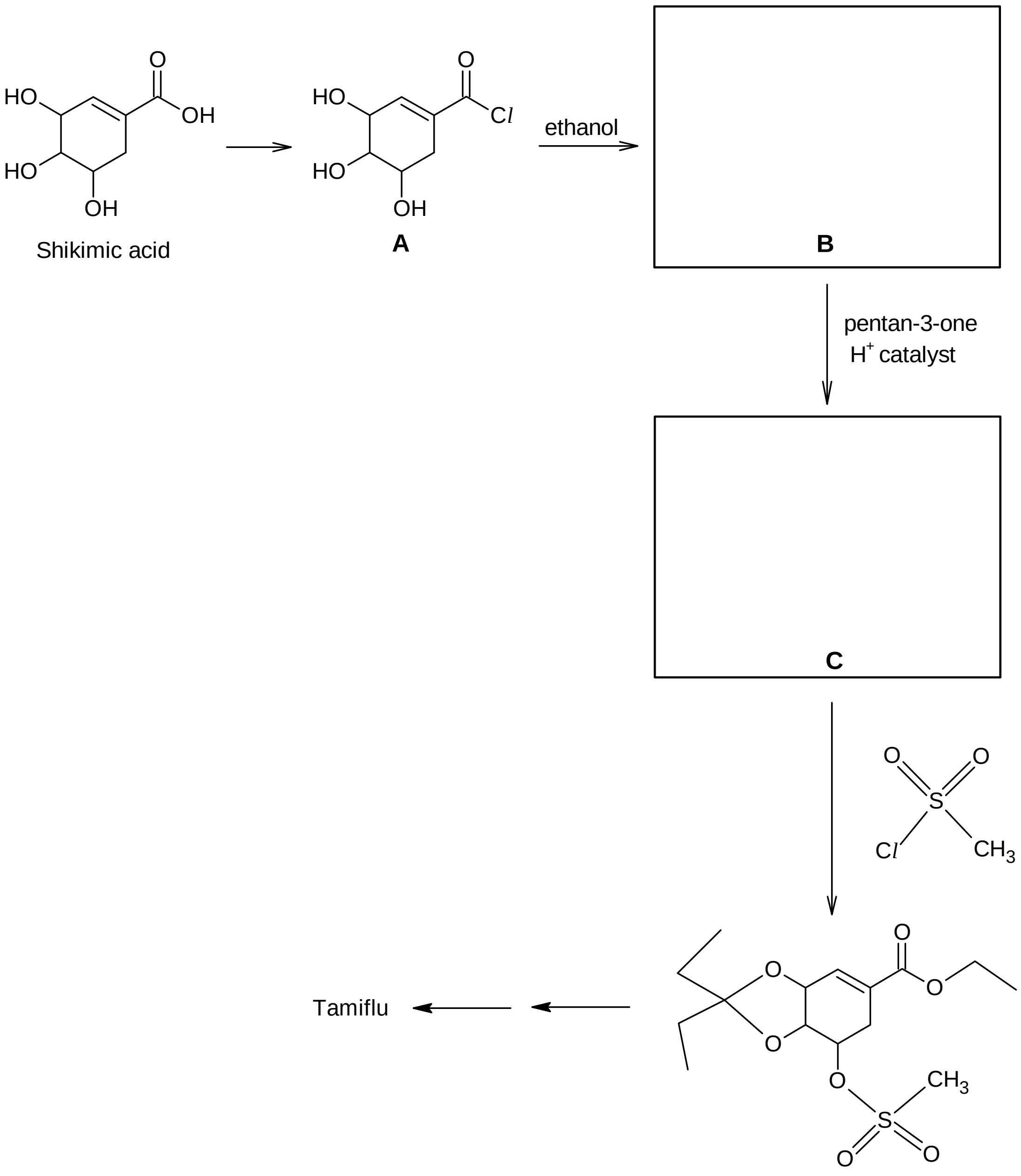
……………………………………………………………………………………[1]

(b) Tamiflu is the anti-influenza drug currently being used to treat ‘Bird–flu’. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected –OH groups of Shikimic acid and ketones helps to control which of the –OH groups reacts to synthesise **C** from **B**.



(i) Draw the structures of **B** and **C** in the boxes provided above.

[2]

(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

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………………………………………………………………………………………[1]

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

$$HCOOH\ (aq) \rightleftharpoons HCOO^{-}\ (aq) + H^{+}\ (aq) \qquad K_a = 1.60 \times 10^{-4}\ mol\ dm^{-3}$$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

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………………………………………………………………………………………[2]

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm^3 of water.

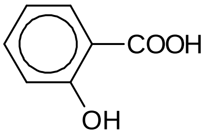
(ii) Calculate the pH of this solution.

[2]

(iii) Hence, calculate the degree of dissociation, α, of methanoic acid in this solution.

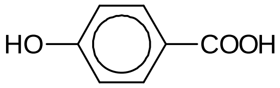
[1]

(d) Salicylic acid occurs naturally in plants.



salicylic acid

pK_{a1} = 2.97



isomer of
salicylic acid

pK_{a1} = 4.54

Explain why salicylic acid is more acidic than its isomer.

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[Total: 15]

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Suggested solutions

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

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The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

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Question No.	**Marks**
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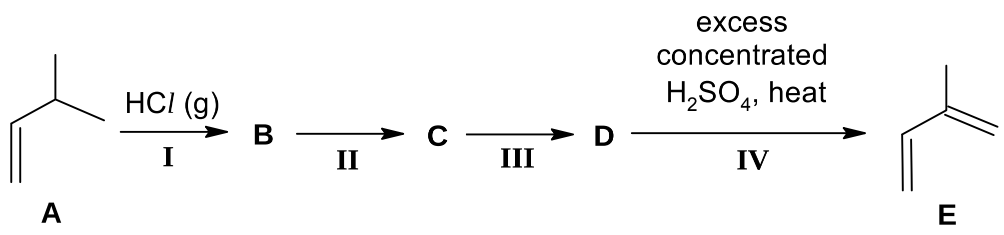
3	**25**
4	**10**
5	**15**
Total	**75**

This question paper consists of **18** printed pages and **0** blank page.

Answer **all** questions in the spaces provided.

1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

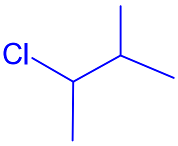
(a) **E** can be synthesised from 3–methylbut–1–ene, **A**, in a 4–step process as follows.

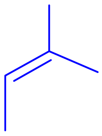


(i) **B** is a major product of step **I**.

Draw the structures of compounds **B**, **C** and **D**.

[3]

B :


C :


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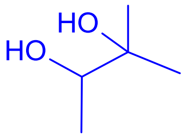


(ii) Suggest the reagents and conditions for steps **II** and **III**.

[2]

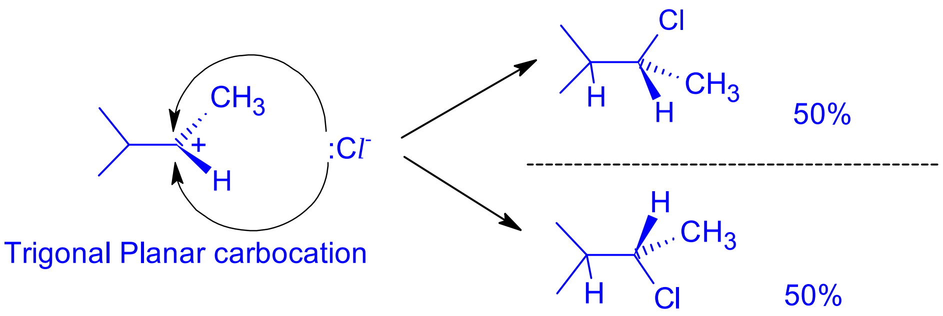
step **II** : alcoholic NaOH heat under reflux

step **III** : cold alkaline $KMnO_4$

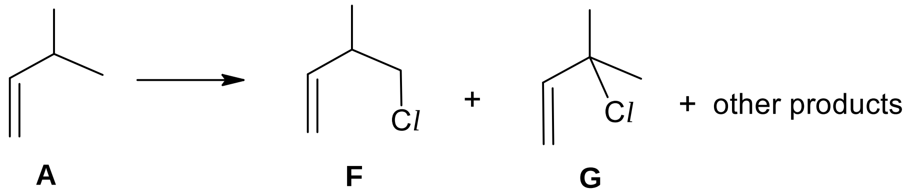
(iii) Predict, with reasoning, whether the mixture of products formed in step **I** is optically active.

[2]

The reaction mixture in **B** is **not optically active**. During electrophilic addition, a **trigonal planar carbocation** is formed. Cl^- has a **50% chance** each of **attacking the carbocation from the top or bottom of the plane**. Hence, resulting in a **racemic mixture** formed.



(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



(i) State the reagents and conditions used to form **F** and **G** from **A**. [1]

Limited Cl_2, uv

(ii) Predict the ratio in which **F** and **G** will be formed. [1]

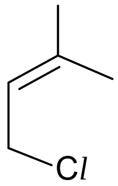
F : **G**
6 : 1

(iii) **Z** was one of the other products formed in the reaction in **(b)**. It was suggested that the radical, •**G**, is involved in the formation of **Z**.

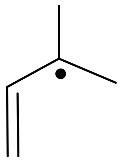
The mechanism of •**G** converting to **Z** is thought to involve 2 steps.

1. Delocalisation of unpaired electron forming •**Z**.
2. •**Z** reacts with Cl_2 to form **Z** and a radical.

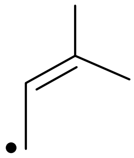
The structures of **Z**, •**G** and •**Z** are as follows.



Z



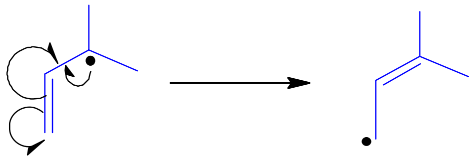
•G



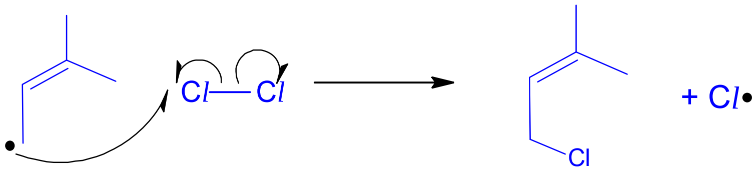
•Z

Use the information above to draw out the mechanism for the conversion of •**G** to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). Use curly half-arrows to indicate the movement of unpaired electrons. [2]

1.



2.



(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

Add 1 cm^3 of **A** and **F** each into separate test tubes. Add **NaOH (aq)** into both test tubes and **heat**, **followed by** adding excess **HNO_3 (aq)** then add **$AgNO_3$ (aq)**.

F : **White ppt** of AgC*l* seen
A : **no white ppt** seen

[Total: 13]

2 **(a)** Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (**J** to **R**) in Periods 2 and 3 of the Periodic Table.

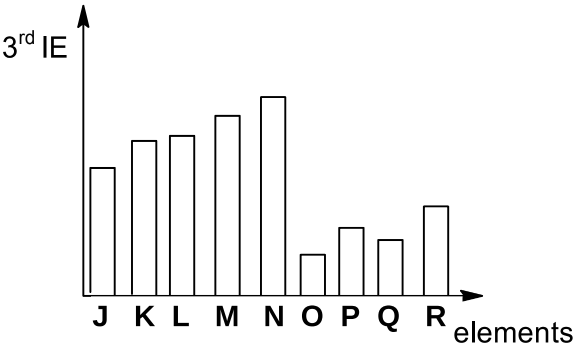


Fig 2.1

(i) Write an equation for the third ionisation energy of element **J**. [1]

$J^{2+}(g) \rightarrow J^{3+}(g) + e^-$

(ii) Identify element **N**. [1]

Mg

(iii) Using your answers in **(a)(i)**, **(a)(ii)** and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3rd IE of **N** compared to **O**.

Electronic configuration: **N^{2+} ($1s^22s^22p^6$)**; **O^{2+} ([Ne]$3s^1$)**

The 3rd ionisation energy of **N** involves the removal of a **2p** electron

The 3rd ionisation energy of **O** involves the removal of a **3s** electron

A **significantly larger amount of energy** is required to remove the **2p** electron in **N^{2+}** which is much more strongly held by the nucleus as it is found in an **inner quantum shell** compared to **3s** electron in **O^{2+}**.

Hence 3rd ionisation energy of **N** is significantly higher than that of **O.**

2. The lower 3rd IE of **Q** than **P**.

[4]

Electronic configuration: **P^{2+} ([Ne]$3s^2$)**; **Q^{2+} ([Ne]$3s^23p^1$)**

The 3rd ionisation energy of P involves the removal of a **3s** electron

The 3rd ionisation energy of Q involves the removal of a **3p** electron

Smaller amount of energy is required to remove the **3p** electron in **Q^{2+}** which is of **higher energy** than **3s** electron in **P^{2+}**. (The 3p electron also experiences increased screening effect provided by the filled 3s subshell.)

Hence 3rd ionisation energy of **Q** is lower than that of **P**

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.

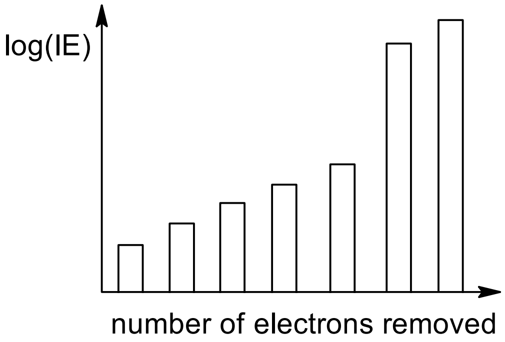


Fig 2.2

(i) Explain the general trend shown in Fig 2.2.

[2]

In an atom of **S**,

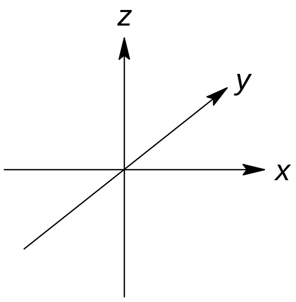
Number of protons unchanged ⇒ **nuclear charge unchanged**

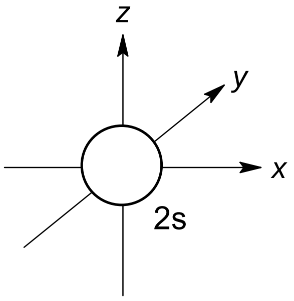
As electrons are removed from the atom, the **increasingly positively charged ion** holds the remaining electrons **more strongly** hence **more energy** is required to remove the remaining electrons resulting in higher I.E

Thus, successive I.E shows an increasing trend.

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.

[1]





(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2.

[1]

Helium has **2 valence electrons** like all other Group 2 elements.

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

[2]

Helium atoms are held by **weak instantaneous dipole induced dipole interactions** while within group 2 elements exist **strong electrostatic forces of attraction between cations and a sea of delocalised electrons**.

Hence, helium has **low melting/boiling point** and it **exist as a gas** while group 2 elements has **high melting/boiling point and exist as a solid** at room temperature. Include energy

OR

Hence, **helium** is a **non-conductor of electricity** due to (**absence of mobile/delocalised electrons**) while **group 2 elements** are **good conductor** of **electricity** due to (**presence of delocalised electrons)**.

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) **(i)** State what is meant by the terms:

Complex

Ligand

[2]

A complex is formed when a **metal ion or atom** forms dative covalent or **coordinate bonds** with **surrounding ion or molecules**.

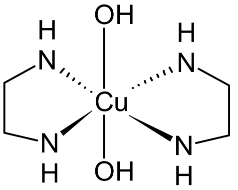
A ligand is a neutral molecule or an anion containing at least one atom with a **lone pair of electrons that can be donated** into **low lying vacant orbital of metal atom/ion to form a coordinate bond**.

(ii) Two of the complexes formed by copper are $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$ and $CuCl_4^{2-}$. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

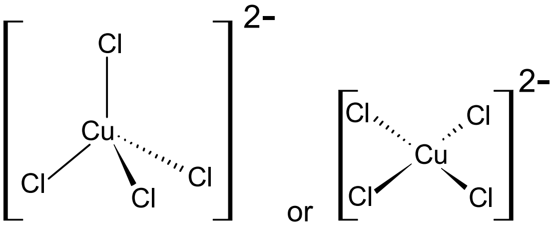
$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$	$CuCl_4^{2-}$
Shape:	Shape:

[3]

$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$
Shape: octahedral



$CuCl_4^{2-}$
Shape: tetrahedral or square planar

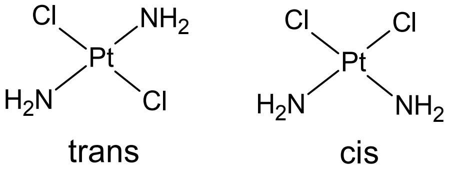


(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

[1]

+2

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.



By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: Cis-trans isomerism

[4]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic configuration of these species.

Cu [Ar]……………

Cu(I) [Ar]……………

[2]

Cu [Ar] $3d^{10}\ 4s^1$
Cu(I) [Ar] $3d^{10}$

(ii) Explain why the following statements are true.

Copper metal is a better electrical conductor than calcium metal.

Copper(II) salts are generally coloured.

[3]

Copper metal are better electrical conductor because both **4s and 3d valence electrons are available for delocalisation**. This increases the number of mobile charge carriers which in turn increases the conductivity of copper metal.

In the presence of ligands, the **degenerate d orbitals are split into two groups of orbital with different energies**. When white light shines on the complex, a d electron **undergoes d-d transition and is promoted to a higher energy partially filled or empty d orbital**. During the transition, the **d electron absorbs a quantum/photon of light of certain wavelength** from the visible region of the electromagnetic spectrum. The **colour observed is the colour of transmitted light** which is a mixture of remaining wavelengths that have not been absorbed. This colour is the complementary colour of the absorbed light.

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the $\Delta H_f^\ominus$ values for some compounds.

Compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
Cu_2O (s)	–168.6
CuO (s)	–157.3
$Cu(NO_3)_2$ (s)	–302.9
NO_2 (g)	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable $\Delta H_f^\ominus$ values from the table to calculate the $\Delta H_r^\ominus$ for this reaction.

$Cu(NO_3)_2\ (s) \rightarrow CuO\ (s) + 2NO_2\ (g) + \frac{1}{2}O_2(g)$

[1]

$\Delta H^\ominus_r = -157.3 + 2(33.2) + 0 - (-302.9)$
$= +212$ kJ mol^{-1}

(ii) Copper(I) oxide can be produced from copper(II) oxide.

$$2CuO\,(s) \rightleftharpoons Cu_2O\,(s) + \tfrac{1}{2}O_2(g) \quad \text{reaction 1}$$

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

[2]

$\Delta H^{\ominus}_r = -168.6 - 2(-157.3)$
$= +146 \text{ kJ mol}^{-1}$

Since the production of copper(I) oxide from copper(II) oxide is an **endothermic process**, it will be favoured by **high temperature** as predicted by **Le Chatelier's Principle**. The equilibrium will **shift to the right** to counter the high temperature.

(iii) For reaction 1, $\Delta S^{\ominus} = +93.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Use this value and your answer in **(c)(ii)** to calculate $\Delta G^{\ominus}$.

[1]

$\Delta G^{\ominus} = 146 - (298)(0.0936)$
$= +118.1 \text{ kJ mol}^{-1}$
$= +118 \text{ kJ mol}^{-1}$

(iv) Write the expression of the equilibrium constant, K_c, for reaction 1. State the units.

[2]

$K_c = [O_2]^{1/2}$
Units: $\text{mol}^{\frac{1}{2}} \text{ dm}^{-\frac{3}{2}}$

(v) For any reaction, $\Delta G^{\ominus}$ and the equilibrium constant, K_c, are related according to the equation,

$$\Delta G^{\ominus} = -2.303RT \log K_c$$

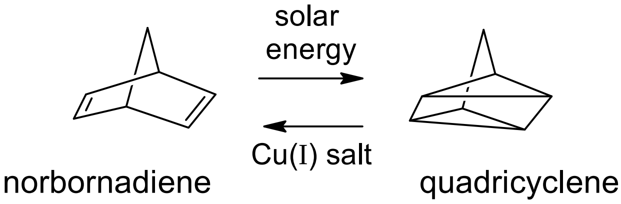
Use this equation to calculate a value of K_c for reaction 1.

[1]

$\log K_c = \frac{-118.1 \times 10^3}{(2.303)(8.31)(298)} = -20.71$

$K_c = 1.95 \times 10^{-21}$

(d) In 1977, Kutal *et al*. conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

[1]

Functional group isomerism

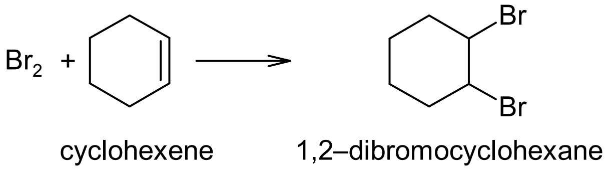
(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

[2]

This system can potentially work as a solar energy storage system. Norbornadiene is first irradiated with solar energy and converted to quadricyclene. Energy can be released when quadricyclene is reacted with copper(I) salts. This means that solar energy can be stored in the covalent bonds of quadricyclene.

[Total: 25]

4 **(a)** Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



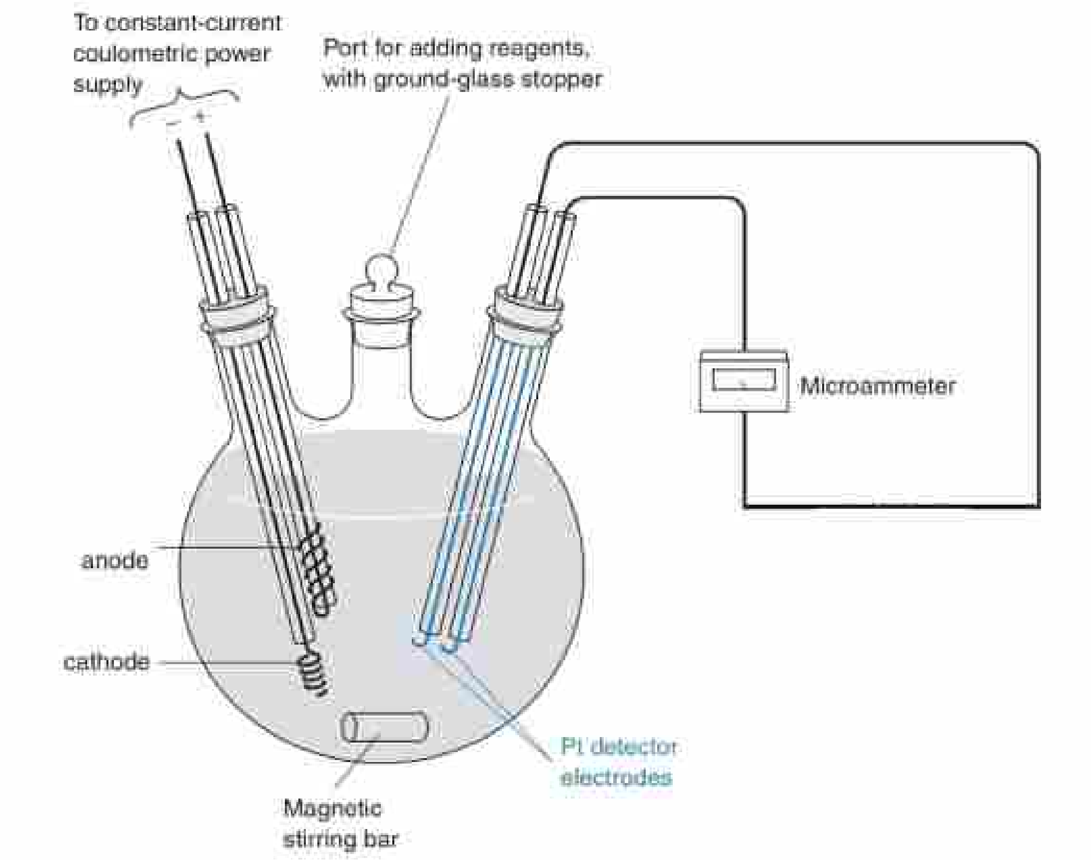
An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^- dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left–hand and right–hand sides respectively.



Br_2 generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

(i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell. [1]

Anode

(ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

$$\text{Detector anode: } 2Br^- \rightarrow Br_2 + 2e^-$$

$$\text{Detector cathode: } Br_2 + 2e^- \rightarrow 2Br^-$$

Suggest why there is no current detected before equivalence point is reached. [1]

Both Br_2 and Br^- must be present for the detector half–reactions to occur.

Prior to the equivalence point, there is Br^- but **no Br_2 is present for reduction at the detector cathode** as any Br_2 formed would have reacted with cyclohexene.

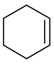
In an experiment, 2 cm^3 of 0.600 x 10^{-3} g cm^{-3} cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used. [1]

mass of cyclohexene = 2 x 0.600 x 10^{-3}
= 1.20 x 10^{-3} g

number of moles of cyclohexene = $\frac{1.20 \times 10^{-3}}{82.0}$
= **1.46 x 10^{-5} mol**

(iv) The experiment was carried out with a constant current of 5 x 10^{-3} A for the electrolytic cell. Determine the time taken for complete titration. [2]

$2e^- \equiv Br_2 \equiv$ 

number of moles of e^- = 1.4634 x 10^{-5} x 2
= 2.9268 x 10^{-5} mol

time taken = $\frac{nF}{I}$
$= \frac{2.9268 \times 10^{-5} \times 96500}{5 \times 10^{-3}}$
= **595 s**

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$$E = 0.32 + 0.029 \log_{10} [I_2], \text{ where } [I_2] \text{ is expressed in mol dm}^{-3}.$$

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

[1]

$0.21 = 0.32 + 0.029 \log_{10} [I_2]$

$[I_2]$ = **$\underline{1.61 \times 10^{-4} \text{ mol dm}^{-3}}$**

(ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

number of moles of $O_3 = 1.6103 \times 10^{-4} \times \frac{10}{1000}$

$= 1.6103 \times 10^{-6}$ mol

$pV = nRT$

$V = \frac{nRT}{p}$

$= \frac{(1.6103 \times 10^{-6})(8.31)(293)}{0.24 \times 101325}$

= **$\underline{1.61 \times 10^{-7} \text{ m}^3}$**

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

[2]

Thermal stability of hydrogen halides **decreases** down the group.

Down the group,

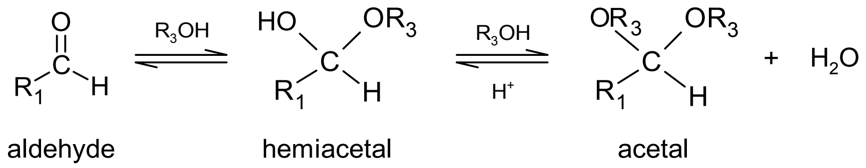
bond energy decreases [BE (H–F) > BE (H–C*l*) > BE (H–Br) > BE (H–I)],

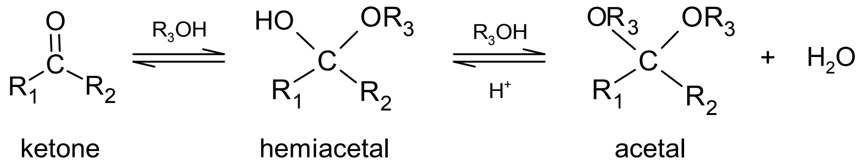
covalent bond strength also **decreases** [H–F > H–C*l* > H–Br > H–I].

Hence, thermal stability **decreases** [H–F > H–C*l* > H–Br > H–I].

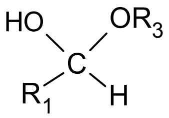
[Total: 10]

5 **(a)** Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.



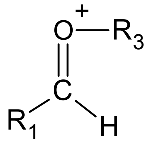


The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



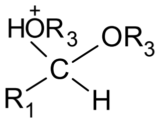
hemiacetal

1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

3. Nucleophilic attack of alcohol, R_3OH, on the oxonium ion to give

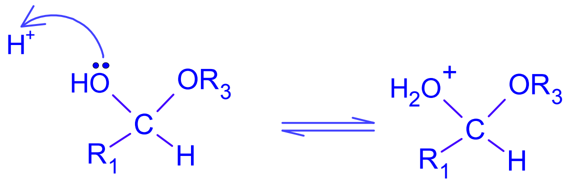


4. Loss of a proton to give the acetal.

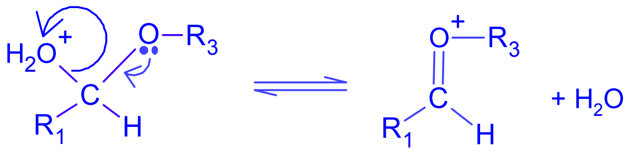
(i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

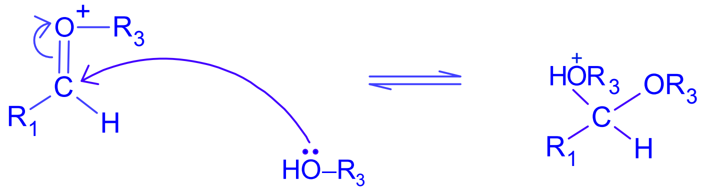
Step 1:



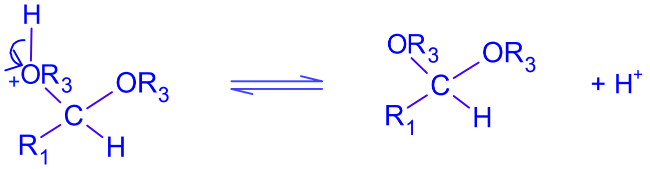
Step 2:



Step 3:



Step 4:



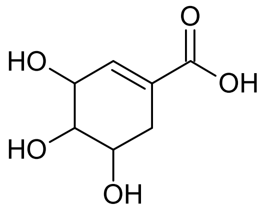
(ii) State the purpose of removing water from the reaction mixture. [1]

By Le Chatelier's Principle, removal of water shifts the position of equilibrium to the right, hence **increasing the yield**.

OR

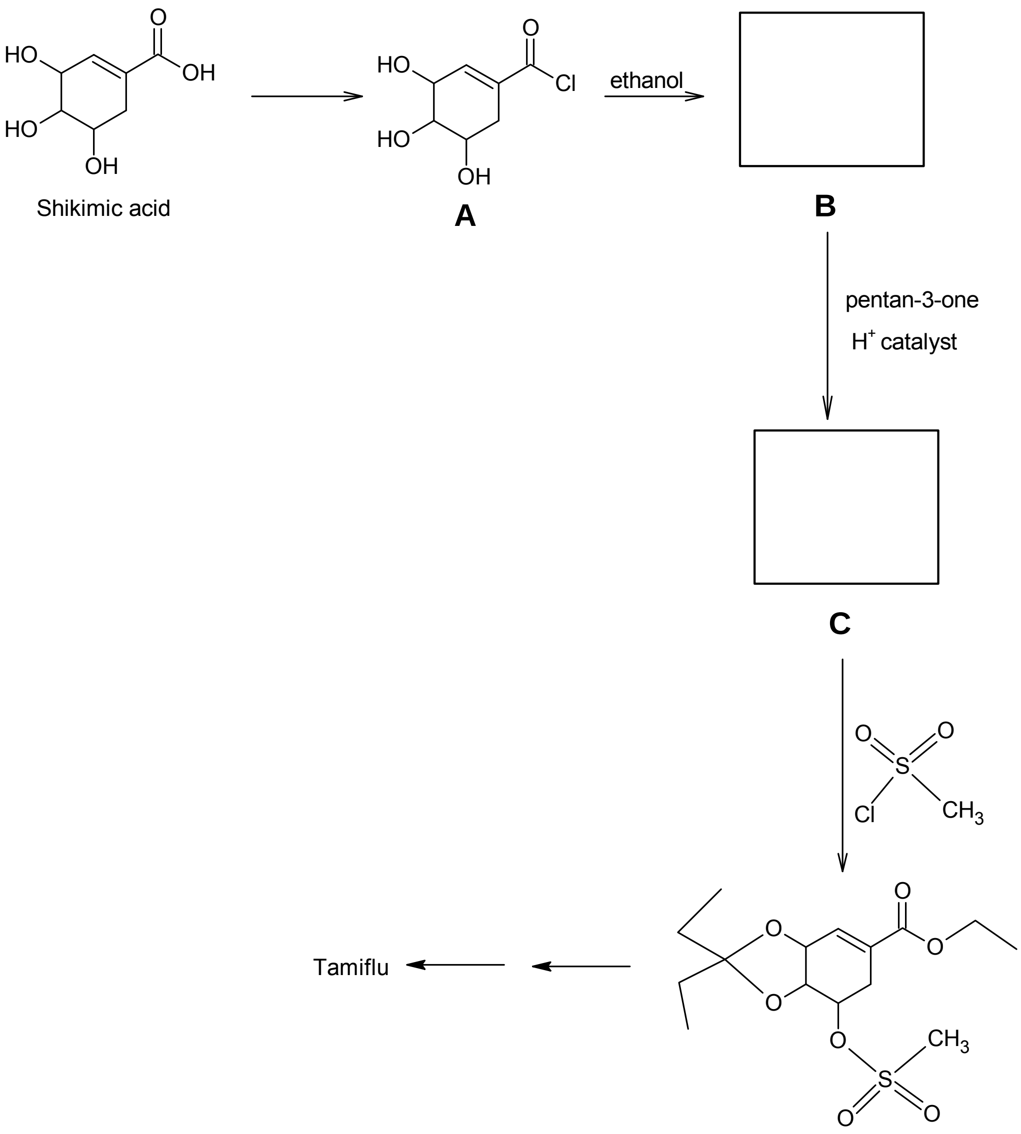
Water is a competing nucleophile to the alcohol, hence other **side products may be formed**.

(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird–flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



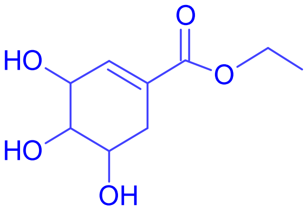
Shikimic acid

Part of the synthetic route is shown below. Formation of acetals between selected –OH groups of Shikimic acid and ketones helps to control which of the –OH groups reacts to synthesise **C** from **B**.

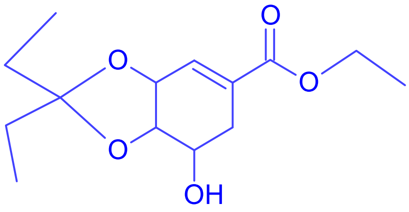


(i) Draw the structures of **B** and **C** in the boxes provided above.

[2]



B



C

(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

[1]

A (acid chloride) is **<u>more reactive</u>** than Shikimic acid.

Using **A** will give a better yield as the reaction is irreversible compared to reversible reaction when Shikimic acid is used. The reaction also requires milder conditions (doing–away with heating and use of catalyst).

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

$$HCOOH\,(aq) \rightleftharpoons HCOO^-\,(aq) + H^+\,(aq) \qquad K_a = 1.60 \times 10^{-4}\ \text{mol dm}^{-3}$$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

[2]

$pK_a = -\lg K_a$

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm^3 of water.

(ii) Calculate the pH of this solution.

[2]

$$[HCOOH] = \frac{0.0100}{0.250}$$

$$= 0.0400\ \text{mol dm}^{-3}$$

$$[H^+] = \sqrt{(0.0400)(1.60 \times 10^{-4})}$$

$$= 2.5298 \times 10^{-3}\ \text{mol dm}^{-3}$$

$pH = -\lg(2.5298 \times 10^{-3})$
$= \underline{\mathbf{2.60}}$

(iii) Hence, calculate the degree of dissociation, α, of methanoic acid in this solution.

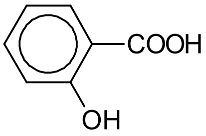
[1]

$$\alpha = \frac{[H^+]}{[HCOOH]}$$

$$= \frac{[2.5298 \times 10^{-3}]}{[0.0400]}$$

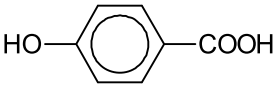
$$= \underline{\mathbf{0.0632}}$$

(d) Salicylic acid occurs naturally in plants.



salicylic acid

pK_{a1} = 2.97



isomer of
salicylic acid

pK_{a1} = 4.54

Explain why salicylic acid is more acidic than its isomer.

[2]

The conjugate base formed from the dissociation of salicylic acid is stabilised by hydrogen bonds between the –OH and $–COO^-$ groups.

The conjugate base formed from the dissociation of the isomer **cannot form such a bond as the –OH and $–COO^-$ groups are too far apart**.

Hence the conjugate base formed from the dissociation of salicylic acid is **stabilised to a greater extent** compared to that of the isomer. The position of the dissociation equilibrium lies more to the right and salicylic acid is a stronger acid than the isomer.

[Total: 15]

Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response

18 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
2 Write your answers on the separate writing papers provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Start each question on a fresh sheet of paper.
[Marks will be deducted if you fail to do so.]
6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.
7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions

Section B

9 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

This question paper consists of **16** printed pages and **0** blank page.

Section A

Answer **all** the questions in this section.

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

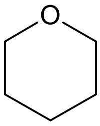
The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow[CH_3OH]{Na} CH_3OCH_3 + HCl$$

(a) **(i)** State the purpose of sodium used in the Williamson ether synthesis. [1]

(ii) Hence, name the mechanism of the reaction. [1]

(iii) Suggest suitable reagent(s) to synthesise each of the following ethers.

- $CH_3CH_2OCH_2CH_3$
- 

[2]

(b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $CH_3CH_2OC(CH_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	CH_3CH_2Br and $(CH_3)_3COH$
B	$(CH_3)_3CBr$ and CH_3CH_2OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning. [2]

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	**Unit**	**DME**	**Diesel Fuel**
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m^{-3}	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg^{-1}	467.1	300
Energy released at burning	MJ kg^{-1}	27.6	42.5

**Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.*

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

(d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al_2O_3 catalyst.

(i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

(ii) State the type of catalysis that Cu-Zn/Al_2O_3 performs and explain briefly how it promotes the synthesis of DME.

[3]

(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \quad \Delta H = -13.1 \text{ kJ mol}^{-1}$$

$$2CH_3OH(l) \rightarrow CH_3OCH_3(l) + H_2O(l) \quad \Delta H = -459.1 \text{ kJ mol}^{-1}$$

Using the thermochemical equations given and any relevant data in part **(c)**, draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]

(e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.

(i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.
[1]

(ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.
[3]

(iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4×10^{-4}, determine the concentration of dimethylamine hydrochloride in the solution.
[3]

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.
[1]

[Total: 25]

2 **(a)** Carbon undergoes combustion in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4.

[2]

(ii) ZnC_2O_4 undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

[1]

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce^{4+}/Ce^{3+} half–cell, using relevant data from the *Data Booklet*.

[1]

(ii) Using relevant data from the *Data Booklet*, deduce if the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

[1]

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is $LaNi_5H_6$ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce $LaNi_5(s)$ and $Ni(OH)_2(s)$, and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in **(c)(i)**, write the overall equation for the reaction that occurs during recharging.

[1]

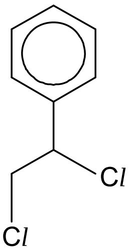
(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

[Total: 12]

3 **(a)** Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound **Y**

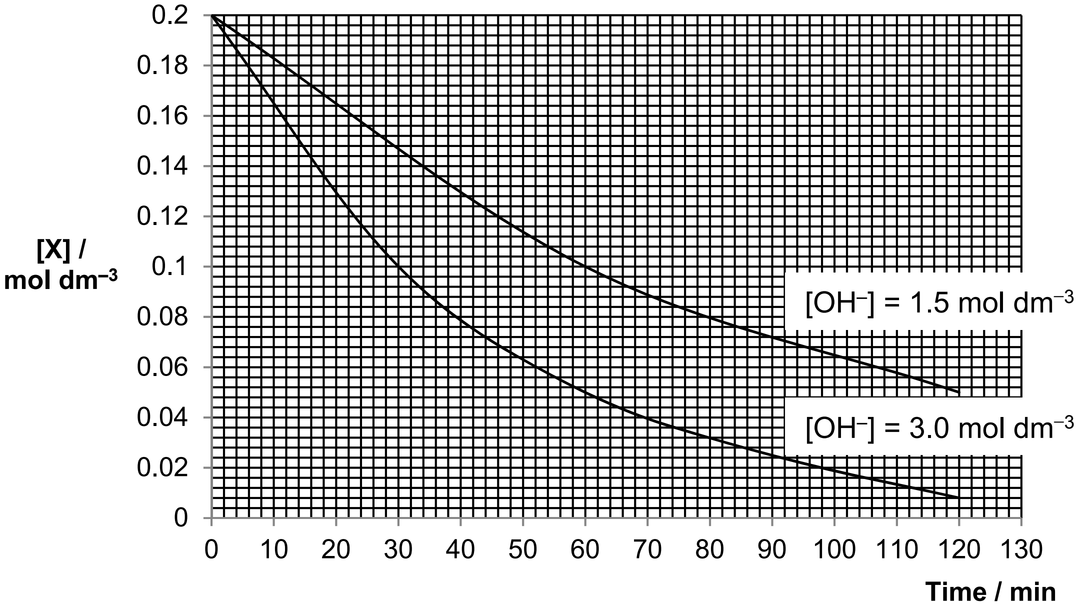
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding $AgNO_3$	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

(i) Deduce the rate equation based on the information given in Experiment **I**.

[3]

(ii) Using your answer in **(a)(i)** and the information given in Experiment **II**, deduce, with reasoning, a possible structure of **X**.

[2]

(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

(b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH^-	
		1° RX in S_N2	3° RX in S_N1
CH_3OH	Protic	1	4
H_2O	Protic	7	150 000
CH_3COOH	Protic	1	1
CH_3COCH_3	Aprotic	5000	–

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

(ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions.

[2]

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction.

[2]

(iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid?

[1]

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / mol^2 dm^{-6}
AgC*l*	1.4 x 10^{-5}	2.0 x 10^{-10}
AgBr	7.1 x 10^{-7}	5.0 x 10^{-13}
AgI	8.9 x 10^{-9}	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide.

[1]

(ii) From the data above, calculate a value for K_{sp} of silver iodide.

[1]

(iii) Using your answer in **(c)(ii)**, calculate the solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$.

[2]

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

(v) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following equation.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT\ \log_{10} K_{sp}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

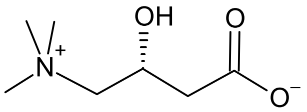
[2]

[Total: 23]

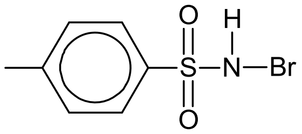
Section B

Answer **one** question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



levocarnitine



bromamine-T

(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of $RuCl_3$, was carried out in aqueous hydrochloric acid.

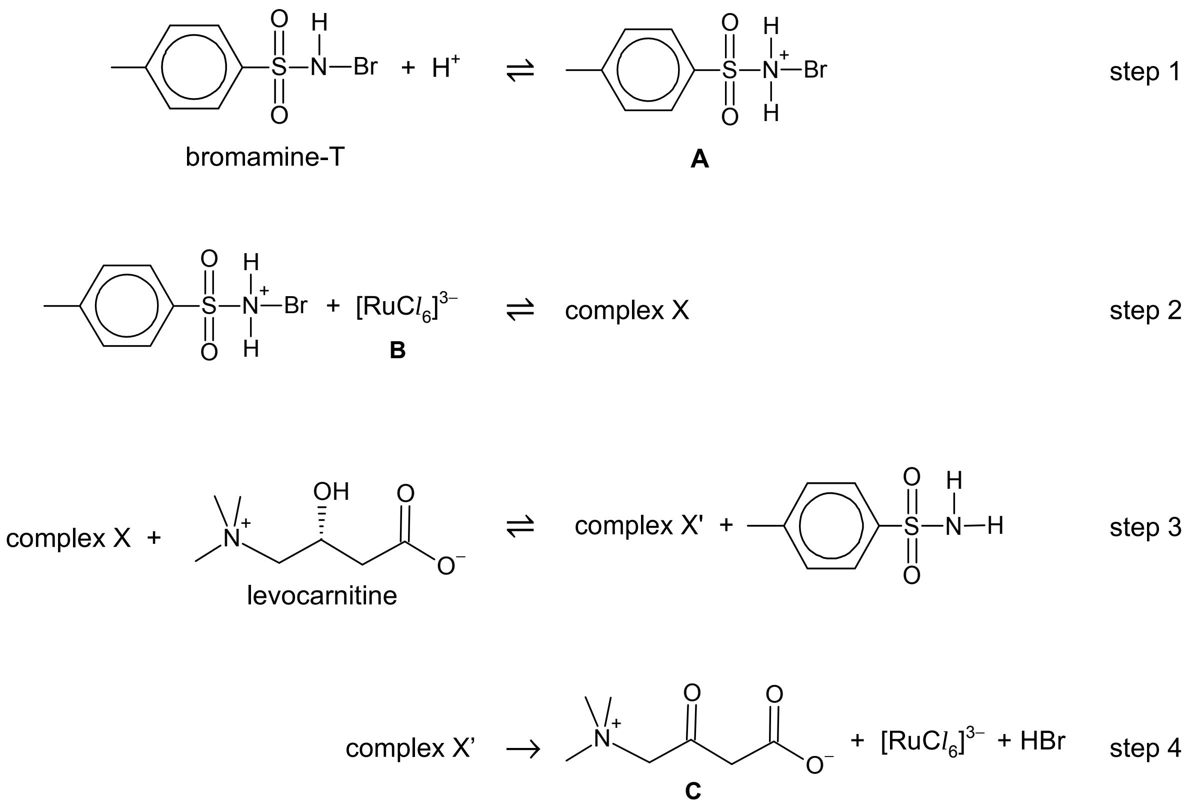
The following equilibrium exists for $RuCl_3$ in aqueous hydrochloric acid.

$$[RuCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [RuCl_6]^{3-} + H_2O$$

Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

[1]

(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number.

[2]

(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, k', for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a, and the pre-exponential factor, A, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.
T is the reaction temperature in Kelvin.
k' is the observed rate constant at a chosen temperature.

(i) Calculate the values of ln k' and $\frac{1}{T}$ for each of the experiments above.

[2]

(ii) Hence plot a graph of ln k' against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

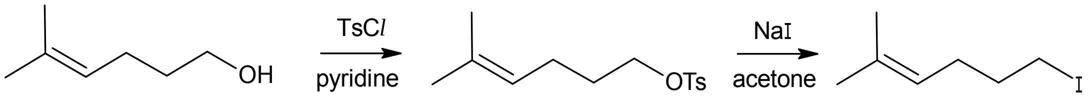
(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]

(d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

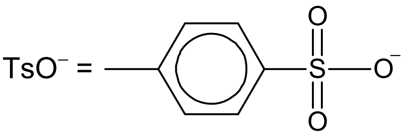
$$\mathrm{ROH} \xrightarrow[\text{pyridine}]{\text{TsC}l} \mathrm{ROTs}$$

This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO^- ion formed compared to OH^-.

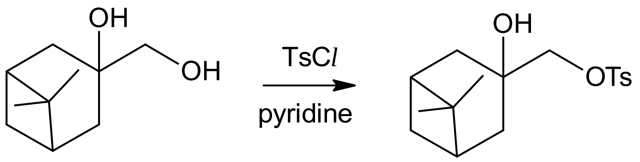
Suggest an explanation for the stability of the TsO^- ion.

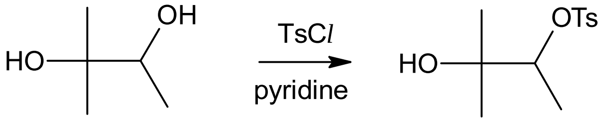


[1]

(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

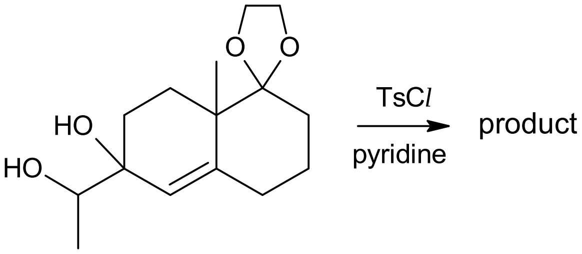
Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.

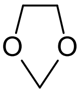




[2]

(iii) Predict the product of the following conversion.



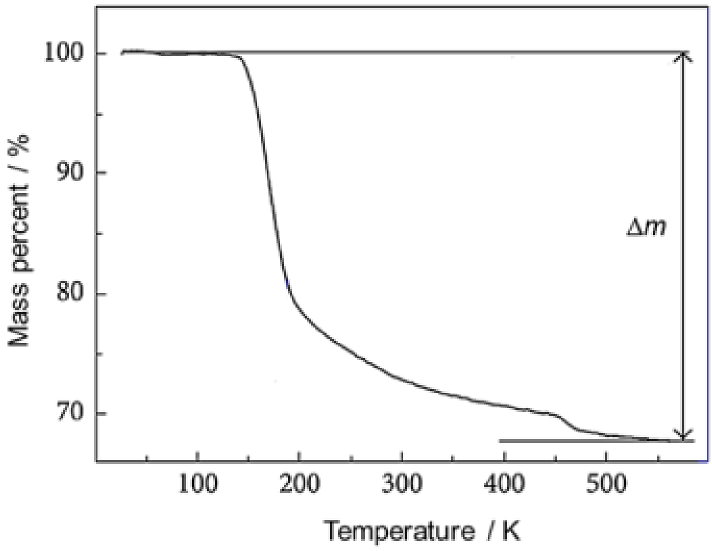
The  ring remains unaltered in the reaction.

[1]

[Total: 20]

5 **(a)** Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $LiB_5O_8.5H_2O$ observed in the graph.

[M_r ($LiB_5O_8.5H_2O$) = 278.9]

[2]

(b) The sample of $LiB_5O_8.5H_2O$ used in **(a)** was synthesised as a system of Li_2O, B_2O_3 and H_2O in the laboratory.

(i) Deduce the molar ratio of Li_2O : B_2O_3 : H_2O in a pure sample of $LiB_5O_8.5H_2O$.

[1]

(ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2.

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ. [2]

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

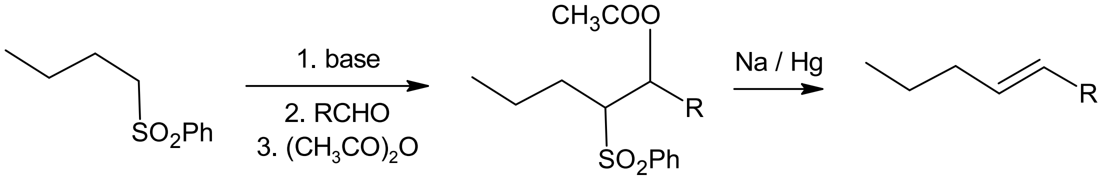
State the change in oxidation number of oxygen as Li_2O_2 is converted into the products. [2]

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is -18.2 kJ mol^{-1}. [2]

(iv) Calculate the pH of the resulting solution formed in **(c)(iii)** given that the K_b of carbonate ion is 1.995×10^{-4} mol dm^{-3}. [3]

(d) Phenylsulfonyl ($PhSO_2$) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.



(i) Suggest the type of reaction occurring in the final step of Julia olefination. [1]

Consider the reaction scheme below involving Julia olefination.

$$\mathbf{A} \xrightarrow[\substack{2.\ C_6H_5CHO \\ 3.\ (CH_3CO)_2O}]{1.\ \text{base}} \mathbf{B} \xrightarrow{Na\ /\ Hg} \underset{(C_{14}H_{16})}{\mathbf{C}} \xrightarrow[\text{heat}]{KMnO_4\ /H^+} \underset{(C_7H_6O_2)}{\mathbf{D}} + \underset{(C_7H_{10}O_6)}{\mathbf{E}}$$

(ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**. [1]

(iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride ($SOCl_2$) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure. [2]

(iv) Hence suggest the structures of compounds **A** to **C**. [3]

[Total: 20]

Suggested solutions

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response **18 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Paper
Cover Sheet
Graph Paper

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.

2 Write your answers on the separate writing papers provided.

3 Write in dark blue or black pen.

4 You may use an HB pencil for any diagrams or graphs.

5 Start each question on a fresh sheet of paper.

[Marks will be deducted if you fail to do so.]

6 At the end of the examination, fasten all your work securely together with the Cover Sheet on top.

7 Do not use staples, paper clips, glue or correction fluid.

Section A

8 Answer **all** questions

Section B

9 Answer **one** question.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

This question paper consists of **13** printed pages and **1** blank page.

Section A

Answer **all** questions.

1 The Williamson ether synthesis is an organic reaction, forming an ether from a halogenoalkane and alcohol in the presence of sodium. This reaction was developed by Alexander Williamson in 1850 and still remains the simplest and most popular method of preparing ethers till today.

The following equation shows the formation of dimethyl ether, a common aerosol propellant.

$$CH_3Cl + CH_3OH \xrightarrow[CH_3OH]{Na} CH_3OCH_3 + HCl$$

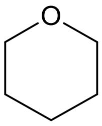
(a) **(i)** State the purpose of sodium used in the Williamson ether synthesis. [1]

Sodium reacts with CH_3OH to form a **stronger nucleophile, CH_3O^-**

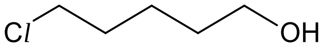
(ii) Hence, name the mechanism of the reaction. [1]

S_N2 / bimolecular nucleophilic substitution

(iii) Suggest suitable reagent(s) to synthesise each of the following ethers.

- $CH_3CH_2OCH_2CH_3$
- 

[2]

- CH_3CH_2OH (in the presence of Na) and CH_3CH_2Cl
-  (in the presence of Na)

(b) Dimethyl ether is known as a symmetrical ether whereas *tert*-butyl ethyl ether, $CH_3CH_2OC(CH_3)_3$ is an example of an unsymmetrical ether. To prepare *tert*-butyl ethyl ether via the Williamson ether synthesis, there are two possible combinations of reagents, as shown in the table below.

Combination	Reagents
A	CH_3CH_2Br and $(CH_3)_3COH$
B	$(CH_3)_3CBr$ and CH_3CH_2OH

Identify the combination of reagents that might favour the mechanism identified in **(a)(ii)** and justify your choice, with reasoning. [2]

Combination **A**

CH_3CH_2Br is a **primary alkyl halide**, and hence it will be **less sterically hindered** for the nucleophile / alkoxide ion to **attack from the back** of the halogen as compared to $(CH_3)_3CBr$, a tertiary alkyl halide.

(c) Since the middle of 1990s, dimethyl ether (DME) has been identified as a reliable diesel alternative for cars. The table below compares the physical and chemical properties of DME and diesel fuel.

Property	**Unit**	**DME**	**Diesel Fuel**
Carbon content	mass %	52.2	86
Hydrogen content	mass %	1 – 3	14
Oxygen content	mass %	34.8	0
Liquid density	kg m^{-3}	667	831
*Auto-ignition temperature	K	508	523
^Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450 – 643
Enthalpy of vaporisation	kJ kg^{-1}	467.1	300
Energy released at burning	MJ kg^{-1}	27.6	42.5

**Auto-ignition temperature is the temperature at which a fuel will ignite spontaneously without an external ignition source.*

^Stoichiometric air/fuel mass ratio is the mass ratio of air to fuel that completely burns the fuel with no excess air.

With reference to the table, suggest one advantage and one disadvantage of using DME as compared to the conventional diesel fuel.

[2]

Advantage: DME has **lower carbon content** than diesel fuel, and thus contribute to **lower carbon dioxide emission** when the same mass is burnt.

Disadvantage: DME releases **less energy at burning** than diesel fuel, and thus is a **less efficient fuel** for the same mass used.

(d) Scientists have recently discovered a new way of synthesising DME by reacting carbon dioxide directly with hydrogen in the presence of Cu-Zn/Al_2O_3 catalyst.

(i) Write the balanced equation for the synthesis of DME from carbon dioxide and hydrogen.

[1]

$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$

(ii) State the type of catalysis that Cu-Zn/Al_2O_3 performs and explain briefly how it promotes the synthesis of DME.

[3]

Heterogeneous catalysis

Both H_2 and CO_2 reactants are gases. The solid catalyst provides a surface for the **gaseous molecules to be *adsorbed*** to the surface, **thus increasing the concentration of the reactants / bringing the molecules closer together** and **weakening the bonds of the reactants molecules**, resulting in a lower E_a.

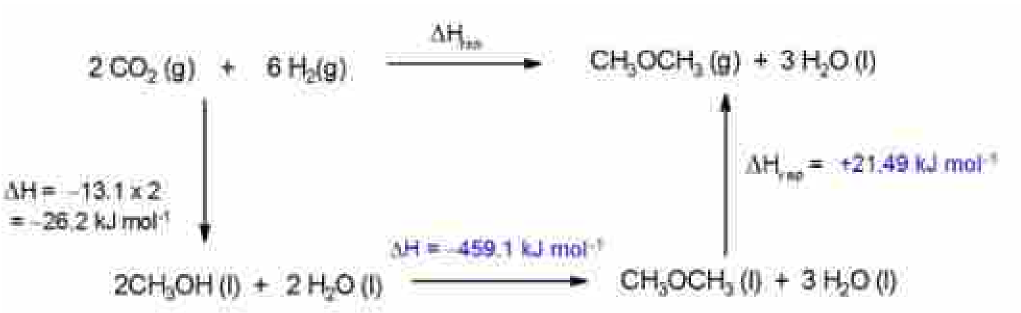
(iii) DME can also be synthesised from carbon dioxide via a two-step reaction in the laboratory.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \quad \Delta H = -13.1 \text{ kJ mol}^{-1}$$

$$2CH_3OH(l) \rightarrow CH_3OCH_3(l) + H_2O(l) \quad \Delta H = -459.1 \text{ kJ mol}^{-1}$$

Using the thermochemical equations given and any relevant data in part **(c)**, draw an energy cycle to determine the enthalpy change of reaction for the synthesis of DME from carbon dioxide and hydrogen at room temperature and pressure.

[5]



$\Delta H_{vap} = 467.1/1000 \times 46 = +21.49 \text{ kJ mol}^{-1}$

By Hess' Law,
$\Delta H_{rxn} = -26.2 - 459.1 + 21.49$
$= \underline{\mathbf{-464 \text{ kJ mol}^{-1}}}$

(e) Both dimethyl ether and dimethyl amine have similar hybridisation around the heteroatoms, O and N, respectively.

(i) State the type of hybridisation of the O and N atoms in dimethyl ether and dimethyl amine respectively.

[1]

sp^3

(ii) Dimethyl ether has a solubility of 7.1 g per litre of water but dimethyl amine has a solubility of 3.54 kg per litre of water instead. Using suitable equation(s), explain briefly the difference in the solubilities between the two compounds.

[3]

DME can form **hydrogen bonds with water molecules** whereas dimethyl amine is a weak base and can partially dissociate in water in to form ions which can form **ion-dipole interactions with water molecules**, hence dimethyl amine has a higher solubility in water.

$$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$$

(iii) A 0.1 mol dm^{-3} solution of dimethyl amine containing an unknown concentration of dimethylamine hydrochloride has a pH of 10.57. Given that the numerical value of K_b of dimethyl amine is 7.4 × 10^{-4}, determine the concentration of dimethylamine hydrochloride in the solution.

[3]

A buffer system is set up.

$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^- \quad K_b = 7.4 \times 10^{-4}$ mol dm^{-3}

pH = 10.57
pOH = 14 – 10.57 = 3.43
$[OH^-] = 10^{-3.43}$ mol dm^{-3}

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

$$7.4 \times 10^{-4} = \frac{[(CH_3)_2NH_2^+]\left[10^{-3.43}\right]}{0.1}$$

$$[(CH_3)_2NH_2^+] = \frac{7.4\times10^{-4}\times0.1}{10^{-3.43}}$$

$= 0.199$ mol dm^{-3}

OR

$$pOH = pK_b + \log_{10}\left(\frac{[(CH_3)_2NH_2^+]}{[(CH_3)_2NH]}\right)$$

$$14 - 10.57 = -\log_{10}(7.4 \times 10^{-4}) + \log_{10}\left(\frac{[(CH_3)_2NH_2^+]}{0.1}\right)$$

$[(CH_3)_2NH_2^+] = 0.199$ mol dm^{-3}

(iv) Explain why trimethyl amine has a higher pK_b than dimethyl amine.

[1]

The **lone pair of electrons on N in trimethyl amine is less available for donation** as it is **more sterically hindered with one more –CH_3 group** than dimethyl amine, hence decreasing its basicity.

[Total: 25]

2 **(a)** Carbon undergoes combustion in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4.

[2]

Mg^{2+} has a **smaller ionic radius and a higher charge density** than Ba^{2+}. Therefore, Mg^{2+} has a **greater polarising power** than Ba^{2+}. Mg^{2+} **distorts the electron cloud of $C_2O_4^{2-}$ anion / weakens the bonds in the $C_2O_4^{2-}$ anion to a greater extent.** Hence MgC_2O_4 is less thermally stable.

(ii) ZnC_2O_4 undergoes a similar reaction when heated strongly, even though zinc is not a Group 2 element.

Write an equation, with state symbols, to represent the thermal decomposition of solid zinc oxalate.

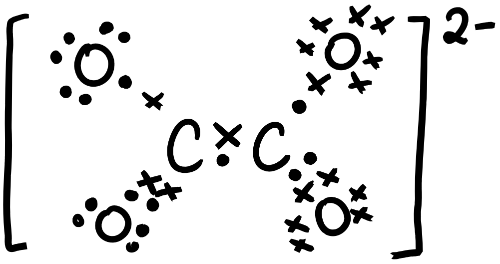
[1]

$ZnC_2O_4(s) \rightarrow ZnO(s) + CO_2(g) + CO(g)$

(iii) Draw the dot–and–cross diagram of $C_2O_4^{2-}$.

State the shape and bond angle around the carbon atoms of the ion.

[3]



Shape: Trigonal Planar about each C atom
Bond Angle: 120°

(b) Zinc can also be used in the manufacturing of rechargeable batteries. Zinc–cerium battery is a type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.

$$Zn + 2Ce^{4+} \rightarrow Zn^{2+} + 2Ce^{3+}$$

(i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the Ce^{4+}/Ce^{3+} half–cell, using relevant data from the *Data Booklet*.

[1]

From the Data Booklet,
$E^{\ominus}(Zn^{2+}/Zn) = -0.76$ V

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$
$2.2 = E^{\ominus}(Ce^{4+}/Ce^{3+}) - (-0.76)$
$E^{\ominus}(Ce^{4+}/Ce^{3+}) = \mathbf{+1.44\ V}$

(ii) Using relevant data from the *Data Booklet*, deduce if the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

[1]

From the Data Booklet,
$E^\ominus(Br_2/Br^-) = +1.07$ V

$E^\ominus_{cell} = +1.07 - (-0.76)$
$= +1.83$ V > 0 (feasible)

Since it is feasible for the battery to discharge electricity, the Ce^{4+}/Ce^{3+} half–cell can be replaced with Br_2/Br^- half–cell.

(c) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is $LaNi_5H_6$ and the other is NiO(OH). The electrolyte is aqueous KOH. During the discharging process, an electrochemical reaction takes place to produce $LaNi_5(s)$ and $Ni(OH)_2(s)$, and releases electrical energy.

(i) Construct a half–equation for the reaction that take place at each electrode during discharging.

[2]

Anode: $LaNi_5H_6(s) + 6OH^-(aq) \rightarrow LaNi_5(s) + 6H_2O(l) + 6e^-$

Cathode: $NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)$

(ii) During recharging, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in **(c)(i)**, write the overall equation for the reaction that occurs during recharging.

[1]

$LaNi_5(s) + 6Ni(OH)_2(s) \rightarrow LaNi_5H_6(s) + 6NiO(OH)(s)$

(iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes to form gaseous products. A safety vent is thus incorporated in the battery to release the excess pressure.

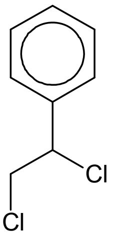
With reference to the *Data Booklet*, suggest a relevant half–equation, with state symbols, for the reaction occurring at one of the electrodes of the Ni–MH battery.

[1]

Anode: $4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$
OR
Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

[Total: 12]

3 **(a)** Compounds **X** and **Y** are dichloroalkanes and constitutional isomers of each other. The structure of **Y** is as shown below.



Compound **Y**

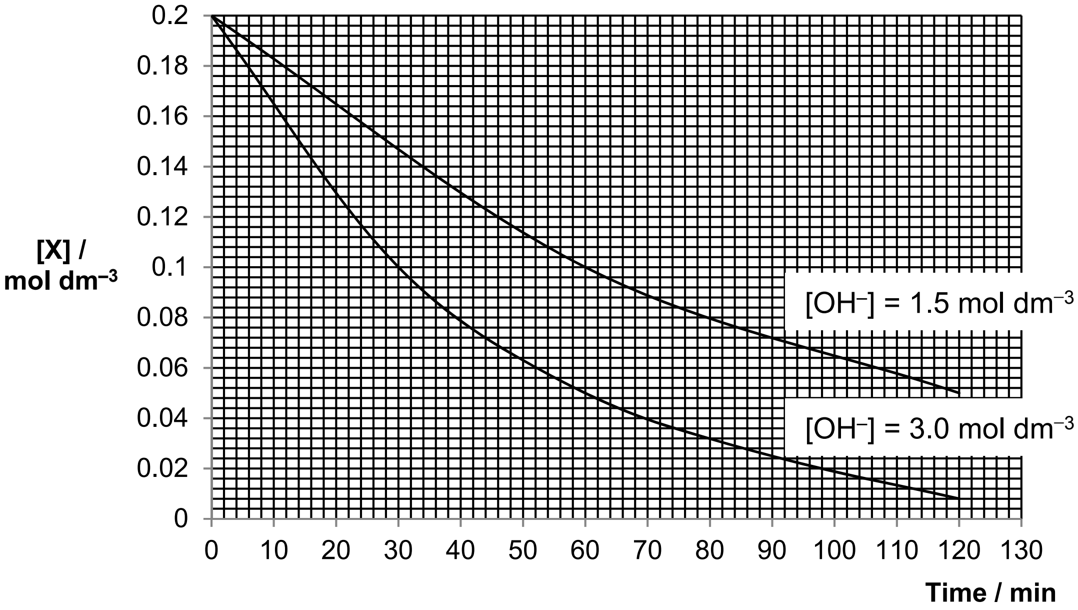
Some additional information is provided about **X**:

- It is not chiral.
- It also contains a benzene ring.
- The two chlorine atoms are not bonded to the same carbon atom.

A series of chemical experiments were also conducted on Compound **X** to further confirm its identity.

Experiment I:

The reaction kinetics of **X** with aqueous sodium hydroxide was determined by monitoring the change in concentration of **X** with time.



Experiment II:

0.25 mol of **X** and **Y** were treated separately with boiling aqueous sodium hydroxide. The products from each compound were then acidified with nitric acid and then treated with silver nitrate solution. The results obtained are shown below.

	Observation upon adding $AgNO_3$	Mass of precipitate / g
X	formation of white precipitate	35.85
Y	formation of white precipitate	71.70

(i) Deduce the rate equation based on the information given in Experiment **I**. [3]

Using [OH^-] = 3.0 mol dm^{-3} graph,
$t_{1/2}$ is constant at 30 min, order of reaction with respect to X is 1.
OR
Using [OH^-] = 1.5 mol dm^{-3} graph,
$t_{1/2}$ is constant at 60 min, order of reaction with respect to X is 1.

Using initial rate method,
Initial rate for graph where [OH^-] = 1.5 mol dm^{-3}
= 0.2/110 = 0.001818 mol dm^{-3} min^{-1}
Initial rate for graph where [OH^-] = 3.0 mol dm^{-3}
= 0.2/52 = 0.003846 mol dm^{-3} min^{-1}

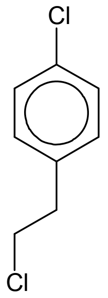
As [OH^-] increases 2 times, initial rate also increases 2 times
Hence, order of reaction with respect to OH^- is 1.

Rate = k [X] [OH^-]

(ii) Using your answer in **(a)(i)** and the information given in Experiment **II**, deduce, with reasoning, a possible structure of **X**. [2]

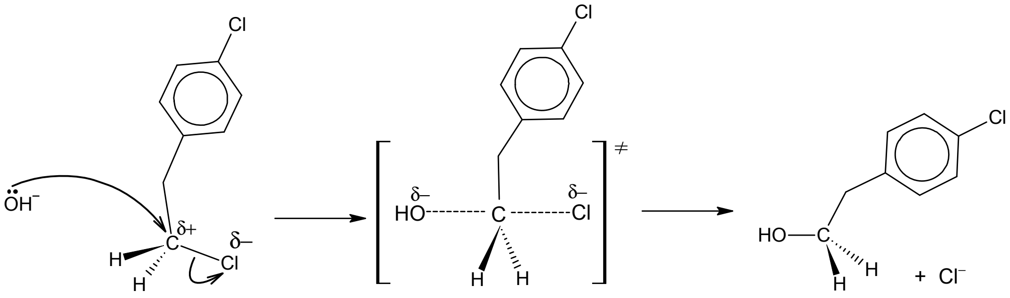
From (a)(i), X undergoes S_N2 mechanism
⇒ X is a primary chloroalkane.

From expt II, 0.25 mol of X forms 0.25 mol of $AgCl$
⇒ There is only one C*l* atom in the alkyl side chain OR there is only one C*l* atom bonded to the benzene ring



(iii) Draw the mechanism for the reaction of **X** with aqueous sodium hydroxide. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]



(b) Depending on the mechanism, the solvent affects the stability of nucleophile and/or reaction intermediates in the nucleophilic substitution of halogenoalkanes (RX). The table below shows the rates of reaction when different halogenoalkanes and solvents are used.

Solvent	Type	Relative rates of reaction with OH^-	
		1° RX in S_N2	3° RX in S_N1
CH_3OH	Protic	1	4
H_2O	Protic	7	150 000
CH_3COOH	Protic	1	1
CH_3COCH_3	Aprotic	5000	–

(i) Suggest, using **only** structure and bonding, the difference between *protic* and *aprotic* solvents, in terms of solvent-solvent interactions.

[1]

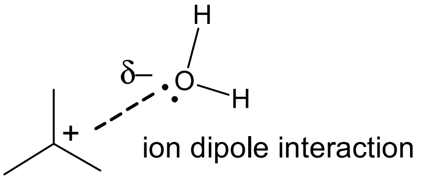
Protic solvent refers to molecules with **H atoms that can be used to form hydrogen bonds**. Aprotic solvents can only form **permanent dipole-permanent dipole interactions between molecules/ have no H atoms that can form hydrogen bonds**.

(ii) Suggest an explanation for the effect of solvent on the relative rate of S_N2 reactions.

[2]

For S_N2 reactions, protic solvents like water can form **hydrogen bond with OH^-** and hence, slowing down the rate of reaction. Aprotic solvents like CH_3COCH_3, do not form hydrogen bond and hence **the lone pair of electron on OH^- is more available to attack the electron deficient C on 1° RX.**

(iii) Explain, with an aid of a diagram, how water increases the rate of S_N1 reaction. [2]



The ion dipole interaction **stabilised the carbocation**.

(iv) Would the rate of S_N1 reaction be faster or slower if hexane was used in place of ethanoic acid? [1]

Slower.

(c) Silver forms a series of halides of general formula AgX. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / mol^2 dm^{-6}
AgC*l*	1.4×10^{-5}	2.0×10^{-10}
AgBr	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

(i) Write an expression for the solubility product, K_{sp} of silver iodide. [1]

$K_{sp} = [Ag^+] [I^-]$

(ii) From the data above, calculate a value for K_{sp} of silver iodide. [1]

$[Ag^+] = [I^-]$
$K_{sp} = (8.9 \times 10^{-9})^2$
$= \underline{\mathbf{7.92 \times 10^{-17}\ mol^2\ dm^{-6}}}$

(iii) Using your answer in **(c)(ii)**, calculate the solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$. [2]

Let solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$ be x mol dm^{-3}.

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

$K_{sp} = [Ag^+][I^-] = (0.0125 + x)(x) = 7.92 \times 10^{-17}$

It can be assumed that $x \ll 0.0125$ such that $(0.0125 + x) \approx 0.0125$

$(0.0125)(x) = 7.92 \times 10^{-17}$

$x = 6.34 \times 10^{-15}$ mol dm^{-3}

Solubility of AgI in 0.0125 mol dm^{-3} $AgNO_3$ = **<u>6.34×10^{-15} mol dm^{-3}</u>**

(iv) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry of the reactions occurring.

[3]

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
White ppt is formed due to the formation of insoluble AgC*l*.

$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^-$
White ppt dissolves due to the formation of a complex ion.

$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
Cream ppt is obtained when NaBr is added to the resultant mixture because K_{sp} of AgBr < K_{sp} of AgC*l* so ionic product still exceeds K_{sp} of AgBr

(v) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following equation.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$$

For silver fluoride, its K_{sp} value is 1.006 at 298 K.

Use the equation given above to deduce if silver fluoride is soluble in water at 298 K. Explain your answer.

[2]

$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$
$= 2.303(8.31)(298)(\log_{10} 1.006)$
$= \mathbf{+14.8\ J\ mol^{-1}}$

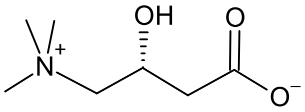
Since $\Delta G^{\ominus}_{ppt} > 0$, precipitation will not occur.
Therefore, AgF is soluble in water at 298 K.

[Total: 23]

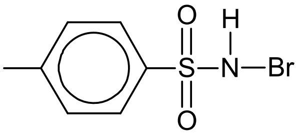
Section B

Answer **one** question from this section.

4 Levocarnitine is a quaternary ammonium compound involved in metabolism in most mammals.



levocarnitine



bromamine-T

(a) A kinetic study on the reaction between levocarnitine and bromamine-T, in the presence of $RuCl_3$, was carried out in aqueous hydrochloric acid.

The following equilibrium exists for $RuCl_3$ in aqueous hydrochloric acid.

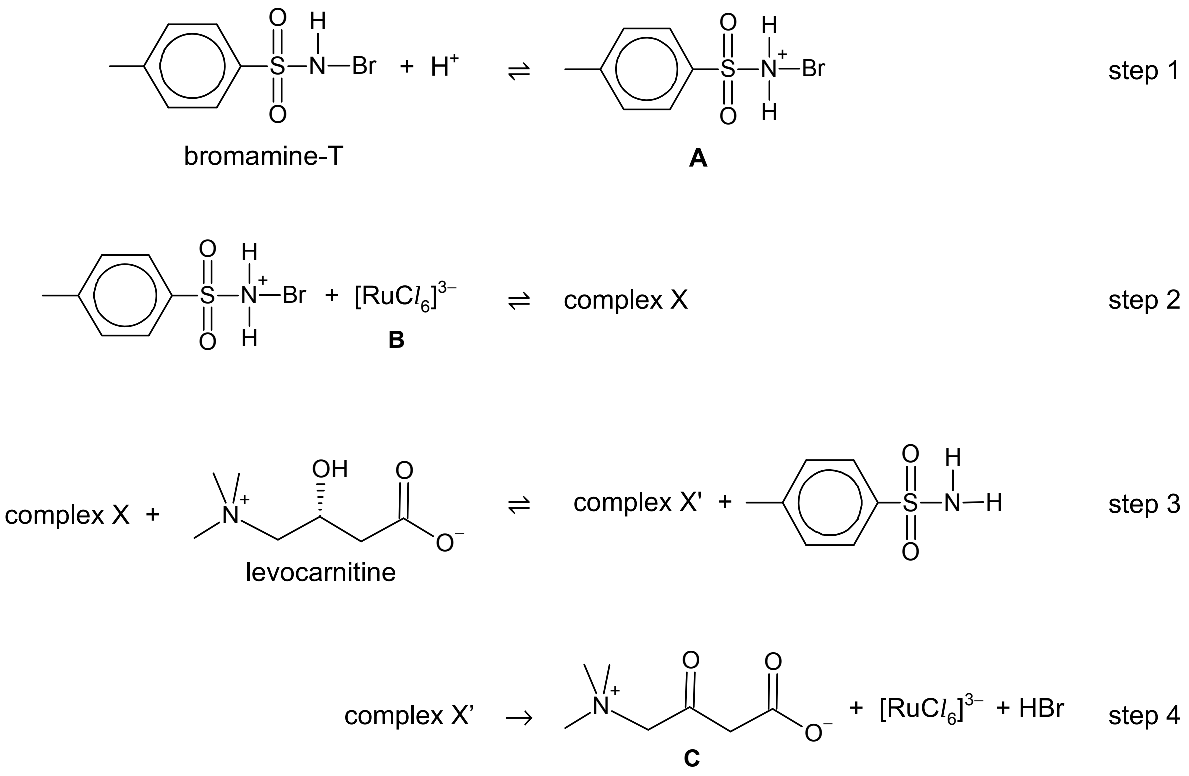
$$[RuCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [RuCl_6]^{3-} + H_2O$$

Explain why $[RuCl_6]^{3-}$ is likely to be the reactive species instead of $[RuCl_5(H_2O)]^{2-}$ in this study.

[1]

By Le Chatelier's Principle, the presence of **chloride ions from aqueous HCl** will shift the **position of equilibrium to the right**, favouring the formation of $[RuCl_6]^{3-}$.

(b) The mechanism for the reaction between levocarnitine and bromamine-T was proposed as follows.



(i) Use the Lewis theory of acids and bases to identify and explain the role of bromamine-T in step 1.

[1]

Bromamine-T acts as a **Lewis base** in step 1 as it **donates its lone pair of electrons** on N atom to H^+.

(ii) The species in the equations shown have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **A**, **B** and **C**.

[3]

A is an **intermediate** as it was **formed in step 1 and then reacted in step 2**.

B is a **catalyst** as it **reacted in step 2 and was regenerated in step 4**.

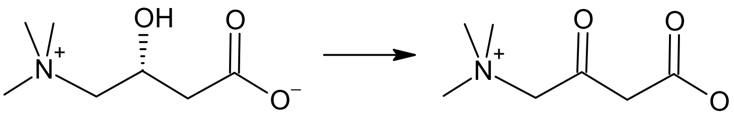
C is a **product** as it was **formed in step 4 and not reacted in other steps**.

(iii) State the type of reaction that levocarnitine had undergone with bromamine-T. Explain your answer in terms of changes in oxidation number.

[2]

Oxidation

The oxidation number of **carbon** (bonded to -OH group) **increased from 0 in levocarnitine** to **+2 in species C**.



levocarnitine

C

(c) A series of experiments were carried out at different temperatures under pseudo-first order conditions with respect to bromamine-T.

The value of the observed rate constant, *k'*, for the catalysed reaction was determined at each temperature and the results are summarised in the table below.

k' / 10^4 s^{-1}	temperature, T / K
1.82	293
3.00	303
4.62	313
7.30	323

The activation energy, E_a, and the pre-exponential factor, *A*, which is a constant, for the reaction can be determined from the equation.

$$k' = Ae^{\frac{-E_a}{RT}}$$

R is the molar gas constant.
T is the reaction temperature in Kelvin.
k' is the observed rate constant at a chosen temperature.

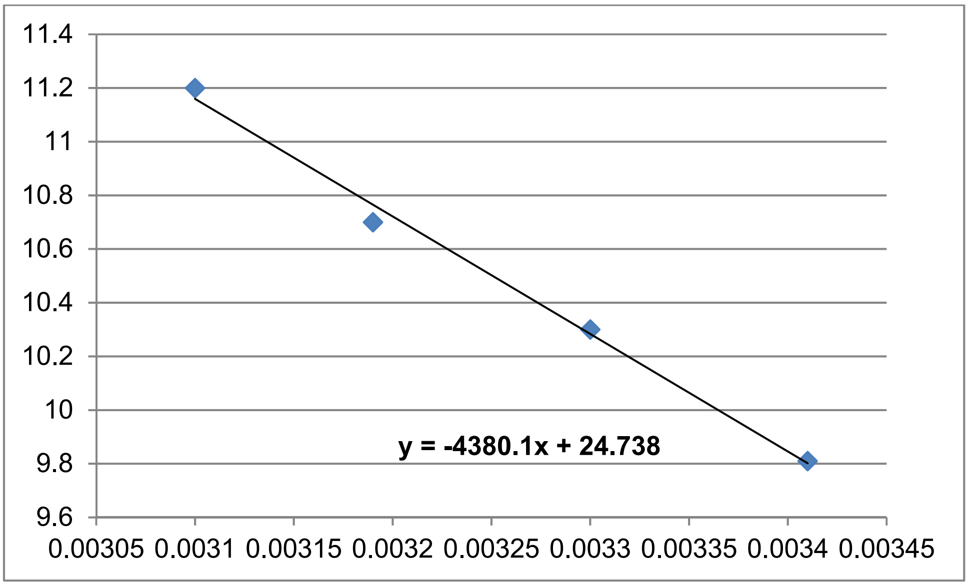
(i) Calculate the values of ln *k*’ and $\frac{1}{T}$ for each of the experiments above.

[2]

k’ / 10^4 s^{-1}	ln *k*’	temperature, T / K	$\frac{1}{T}$ / K^{-1}
1.82	9.81	293	0.00341
3.00	10.3	303	0.00330
4.62	10.7	313	0.00319
7.30	11.2	323	0.00310

(ii) Hence plot a graph of ln *k*’ against $\frac{1}{T}$ and determine E_a from the gradient of the best-fit line which is $\frac{-E_a}{R}$.

[4]

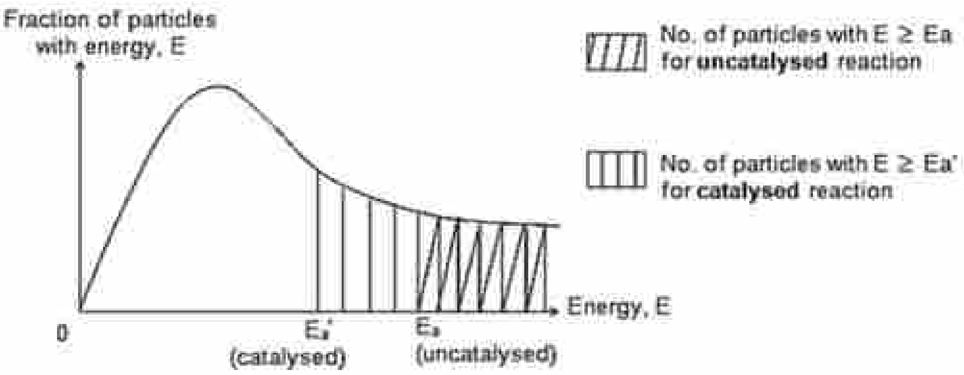


Gradient = $\frac{-E_a}{R}$ = –4380.1 K

Hence E_a = 36399 J mol^{-1} = **36.4 kJ mol^{-1}**

(iii) How would you expect the activation energy and rate of the reaction to be different if the reaction was uncatalysed? Explain your answer with the aid of a Boltzmann distribution curve.

[3]



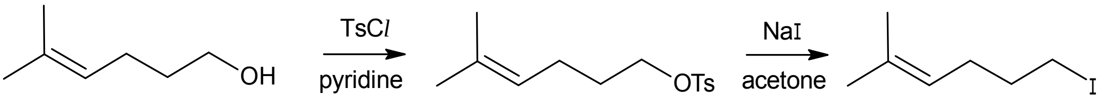
The activation energy will be **higher** and the rate of reaction **slower** if the reaction was uncatalysed.

When a catalyst is used,
- reaction takes place via an alternative pathway that requires a lower activation energy
- there are more reactant particles with energy ≥ E_a and frequency of effective collisions increases
- rate of reaction increases, since the rate of reaction is proportional to the frequency of effective collisions.

(d) Tosyl chlorides (TsC*l*) are often used to convert alcohols (ROH) into alkyl tosylates (ROTs) as shown below.

$$\mathrm{ROH} \xrightarrow[\text{pyridine}]{\mathrm{TsC}l} \mathrm{ROTs}$$

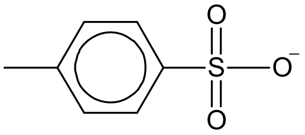
This conversion allows alcohols to undergo nucleophilic substitution reactions by converting the poor leaving group (OH) into a good leaving group (OTs). An example of this application is given below.



(i) The tosylate group is a better leaving group than the alcohol group due the greater stability of the TsO$^-$ ion formed compared to OH$^-$.

Suggest an explanation for the stability of the TsO$^-$ ion.

TsO$^-$ =

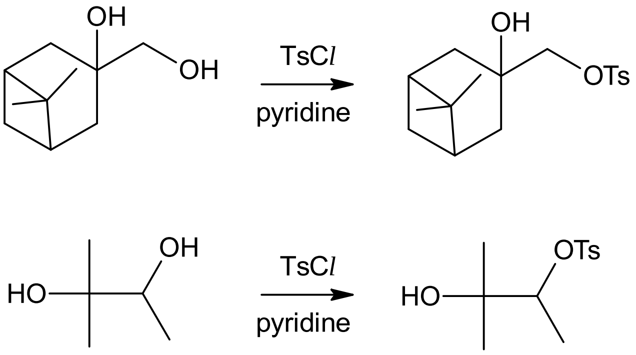


[1]

TsO$^-$ is **resonance stabilised** as the **negative charge on oxygen is delocalised into the adjacent S=O bond**.

(ii) The conversion of alcohols into alkyl tosylates using tosyl chlorides is selective in nature.

Consider the following examples involving diols and suggest a factor that affects the selectivity of the conversion. Explain your answer.

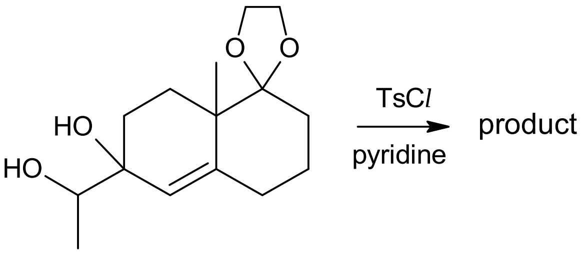


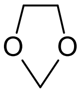
[2]

Degree of substitution of alcohol OR degree of **steric hindrance around alcohol** group.

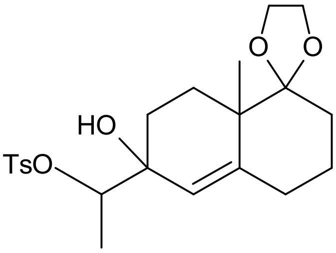
Tosyl group is a **bulky group** so TsC*l* can **approach the less hindered/ less substituted alcohol more easily**.

(iii) Predict the product of the following conversion.



The  ring remains unaltered in the reaction.

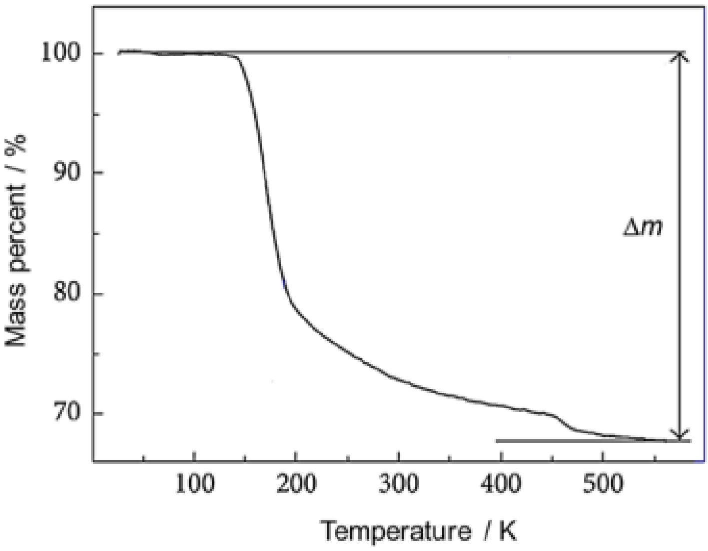
[1]



[Total: 20]

5 **(a)** Thermogravimetric analysis (TGA) is a technique where the mass of a sample in a controlled atmosphere is recorded as a function of temperature as the temperature of the sample is increased.

A sample of lithium pentaborate pentahydrate ($LiB_5O_8.5H_2O$) was subject to TGA and the graph obtained is shown below.



Suggest an explanation, supported with relevant calculations, for the loss in mass (Δm) of $LiB_5O_8.5H_2O$ observed in the graph.

[M_r ($LiB_5O_8.5H_2O$) = 278.9]

[2]

The mass loss is likely due to the **loss of the five water molecules** in $LiB_5O_8.5H_2O$.

% mass loss = $\frac{5 \times 18}{278.9} \times 100$ = **32.3 %** which agrees well with the value obtained from the graph (≈ 32.5 %).

(b) The sample of $LiB_5O_8.5H_2O$ used in **(a)** was synthesised as a system of Li_2O, B_2O_3 and H_2O in the laboratory.

(i) Deduce the molar ratio of $Li_2O : B_2O_3 : H_2O$ in a pure sample of $LiB_5O_8.5H_2O$.

[1]

Since $LiB_5O_8.5H_2O \equiv \frac{1}{2} Li_2O \equiv \frac{5}{2} B_2O_3 \equiv 5H_2O$,

molar ratio of $Li_2O : B_2O_3 : H_2O$ = **1 : 5 : 10**

(ii) Aqueous sodium hydroxide can be used to react with B_2O_3 to determine its actual amount in the sample.

Given that B_2O_3 and Al_2O_3 have similar reactions with aqueous sodium hydroxide under appropriate conditions, write a balanced equation for the reaction between B_2O_3 and aqueous sodium hydroxide.

[1]

$B_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[B(OH)_4]$

(c) Li_2O can be produced from the thermal decomposition of lithium peroxide, Li_2O_2.

(i) State and explain how the lattice energies of Li_2O and Li_2O_2 would differ.

[2]

$\Delta H_{latt}^{\ominus}(Li_2O)$ will be **more exothermic** than that of $\Delta H_{latt}^{\ominus}(Li_2O_2)$

For ionic compounds, $|\Delta H_{latt}| \propto \left|\frac{q_+q_-}{r_+ + r_-}\right|$

cationic charge (q_+) and radius (r_+) are the **same** for both compounds.
anionic charge (q_-) is the **same** for both compounds.
Anionic radius (r_-): $O^{2-} < O_2^{2-}$

(ii) Lithium peroxide reacts with carbon dioxide according to the equation shown below.

$$2Li_2O_2(s) + 2CO_2(g) \rightarrow 2Li_2CO_3(s) + O_2(g)$$

State the change in oxidation number of oxygen as Li_2O_2 is converted into the products.

[2]

The oxidation number of O **increases from –1 in Li_2O_2 to 0 in O_2**.

The oxidation number of O **decreases from –1 in Li_2O_2 to –2 in Li_2CO_3**.

(iii) Calculate the highest temperature reached when the 2.50 g of lithium carbonate was dissolved in 30 cm^3 of water at room temperature. The standard enthalpy change of solution of lithium carbonate is -18.2 kJ mol^{-1}.

[2]

Moles of $Li_2CO_3 = 2.50 / (6.9 \times 2 + 12 + 16 \times 3) = 0.033875$ mol
$q = 18.2 \times 10^3 \times 0.033875 =$ **616.53 J**

$\Delta T = q / mc = 616.53 / (30 \times 4.18) = 4.9165$ °C/K
Highest temperature = 20 + 4.9165 = **24.9 °C** OR **298 K**

(iv) Calculate the pH of the resulting solution formed in **(c)(iii)** given that the K_b of carbonate ion is 1.995×10^{-4} mol dm^{-3}.

[3]

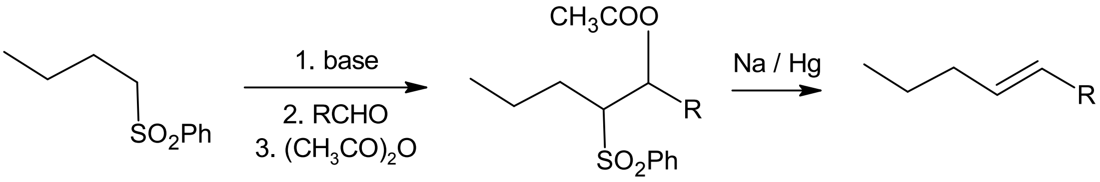
$[CO_3^{2-}] = \frac{0.033875}{0.030} = 1.129$ mol dm^{-3}

$$[OH^-] = \sqrt{\left(K_b \times [CO_3^{2-}]\right)}$$
$$= \sqrt{(1.995 \times 10^{-4} \times 1.129)}$$
$$= 0.01501 \text{ mol dm}^{-3}$$

pH = 14 – pOH = 14 + $\log_{10}(0.01501)$ = **12.2**

(d) Phenylsulfonyl ($PhSO_2$) and acetate (CH_3COO) groups on adjacent carbons in a starting material can be lost to form an alkene via Julia olefination.

An example of Julia olefination is as follows.



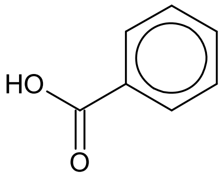
(i) Suggest the type of reaction occurring in the final step of Julia olefination. [1]

Elimination

Consider the reaction scheme below involving Julia olefination.

$$\mathbf{A} \xrightarrow[\substack{2.\ C_6H_5CHO \\ 3.\ (CH_3CO)_2O}]{1.\ \text{base}} \mathbf{B} \xrightarrow{Na\ /\ Hg} \underset{(C_{14}H_{16})}{\mathbf{C}} \xrightarrow[\text{heat}]{KMnO_4\ /H^+} \underset{(C_7H_6O_2)}{\mathbf{D}} + \underset{(C_7H_{10}O_6)}{\mathbf{E}}$$

(ii) Compound **D** effervesces with sodium carbonate. Suggest the structure of **D**. [1]



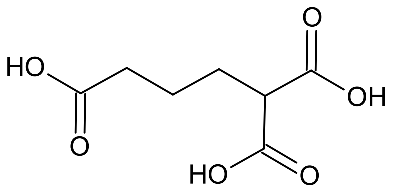
D
($C_7H_6O_2$)

(iii) Compound **E** is non-cyclic and has six carbons in the longest continuous carbon chain. It also does **not** contain any chiral carbon.

One mole of **E** reacts with three moles of thionyl chloride ($SOCl_2$) to liberate acidic gas.

Identify the functional group present in **E** and suggest its structure. [2]

Functional group: **carboxylic acid**

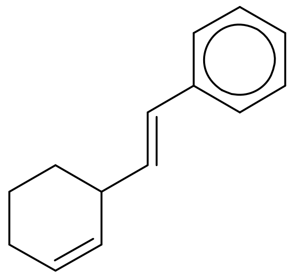


E

$(C_7H_{10}O_6)$

(iv) Hence suggest the structures of compounds **A** to **C**.

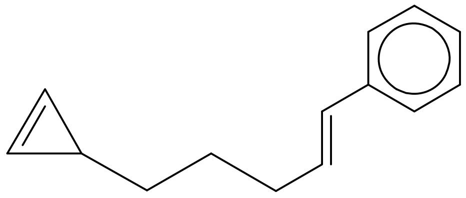
[3]



C

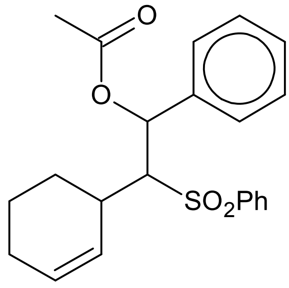
$(C_{14}H_{16})$

OR



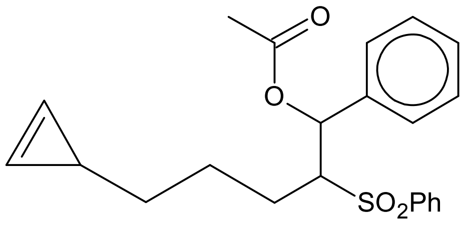
C

$(C_{14}H_{16})$

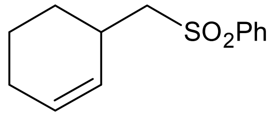


B

OR

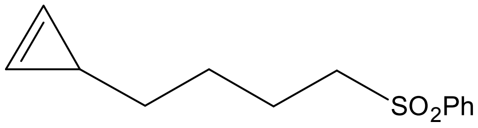


B



A

OR



A

[Total: 20]

Dunman High School

Year 6 H2 Chemistry 2018

Preparation List for Prelim Practical Exam

Chemicals Required

Label	Per candidate / cm^3	Identity
FA 1	1.5	Triacetin
FA 2	5	0.5% sodium carbonate solution in ethanol
FA 3	5	8% lipase solution
FA 4	5	Bromocresol purple solution
FA 5	250	0.5 mol dm^{-3} sodium chloride
FA 6	250	0.1 mol dm^{-3} copper(II) sulfate
FA 7	2	Fehling's solution II
FA 8	2	Formaldehye
FA 9	10	0.5 mol dm^{-3} sulfuric acid
-	10	Concentrated hydrochloric acid
-	Sufficient	Aluminium foil

Apparatus Required

S/N	Apparatus	Quantity per student
1	Funnel	1
2	250 cm^3 glass beaker	2
3	Graphite electrodes	2
4	DC power supply	1
5	Electrical wire with crocodile clips	2
6	Retort stand with boss clamp	1
7	Boiling tube	2
8	Test-tube	11
9	Test tube holder & rack	1
10	Delivery tube with test tube size stopper	1
11	Spatula	1
12	UI solution	1 bottle
13	UI paper	sufficient
14	1ml dropper	1
15	1ml syringe	2
16	Stopwatch	1
17	Bromocresol purple	1 bottle
18	Distilled water	
19	Lighter	1
20	Gauze and tripod	1

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2018
Year 6

H2 CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018
2 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Do not use staples, paper clips, glue or correction fluid.
6 **You are to start with Question 1 FIRST.**
7 Protective eye goggles and gloves must be worn at ALL TIMES.

Answer **ALL** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 17 and 18.

The number of marks is given in brackets, [ ], at the end of each question or part question.

Shift
Laboratory

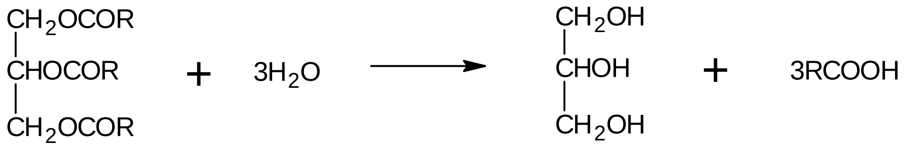
For Examiner's Use	
Question No.	**Marks**
1	**14**
2	**13**
3	**28**
Total	**55**

This question paper consists of **18** printed pages and **0** blank page.

Answer **all** questions in the spaces provided.

1 Investigation of reaction kinetics between triacetin and lipase

Lipase is an enzyme that breaks down, hydrolyses, the lipids present in animal fats and vegetable oils. It does so by hydrolysing ester bonds. A general reaction scheme for this process is shown below; the size of the R group and its level of saturation will depend on the lipid used.

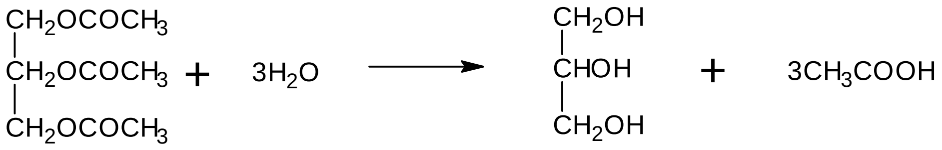


$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH$$

glycerol fatty acid

Olive oil is often used as a substrate in testing for lipase, with the oleic acid released being titrated with sodium hydroxide solution. Oleic acid, $C_{17}H_{33}COOH$, is a mono–unsaturated fatty acid.

In this experiment, glycerol triethanoate (triacetin) is used as the substrate. Lipase breaks this substrate down into glycerol and ethanoic acid as shown below.



$$\begin{array}{l} CH_2OCOCH_3 \\ | \\ CH_2OCOCH_3 \\ | \\ CH_2OCOCH_3 \end{array} + 3H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3COOH$$

glycerol triethanoate
(triacetin)

The ethanoic acid produced lowers the pH of the solution. This change can be detected by using a suitable acid–base indicator, bromocresol purple which changes from purple at high pH value to yellow at lower pH value. Sodium carbonate is added to the triacetin to ensure that the pH is high enough at the start of the experiment. Only after the sodium carbonate has all reacted with the liberated ethanoic acid will the ethanoic acid concentration rise and the pH value decreases. The reaction time is measured from the initial point of mixing the solutions until the end–point of the indicator is reached.

The following reagents are provided for this experiment.

FA 1 is triacetin
FA 2 is 0.5% sodium carbonate solution
FA 3 is 8% lipase solution
FA 4 is bromocresol purple solution

Procedure

1. To a test-tube, add 2 drops of **FA 2** followed by 1 drop of **FA 4**.

2. Using a dropper, add 5 drops of **FA 1** to the test tube.

3. Using a 250 cm^3 beaker, collect 200 cm^3 of warm water from the dispenser.

4. **Swirl the bottle** containing **FA 3** before using a syringe to transfer 0.20 cm^3 of **FA 3** into the test tube. Start the stopwatch immediately and place the test tube into the warm water bath.

5. **Shake the test tube continuously**. This is necessary to ensure that **FA 1** and **FA 3** are continually mixed.

6. Record the reaction time, ***t*** (in seconds) when the mixture turns yellow. This will be a gradual process.

7. Repeat steps 1 – 6 for four other test tubes, using different volumes of **FA 3** as shown in the table below.

Test Tube	Volume of **FA 3** / cm^3
1	0.20
2	0.40
3	0.60
4	0.80
5	1.00

8. Calculate the value of reaction rate, $\frac{1}{t}$, for each experiment.

(a) **Results:**

(i)

[4]

(ii) Plot the reaction rate, $\frac{1}{t}$, against the volume of **FA 3** used.

[3]

(iii) By considering the graph in **(a)(ii)**, deduce the order of reaction with respect to lipase, **FA 3**. Explain your deduction.

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………………………………………………………………………………………………..[3]

(iv) The **weighted reaction time** can be obtained by multiplying the appropriate conversion factor to the reaction time, ***t*** (in seconds).

Test Tube	Conversion factor	Weighted reaction time / s
1	0.20	
2	0.40	
3	0.60	
4	0.80	
5	1.00	

Based on your deduction in **(a)(iii)**, sketch the expected graph of **weighted reaction time, in seconds,** against the volume of **FA 3** used. Explain your sketch.

[1]

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………………………………………………………………………………………………..[1]

(b) Explain how the volumes of **FA 1**, **FA 2** and **FA 3** should change in the procedure in order to investigate the relationship between substrate concentration and the rate of reaction. You are **not** required to give exact figures.

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……………………………………………………………………………………………………[2]

[Total: 14]

2 Planning

An ideal gas is a theoretical idea – a gas in which there are no attractive forces between the molecules, and in which the molecules take up no space. The ideal gas law is usually stated as $pV = nRT$, where

- p is the pressure
- V is the volume
- n is the number of moles
- T is the temperature in K

of the gas, and

- R is the ideal gas constant.

The value of R is determined experimentally by measuring the other variables in the equation, and solving mathematically to get the value of the constant. R is the same for all gases – provided the gas has ideal behaviour.

In this experiment you will determine the ideal gas constant using H_2 gas. The H_2 will be generated using the reaction between magnesium and hydrochloric acid.

$$\text{Mg(s)} + 2\text{HC}l\text{(aq)} \rightarrow \text{MgC}l_2\text{(aq)} + \text{H}_2\text{(g)}$$

You may assume you are provided with:

- a two-necked round bottom flask,
- a rubber tubing,
- a water tub,
- 0.1 mol dm^{-3} hydrochloric acid,
- thermometer,
- barometer (instrument used to measure pressure),
- one piece of magnesium ribbon strip of about 0.06 g,
- apparatus normally found in a school laboratory

(a) Your plan should contain the following:

- the procedure that you would follow and the measurements that you would take
- a tabulation of the experimental data to be collected
- the reactants and conditions that you would use
- the mass of magnesium that you would use and the volume of hydrochloric acid that you would measure. Assume that the molar volume of gas under experimental conditions is 24.0 dm^3 mol^{-1}.
  [A_r: Mg, 24.3]

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……[7]

(b) State two basic assumptions of an ideal gas.

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……………………………………………………………………………………………………[2]

(c) Real gases do not obey the ideal gas law exactly. Sketch a **fully labelled** graph representing the deviation from ideality for one mole of each of the following gases.

- ideal gas
- H_2 gas
- CH_4 gas

[4]

[Total: 13]

3 Investigation of chemical reactions of electrolytes

You are provided with the following.
FA 5 is sodium chloride solution
FA 6 and **FA 9** are aqueous electrolytes, each containing one cation and one anion.

(a) Electrolysis of FA 5

1. Set up the apparatus and circuit as shown in Fig. 3.1.

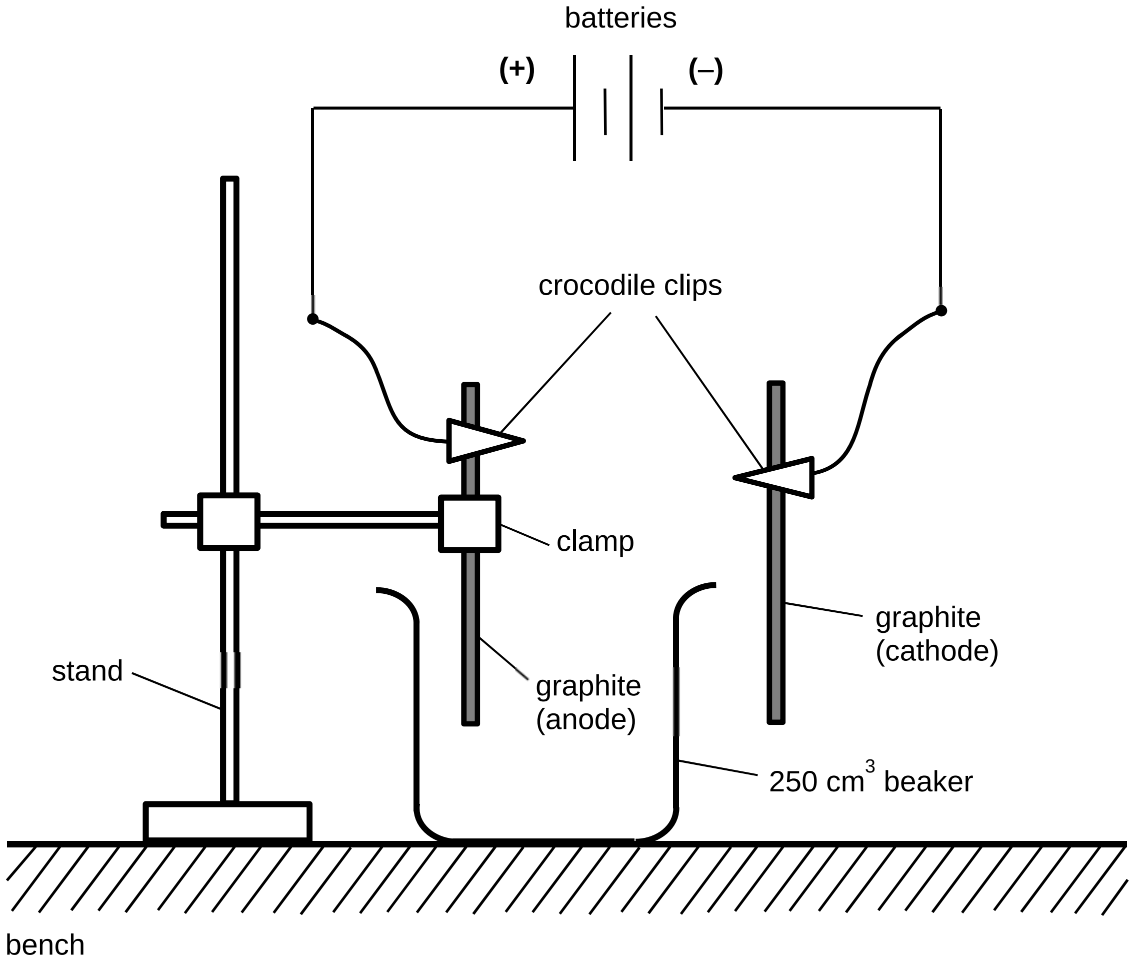

Fig 3.1

2. Transfer about 200 cm^3 of **FA 5** into the glass beaker.
3. Ensure that the graphite (anode) is partially submerged in **FA 5** by adjusting the height of the clamp.
4. Immerse one end of the graphite (cathode) in **FA 5** for a few minutes and record your observations in Table 3.1. You do **not** need to collect and test any gases evolved.

Table 3.1

electrolyte	observations at the electrodes
FA 5	anode:
	cathode:

[1]

5. Perform the tests described in Table 3.2, and record your observations in the table.

Table 3.2

tests		observations
1.	Add one drop of Universal Indicator solution to **FA 5** near the **cathode**.	
2.	Place a piece of moist blue litmus paper near the **anode**. Observe until no further change is seen.	

[2]

6. Remove both electrodes from **FA 5** and rinse them thoroughly with deionised water.

Consider your observations in Table 3.2.

(i) Explain, with the aid of an equation, the observations made in test 1 in Table 3.2.

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…………………………………………………………………………………………….[2]

(ii) With reference to the data below, suggest an explanation for your observations in test 2 in Table 3.2, in terms of *E* values.

electrode reaction	$E^\ominus$ / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

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…………………………………………………………………………………………….[3]

(b) (i) Qualitative analysis of FA 6

FA 7 is a solution of potassium sodium tartrate tetrahydrate in sodium hydroxide.
FA 8 is an organic compound with only one functional group.

Perform the tests described in Table 3.3, and record your observations in the table. You do **not** need to test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.3

tests		observations
1.	To 1 cm depth of **FA 6** in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	
2.	To 1 cm depth of **FA 6** in a test-tube, add an equal volume of **FA 7**. Add 1 cm depth of **FA 8** and shake the mixture thoroughly. Warm the mixture in a water bath. Observe the mixture until no further changes are seen.	

[4]

Identify the cation present in **FA 6** and the functional group present in **FA 8**.

Cation present in **FA 6**: ……………………………………………………………………[1]

Functional group present in **FA 8**: ……………………….......................................[1]

(ii) **Electrolysis of FA 6**

1. Repeat steps **1** to **3** of the procedure in **3(a)** using **FA 6**.
2. Immerse one end of the graphite (cathode) in **FA 6** for a few minutes until it is coated with a **thin layer of solid** and record your observations in Table 3.4. You do **not** need to identify any gases evolved.
3. Remove the graphite (cathode) from **FA 6** and rinse it with deionised water.
4. Retain the graphite (cathode) for further tests in **(b)(iii)**.

Table 3.4

electrolyte	observations at the electrodes
FA 6	anode:
	cathode:

[1]

(iii) Investigation of some chemical reactions involving the solid deposited

Perform the tests described in Table 3.5, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.5

	tests	observations
1.	Put the graphite (cathode) from **(b)(ii)** in a boiling tube. **Carry out the following steps in the fume hood.** Cautiously add 2 cm depth of **concentrated hydrochloric acid** to the boiling tube and shake the mixture thoroughly to dissolve, as much as possible, the solid coated on the electrode. Add an equal volume of **FA 6** to the boiling tube.	
Decant the solution into another boiling tube and retain it for tests 2 and 3.		
2.	Put about 2 cm depth of the solution from test 1 into a test-tube. Add an equal volume of potassium iodide and shake the mixture thoroughly. Filter the mixture.	
3.	Put about 2 cm depth of the solution from test 1 into a test-tube. Add 1 cm depth of deionised water to the test-tube. Then add a small piece of aluminium foil and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	

[6]

(c) Consider your observations in Table 3.5.

(i) Explain the colour changes you observed in test 1 in Table 3.5, in terms of the ions present in the solutions.

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…………………………………………………………………………………………..[2]

(ii) State the role of potassium iodide in test 2 in Table 3.5. Explain your answer in terms of oxidation state changes.

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…………………………………………………………………………………………..[1]

(d) **Identification of ions present in FA 9**

(i) Perform the tests described in Table 3.6, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.6

tests		observations
1.	Test the **FA 9** solution using Universal Indicator paper.	
2.	To 2 cm depth of **FA 9** in a test-tube, add barium nitrate dropwise, with shaking, until no further change is seen.	

[2]

(ii) Suggest the identity of **FA 9**. Describe one chemical test using a reagent from the Qualitative Analysis Notes provided to confirm the identity of the **cation** in **FA 9**.

Identity of **FA 9**: ……………………………………………………………………………[1]

Chemical test: ……………………………………………………………………………

…………………………………………………………………………………………..

…………………………………………………………………………………………..

……………………………………………………………………………………………[1]

[Total: 28]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^{-}(aq)$	gives white ppt. with $Ag^{+}(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^{-}(aq)$	gives pale cream ppt. with $Ag^{+}(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^{-}(aq)$	gives yellow ppt. with $Ag^{+}(aq)$ (insoluble in $NH_3(aq)$)
nitrate, NO_3^{-} (aq)	NH_3 liberated on heating with $OH^{-}(aq)$ and A*l* foil
nitrite, NO_2^{-} (aq)	NH_3 liberated on heating with $OH^{-}(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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Suggested solutions

DUNMAN HIGH SCHOOL
Preliminary Examinations 2018
Year 6

H2 CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018
2 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Give details of the practical shift and laboratory where appropriate, in the boxes provided.
3 Write in dark blue or black pen.
4 You may use an HB pencil for any diagrams or graphs.
5 Do not use staples, paper clips, glue or correction fluid.

Answer **ALL** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.

The number of marks is given in brackets, [ ], at the end of each question or part question.

Shift
Laboratory

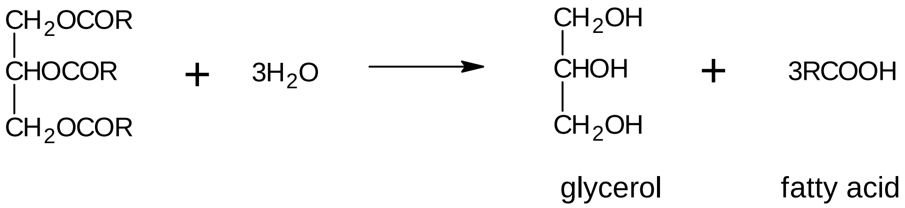
For Examiner's Use	
Question No.	**Marks**
1	**14**
2	**13**
3	**28**
Total	**55**

This question paper consists of **18** printed pages and **0** blank page.

Answer **all** questions in the spaces provided.

1 Investigation of reaction kinetics between triacetin and lipase

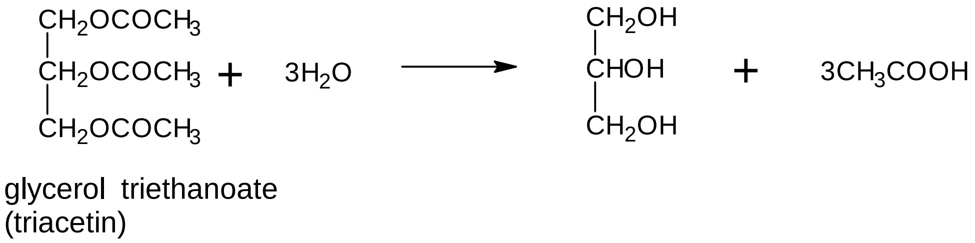
Lipase is an enzyme that breaks down, hydrolyses, the lipids present in animal fats and vegetable oils. It does so by hydrolysing ester bonds. A general reaction scheme for this process is shown below; the size of the R group and its level of saturation will depend on the lipid used.



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH$$

Olive oil is often used as a substrate in testing for lipase, with the oleic acid released being titrated with sodium hydroxide solution. Oleic acid, $C_{17}H_{33}COOH$, is a mono–unsaturated fatty acid.

In this experiment, glycerol triethanoate (triacetin) is used as the substrate. Lipase breaks this substrate down into glycerol and ethanoic acid as shown below.



$$\begin{array}{l} CH_2OCOCH_3 \\ | \\ CH_2OCOCH_3 \\ | \\ CH_2OCOCH_3 \end{array} + 3H_2O \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3COOH$$

The ethanoic acid produced lowers the pH of the solution. This change can be detected by using a suitable acid–base indicator, bromocresol purple which changes from purple at high pH value to yellow at lower pH value. Sodium carbonate is added to the triacetin to ensure that the pH is high enough at the start of the experiment. Only after the sodium carbonate has all reacted with the liberated ethanoic acid will the ethanoic acid concentration rise and the pH value decreases. The reaction time is measured from the initial point of mixing the solutions until the end–point of the indicator is reached.

The following reagents are provided for this experiment.

FA 1	is triacetin
FA 2	is 0.5% sodium carbonate solution
FA 3	is 8% lipase solution
FA 4	is Bromocresol purple solution

Procedure

1. To a test-tube, add 2 drops of **FA 2** followed by 1 drop of **FA 4**.
2. Using a dropper, add 5 drops of **FA 1** to the test tube.
3. Using a 250 cm^3 beaker, collect 200 cm^3 of warm water from the dispenser.
4. **Swirl the bottle** containing **FA 3** before using a syringe to transfer 0.20 cm^3 of **FA 3** into the test tube. Start the stopwatch immediately and place the test tube into the warm water bath.
5. **Shake the test tube continuously**. This is necessary to ensure that **FA 1** and **FA 3** are continually mixed.
6. Record the reaction time, ***t*** (in seconds) when the mixture turns yellow. This will be a gradual process.
7. Repeat steps 1 – 6 for four other test tubes, using different volumes of **FA 3** as shown in the table below.

Test Tube	Volume of **FA 3** / cm^3
1	0.20
2	0.40
3	0.60
4	0.80
5	1.00

8. Calculate the value of reaction rate, $\frac{\mathbf{1}}{\boldsymbol{t}}$, for each experiment.

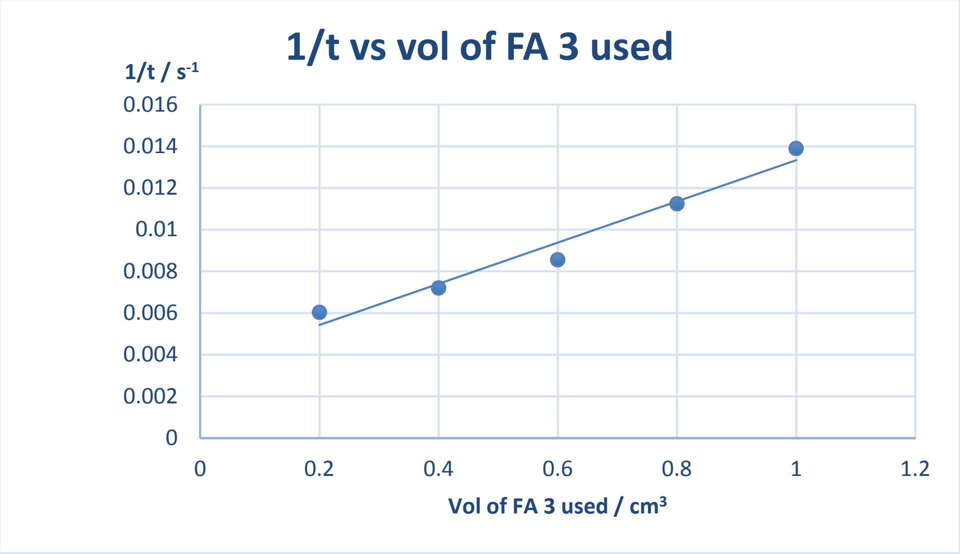
(a) Results:

(i)

Test Tube	Reaction time ‘t’ / s	1/t / s^{-1}
1	166	0.00602
2	139	0.00719
3	117	0.00854
4	89	0.0112
5	72	0.0138

[4]

(ii) Plot the reaction rate, $\frac{1}{t}$, against the volume of **FA 3** used.



[3]

(iii) By considering the graph in **(a)(ii)**, deduce the order of reaction with respect to lipase, **FA 3**. Explain your deduction.

[3]

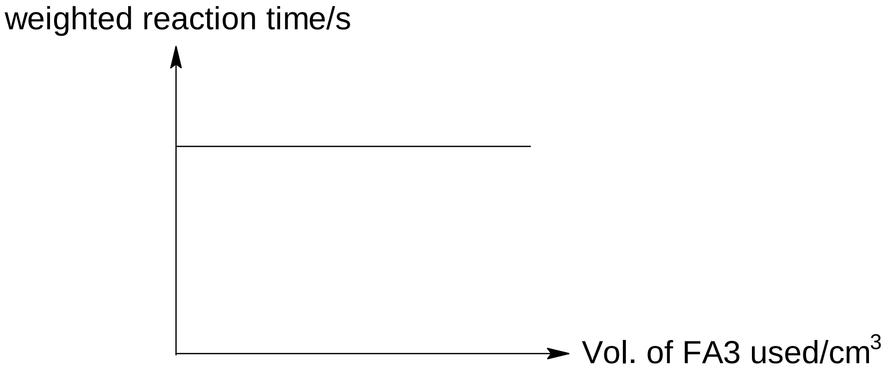
A best fit <u>linear graph</u> was obtained. This suggest that the relative rate as represented by 1/t **<u>increases proportionately</u>** with increasing volume of lipase used. The increasing volume of lipase used can be treated as increasing concentration since volume of all other reagents are maintained the same.
Hence, the **<u>order of reaction with respect to lipase is 1</u>**.

(iv) The **weighted reaction time** can be obtained by multiplying the appropriate conversion factor to the reaction time, ***t*** (in seconds).

Test Tube	Conversion factor	Weighted reaction time / s
1	0.20	
2	0.40	
3	0.60	
4	0.80	
5	1.00	

Based on your deduction in **(a)(iii)**, sketch the expected graph of **weighted reaction time, in seconds,** against the volume of **FA 3** used. Explain your sketch.

[2]



Since the **weighted factor is the same magnitude as the volume of FA3 used** and that **order of reaction with respect to FA3 is one**, a straight line with zero gradient is expected.

(b) Explain how the volumes of **FA 1**, **FA 2** and **FA 3** should change in the procedure in order to investigate the relationship between substrate concentration and the rate of reaction. You are **not** required to give exact figures.

[2]

The **volume of FA 1 (triacetin) must change with each experiment** eg it should increase from test tube 1 to 5 while the **volume of FA 3 (lipase) should be kept constant for all 5 test tubes**. The **volume of FA 2 (sodium carbonate) solution should be kept constant for all 5 test tubes**. Any changes in rate of reaction could then be attributed to the change in substrate concentration.

[Total: 14]

2 Planning

An ideal gas is a theoretical idea – a gas in which there are no attractive forces between the molecules, and in which the molecules take up no space. The ideal gas law is usually stated as $pV = nRT$, where

- p is the pressure
- V is the volume
- n is the number of moles
- T is the temperature in K

of the gas, and

- R is the ideal gas constant.

The value of R is determined experimentally by measuring the other variables in the equation, and solving mathematically to get the value of the constant. R is the same for all gases – provided the gas has ideal behaviour.

In this experiment you will determine the ideal gas constant using H_2 gas. The H_2 will be generated using the reaction between magnesium and hydrochloric acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

You may assume you are provided with:

- a two-necked round bottom flask,
- a rubber tubing,
- a water tub,
- 0.1 mol dm^{-3} hydrochloric acid,
- thermometer,
- barometer (instrument used to measure pressure),
- one piece of magnesium ribbon strip of about 0.06 g,
- apparatus normally found in a school laboratory

(a) Your plan should contain the following:

- the procedure that you would follow and the measurements that you would take
- a tabulation of the experimental data to be collected
- the reactants and conditions that you would use
- the mass of magnesium that you would use and the volume of hydrochloric acid that you would measure. Assume that the molar volume of gas under experimental conditions is 24.0 dm^3 mol^{-1}.
  [A_r: Mg, 24.3]

[7]

Pre-Calculations:

If 0.06 g of Mg was used,

No. of moles of HC*l* required = $\frac{0.06}{24.3} \times 2 = 4.938 \times 10^{-3}$ mol

Volume of HC*l* required = 49.38 cm^3 (volume of HC*l* used must be greater than 49.4 cm^3)

Volume of H_2 evolved = $2.469 \times 10^{-3} \times 24000 = 59.3$ cm^3 (assuming r.t.p.)

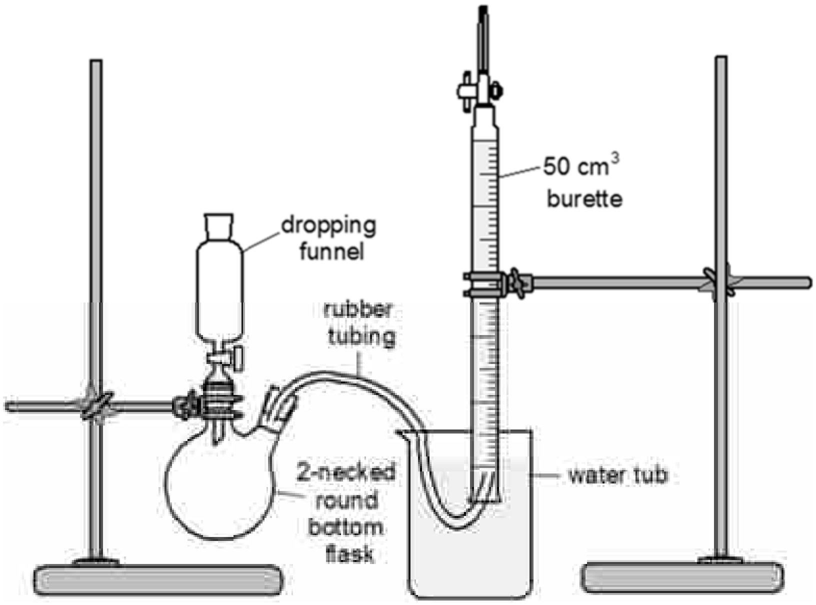
Maximum mass of Mg allowed to evolve 50 cm^3 of H_2:

No. of moles of Mg = $\frac{0.05}{24} = 2.083 \times 10^{-3}$ mol

Mass of Mg = $2.083 \times 10^{-3} \times 24.3 = 0.0506$ g

Minimum volume of HC*l* required = $\frac{2.083 \times 10^{-3} \times 2}{0.1} = 0.0417$ dm^3 = 41.7 cm^3

Procedure:



1) Cut the magnesium strip to three roughly equal pieces. **Using a weighing balance, weigh each piece of magnesium strip in a weighing bottle**. Each strip should weigh about 0.02 g.

2) Place one piece of cut **magnesium strip into the two-necked round bottom flask.**

3) Secure the two-necked round bottom flask with a retort stand.

4) Using a 50 cm^3 measuring cylinder, **measure out 25 cm^3 of 0.1 mol dm^{-3} hydrochloric acid**. Transfer the 25 cm^3 of 0.1 mol dm^{-3} hydrochloric acid to a dropping funnel.

5) **Connect the dropping funnel** to one of the necks of the two-necked round bottom flask.

6) Fill the water tub with tap water.

7) **Submerge the mouth of an inverted 50.00 cm^3 burette (filled with water) in the water tub** and secure the burette with a second retort stand. Adjust the water level in the burette until it is between 48.00 cm^3 and 50.00 cm^3. Note and record the **initial reading of the burette**.

8) **Connect one end of a rubber tubing** (with stopper) to the other neck of the two-necked round bottom flask and place the other end inside the inverted burette.

9) Measure and record the **ambient temperature using the thermometer**.

10) Measure and record the **pressure of the room using the barometer**.

11) Open the tap of the dropping funnel fully and gently swirl the two-necked round bottom flask. Close the tap immediately when all the hydrochloric acid is added.

12) **Note the final reading of the burette when all effervescence has ceased**.

13) **Repeat Steps 2 to 12 with the other two pieces of magnesium.**

Tabulation of data:

Experiment	Mass of empty weighing bottle /g	Mass of weighing bottle and Mg strip /g	Mass of Mg strip used / g	Final burette reading / cm^3	Initial burette reading / cm^3	Volume of H_2 produced / cm^3	Temperature / °C	Barometer reading / kPa
1								
2								
3								

(b) State two basic assumptions of an ideal gas.

[2]

The gas particles have **negligible volume compared to the volume of the container**.

There are **no intermolecular forces of attraction** between gas particles.

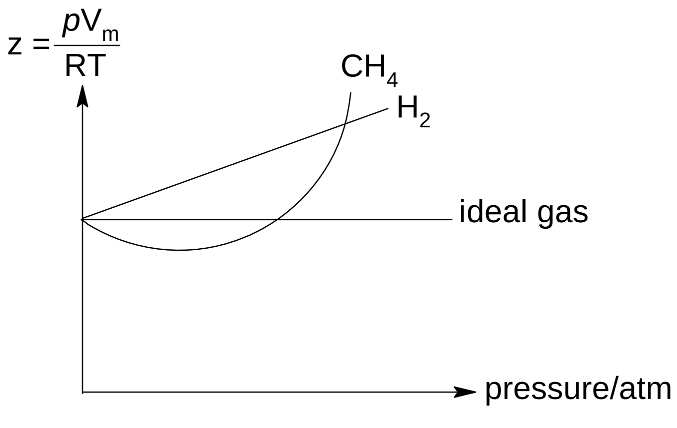
The collisions which occur between gas particles and with walls of the container are **perfectly elastic**.

The gas particles are in **constant random motion.**

(c) Real gases do not obey the ideal gas law exactly. Sketch a **fully labelled** graph representing the deviation from ideality. Your sketch should include:

- ideal gas
- H_2 gas
- CH_4 gas

[4]



[Total: 13]

3 Investigation of chemical reactions of electrolytes

You are provided with the following.
FA 5 is sodium chloride solution.
FA 6 and **FA 9** are aqueous electrolytes, each containing one cation and one anion.

(a) Electrolysis of FA 5

1. Set up the apparatus and circuit as shown in Fig. 3.1.

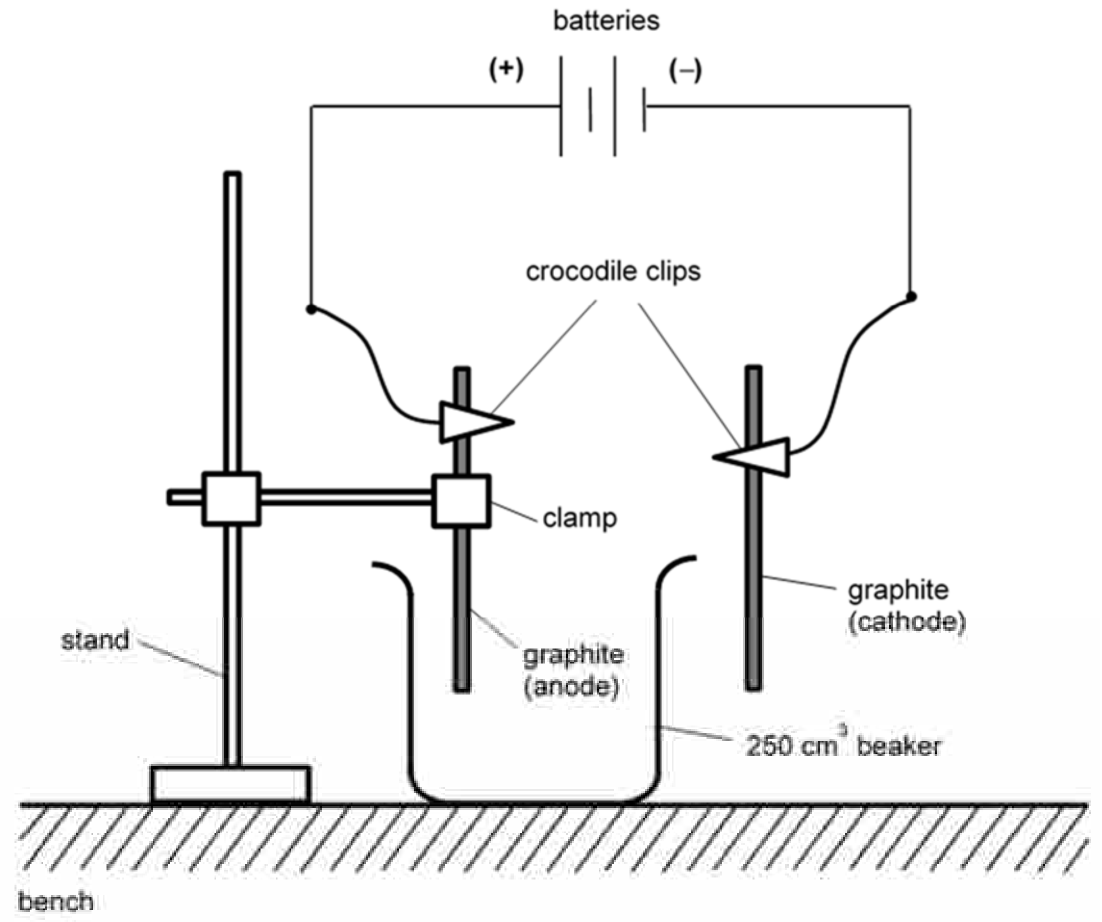


Fig 3.1

2. Transfer about 200 cm^3 of **FA 5** into the glass beaker.
3. Ensure that the graphite (anode) is partially submerged in **FA 5** by adjusting the height of the clamp.
4. Immerse one end of the graphite (cathode) in **FA 5** for a few minutes and record your observations in Table 3.1. You do **not** need to collect and test any gases evolved.

Table 3.1

electrolyte	observations at the electrodes
FA 5	anode: **effervescence / bubbles** of greenish yellow, pungent gas observed
	cathode: vigorous **effervescence /** more **bubbles** of colourless, odourless gas observed

[1]

5. Perform the tests described in Table 3.2, and record your observations in the table.

Table 3.2

tests		observations
1.	Add one drop of Universal Indicator solution to **FA 5** near the **cathode**.	**Green** Universal Indicator solution turned **purple/violet**.
2.	Place a piece of moist blue litmus paper near the **anode**. Observe until no further change is seen.	**Gas evolved** turned moist blue litmus paper red and then **bleached** it.

[2]

6. Remove both electrodes from **FA 5** and rinse them thoroughly with deionised water.

Consider your observations in Table 3.2.

(i) Explain, with the aid of an equation, the observations made in test 1 in Table 3.2. [2]

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Water is preferentially reduced at the cathode, producing hydrogen gas and **hydroxide ions** which make the solution near the cathode **basic**.

(ii) With reference to the data below, suggest an explanation for your observations in test 2 in Table 3.2, in terms of *E* values.

electrode reaction	$E^\ominus$ / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

The observations from test 2 of Table 3.2 suggest that **chlorine gas is produced at the anode**.

Thus **FA 5** could be concentrated sodium chloride solution with a **high concentration of chloride ions** (> 1 mol dm^{-3}) so that by **Le Chatelier's Principle, the position of the $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ equilibrium will shift to the left** to favour the backward oxidation reaction.

Then **$E(Cl_2/Cl^-)$ becomes less positive than $E^\ominus(O_2/H_2O) = +1.23$ V** and chloride ion is preferentially oxidised at the anode.

[3]

(b) (i) Qualitative analysis of FA 6

FA 7 is a solution of potassium sodium tartrate tetrahydrate in sodium hydroxide.
FA 8 is an organic compound with only one functional group.

Perform the tests described in Table 3.3, and record your observations in the table. You do **not** need to test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.3

	tests	observations
1.	To 1 cm depth of **FA 6** in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	Blue ppt formed, soluble in excess aqueous ammonia to give dark blue solution.
2.	To 1 cm depth of **FA 6** in a test-tube, add an equal volume of **FA 7**.	Blue ppt formed, soluble in excess **FA 7** to give dark blue solution.
	Add 1 cm depth of **FA 8** and shake the mixture thoroughly.	Dark blue solution turned lighter blue (due to dilution).
	Warm the mixture in a water bath. Observe the mixture until no further changes are seen.	Effervescence of gas Blue solution turned purple and then colourless. Brick-red / red-brown precipitate formed.

[4]

Identify the cation present in **FA 6** and the functional group present in **FA 8**.

[2]

FA 6: **$Cu^{2+}(aq)$**
FA 8: (aliphatic) **Aldehyde**

(ii) Electrolysis of FA 6

1. Repeat steps **1** to **3** of the procedure in **3(a)** using **FA 6**.
2. Immerse one end of the graphite (cathode) in **FA 6** for a few minutes until it is coated with a **thin layer of solid** and record your observations in Table 3.4. You do **not** need to identify any gases evolved.
3. Remove the graphite (cathode) from **FA 6** and rinse it with deionised water.
4. Retain the graphite (cathode) for further tests in **(b)(iii)**.

Table 3.4

electrolyte	observations at the electrodes
FA 6	anode: **bubbles** of colourless, odourless gas observed
	cathode: **pink/red-brown solid** deposited

[1]

(iii) Investigation of some chemical reactions involving the solid deposited

Perform the tests described in Table 3.5, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.5

tests		observations
1.	Put the graphite (cathode) from **(b)(ii)** in a boiling tube.	
	Carry out the following steps in the fume hood.	
	Cautiously add 2 cm depth of **concentrated hydrochloric acid** to the boiling tube and shake the mixture thoroughly to dissolve, as much as possible, the solid coated on the electrode.	Pink/red-brown solid dissolved to give yellow solution.
	Add an equal volume of **FA 6** to the boiling tube.	Yellow solution turned green.
Decant the solution into another boiling tube and retain it for tests 2 and 3.		
2.	Put about 2 cm depth of the solution from test 1 into a test-tube.	
	Add an equal volume of potassium iodide and shake the mixture thoroughly.	Green solution turned brown/orange. White/cream precipitate formed.
	Filter the mixture.	Brown/orange solution as filtrate and White/cream solid as residue.
3.	Put about 2 cm depth of the solution from test 1 into a test-tube.	

	Add 1 cm depth of deionised water to the test-tube. Then add a small piece of aluminium foil and shake the mixture thoroughly. Observe the mixture until no further changes are seen.	Green solution turned pale blue/pale green. Effervescence of a colourless, odourless gas that extinguished a lighted splint with a 'pop' sound. The gas is hydrogen. Aluminium foil dissolved and red-brown solid formed on its surface. Pale blue/ pale green solution decolourised.

[6]

(c) Consider your observations in Table 3.5.

(i) Explain the colour changes you observed in test 1 in Table 3.5, in terms of the ions present in the solutions.

Copper deposited on the electrode dissolved in concentrated HC*l* to form **$[CuCl_4]^{2-}$** ions which gave the yellow solution.

FA 6 is blue due to the presence of **$[Cu(H_2O)_6]^{2+}$** ions in the solution.

On adding **FA 6** to the yellow solution, **a mixture of $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$** ions gave a green solution.

[2]

(ii) State the role of potassium iodide in test 2 in Table 3.5. Explain your answer in terms of oxidation state changes.

Potassium iodide is a **reducing agent** in test 2. The **oxidation number of iodine increased from –1 in I^- to 0 in I_2** while the oxidation number of copper deceased from +2 in Cu^{2+} to +1 in Cu^+.

[1]

(d) Identification of ions present in FA 9

(i) Perform the tests described in Table 3.6, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.6

tests		observations
1.	Test the **FA 9** solution using Universal Indicator paper.	Green UI paper turned dark brown and solution is **pH 1**
2.	To 2 cm depth of **FA 9** in a test-tube, add barium nitrate dropwise, with shaking, until no further change is seen.	white ppt formed

[2]

(ii) Suggest the identity of **FA 9**. Describe one chemical test using a reagent from the Qualitative Analysis Notes provided to confirm the identity of the **cation** in **FA 9**.

[2]

FA 9 is dilute **sulfuric acid**.

Add **CO_3^{2-}**(aq) ions to **FA 9** and **CO_2 will be liberated, forming white ppt with $Ca(OH)_2$(aq)**, if H^+ is present.

[Total: 29]

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

24 September 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, civics group and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

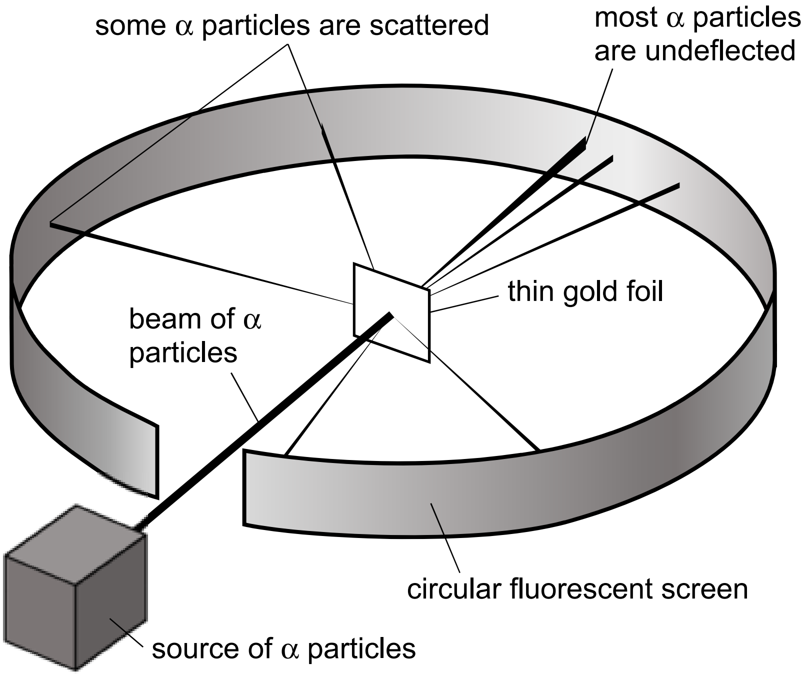
Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this question paper.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **12** printed pages.

1 Following J. J. Thomson's discovery of the electron in 1897, Ernest Rutherford devised the celebrated gold foil experiment, which led to a better understanding of the structure of the atom. In the experiment, a beam of heavy α particles, ${}^{4}_{2}He^{2+}$, was fired at a piece of thin gold foil as target.

As expected, most of the α particles passed straight through the gold foil undeflected. However, some α particles are scattered, and a small number in fact deflected right back to the source.



Which of the following conclusions **cannot** be drawn from the gold foil experiment?

A Atom is mostly empty space.

B Atom possesses a region of positive charge.

C Electrons in atom orbit around a dense positively charged region.

D The positive charge in an atom is concentrated within a very small volume.

2 The most common oxidation state of americium, Am, in aqueous solution is +*n*.

Recently, Cu^{3+} has been shown to quantitatively oxidise Am^{n+}(aq) in dilute HNO_3 to the +2*n* oxidation state, while itself is reduced to Cu^{2+}.

In an experiment, 25.0 cm^3 of 0.0100 mol dm^{-3} Am^{n+}(aq) was found to require 15.0 cm^3 of 0.0500 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium containing species formed?

A Am^{2+} **B** AmO_2 **C** AmO_2^{+} **D** AmO_2^{2+}

3 In which sequences are the molecules quoted in order of increasing bond angle around the central atom within the molecule?

A	OF_2	CH_4	SF_6
B	H_2O	O_3	N_2O
C	PF_3	BF_3	IF_3
D	NO_2	SO_2	CO_2

4 Unlike the reaction of ammonia with hydrogen chloride to give ammonium chloride, the reaction of ammonia with hydrogen fluoride produces colourless crystals of ammonium bifluoride, NH_4HF_2, which contains the bifluoride ion, HF_2^-:

$$NH_3(g) + 2HF(g) \rightarrow NH_4HF_2(s)$$

Which of the following chemical bonds are present in the ammonium bifluoride crystals?

1 ionic bond

2 dative bond

3 hydrogen bond

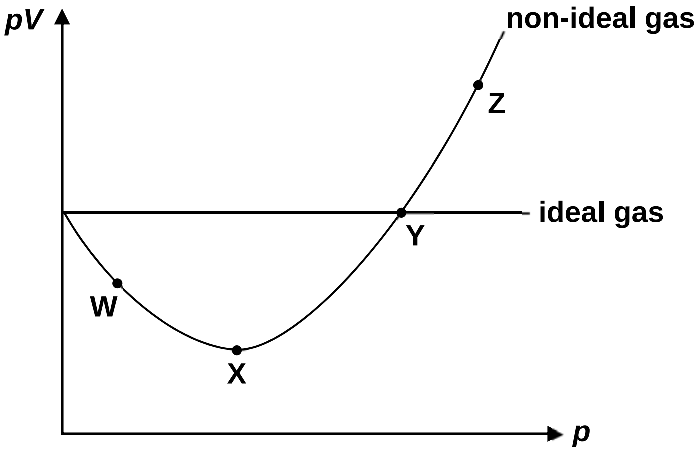
A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

5 The value of pV is plotted against p for two gases, an ideal gas and a non-ideal gas, where p is the pressure and V is the volume of the gas.



At which points on the graph, is the intermolecular forces of attraction within the non-ideal gas, the dominant factor accounting for deviation from ideal gas behavior?

A **W** only

B **W** and **X** only

C **W**, **X** and **Y** only

D **W**, **X** and **Z** only

6 There are conflicting interpretations for the origin of the acidity of aqueous boric acid, $B(OH)_3$. Some believe that the acidity is exclusively from the following equilibria:

$$B(OH)_3(aq) + H_2O(l) \qquad B(OH)_4^-(aq) + H^+(aq)$$

Which of the following statements pertaining to this interpretation of the acidity of boric acid is **incorrect**?

A Boric acid is an Arrhenius acid.

B Boric acid is a Brønsted-Lowry acid.

C Boric acid is a Lewis acid.

D Boric acid is a weak monobasic acid.

7 Chlorides of Period 3 elements dissolve in water to form aqueous solutions.

Which of the following sequence shows the order of increasing pH of the resultant solutions formed when these compounds are dissolved in water?

A $Al_2Cl_6 < MgCl_2 < NaCl$

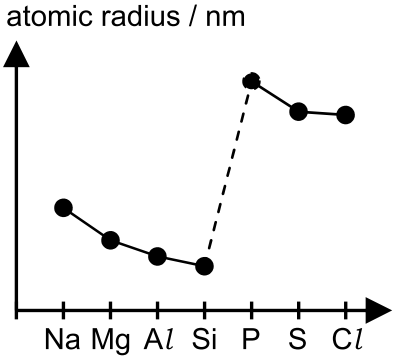
B $MgCl_2 < Al_2Cl_6 < SiCl_4$

C $PCl_5 < MgCl_2 < Al_2Cl_6$

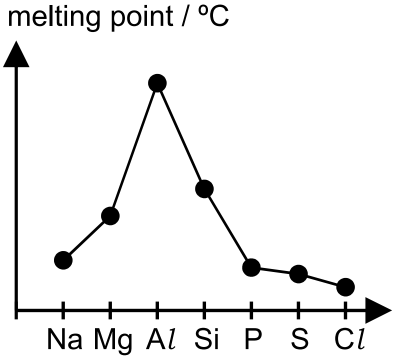
D $SiCl_4 < Al_2Cl_6 < PCl_5$

8 For the elements in Period 3 of the Periodic Table, which of the following sketches shows the correct trend in the stated property?

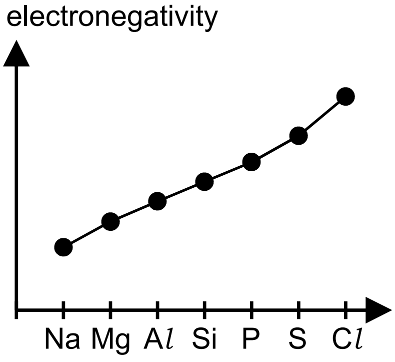
A



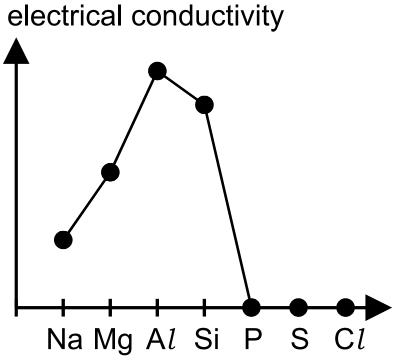
B



C



D



9 Sodium reacts with water to form sodium hydroxide and hydrogen.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H_1^\circ$$

What information is needed in order to calculate the standard enthalpy change of reaction, ΔH_1°?

1 ΔH_c° for $H_2(g)$

2 ΔH_c° for $H_2O(l)$

3 ΔH_f° for $NaOH(aq)$

4 ΔH_c° for $Na(s)$

A **1** and **2** only

B **1** and **3** only

C **2** and **3** only

D **1**, **2** and **4** only

10 Which reaction represents a standard enthalpy change at 298 K?

A $\frac{1}{2}O_2(g) \rightarrow O(g)$

B $C(g) + O_2(g) \rightarrow CO_2(g)$

C $2C(s) + 6H(g) \rightarrow C_2H_6(g)$

D $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

11 The reaction between $A(aq)$ and $B(aq)$ has a rate constant of 9×10^{-3} $mol^{-2}\,dm^6\,s^{-1}$.

Which one of the following is a possible rate equation for this reaction?

A $\text{rate} = k[B(aq)]$

B $\text{rate} = k[A(aq)]^2$

C $\text{rate} = k[A(aq)][B(aq)]^2$

D $\text{rate} = k[A(aq)]^2[B(aq)]^2$

12 The half-life of the first order gaseous reaction in which X_2 molecules become converted into X atoms is 20 minutes.

1 mol of X_2 is put into a sealed vessel at pressure *p*.

Which of the following will be correct when 87.5% of X_2 has been converted into X atoms?

1 60 minutes have elapsed.

2 1.75 mol of X atoms have been formed.

3 The total pressure is $\frac{15p}{8}$ (at constant temperature).

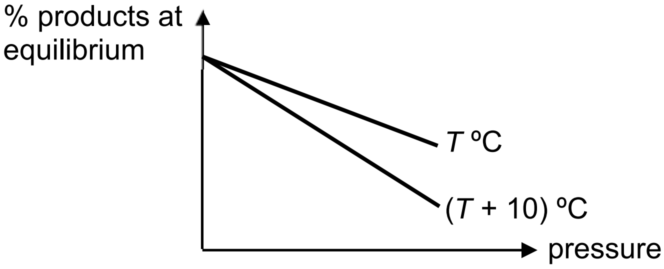
A **1** only is correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1**, **2** and **3** are correct

13 The graphs below show how the percentage of gaseous products present at equilibrium vary with temperature and pressure.



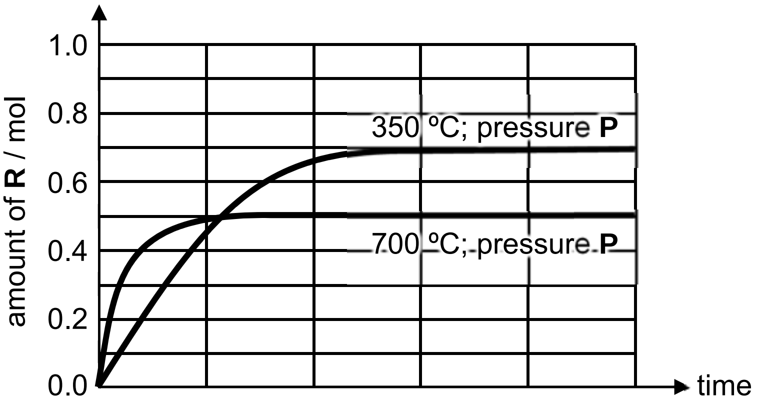
Which one of the following reactions could the graph represent?

A	$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	ΔH = +57 kJ mol^{-1}
B	$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	ΔH = +53 kJ mol^{-1}
C	$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$	ΔH = –221 kJ mol^{-1}
D	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	ΔH = –92 kJ mol^{-1}

14 **L** and **M** can react together to reach equilibrium in the reaction below.

$$\mathbf{L}(g) + \mathbf{M}(g) \rightleftharpoons \mathbf{Q}(g) + \mathbf{R}(g)$$

In an experiment, 1.0 mole each of **L** and **M** were reacted at constant pressure **P** and temperature 350 °C. The amount of **R** present in the mixture at intervals of time was recorded. The experiment was repeated at the same pressure **P**, but at a temperature of 700 °C. The results for both experiments are shown below.



Which one of the following information **cannot** be deduced from the graph?

A The value of K_p at 350 °C.

B The forward reaction is exothermic.

C The activation energy of the forward reaction is high.

D The equilibrium is achieved at a faster rate at higher temperatures.

15 The table gives the concentrations and pH values of the aqueous solutions of three compounds, **X**, **Y** and **Z** at 25 °C. Each compound could be an acid or a base.

	X	**Y**	**Z**
concentration	1.00×10^{-4} mol dm^{-3}	1.00 mol dm^{-3}	1.00 mol dm^{-3}
pH	4	3	14

A final year student made the following conclusions:

1 **X** is a strong acid and **Z** is a strong base.

2 The extent of dissociation of **X**(aq) is higher than in **Y**(aq).

3 Mixture of equal volume of **Y** and **Z** will give a resulting solution of pH > 7.

Which of the above conclusions are **correct**?

A Conclusion **1** only

B Conclusion **2** only

C Conclusions **2** and **3** only

D All three conclusions are correct

16 In which of the following solution will solid silver phosphate, Ag_3PO_4, be the least soluble at 25 °C?

Given that the numerical value of $K_{sp}(Ag_3PO_4) = 8.89\times10^{-17}$.

A pure water

B 0.10 mol dm^{-3} $AgNO_3(aq)$

C 0.10 mol dm^{-3} $NH_3(aq)$

D 0.10 mol dm^{-3} $Na_3PO_4(aq)$

17 Which compound exhibits both *cis-trans* and enantiomerism?

A $CH_3CH_2CHBrCH{=}CHBr$

B $CH_3CH{=}CHCH_2CH_3$

C $CH_3CHBrCH{=}CH_2$

D $CH_3CBr{=}CBrCH_3$

18 Which structural formula represents 2,2-dimethylpentane?

A $(CH_3)_3CCH(CH_3)_2$

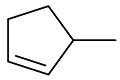
B $(CH_3)_3CCH_2C(CH_3)_3$

C $CH_3CH_2CH_2C(CH_3)_3$

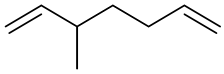
D $(CH_3)_2CHCH_2CH(CH_3)_2$

19 Which of the following hydrocarbons would give the same organic product upon oxidation with hot acidified $KMnO_4$?

1



2



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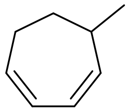


A **1**, **2** and **3** are correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1** and **3** only are correct

20 Which of the following compounds reacts with benzene under suitable conditions to form $C_6H_5COC_6H_5$?

A C_6H_5CHO

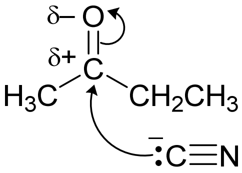
B C_6H_5COOH

C $C_6H_5CH_2OH$

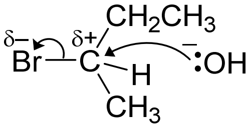
D C_6H_5COCl

21 The **rate-determining step** of two different reaction mechanisms are shown below:

first
reaction mechanism



second
reaction mechanism



What do both reaction mechanism steps have in common?

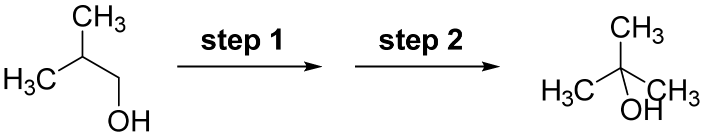
A Intermediates are formed.

B They involve addition of nucleophile.

C The overall rate of reaction is second order.

D The products formed can rotate plane polarised light.

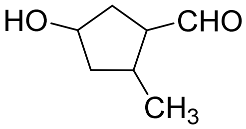
22 2-methylpropan-1-ol can be converted into 2-methylpropan-2-ol in two steps.



Which one of the following sequences may be used for the conversion?

	step 1	step 2
A	PCl_5 at r.t.p.	NaOH(aq), heat
B	conc. H_2SO_4, heat	alkaline $KMnO_4$, cold
C	Al_2O_3 with heating	H_2O with H_3PO_4 at high temperature and pressure
D	alcoholic NaOH	dilute H_2SO_4

23 Tollens' reagent is added to the following organic compound and warmed. What are the products formed as a result?



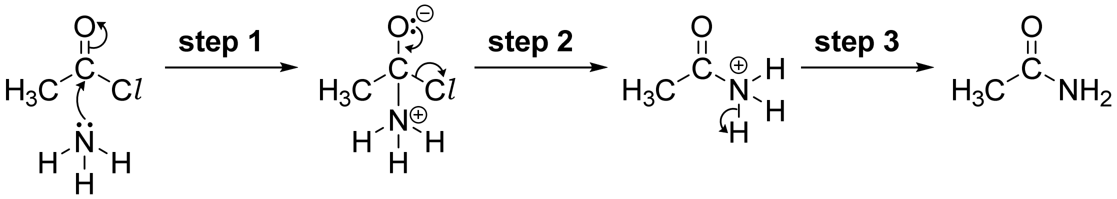
A Silver mirror and an organic compound containing a carboxylic acid

B Silver mirror and an organic compound containing a carboxylate salt

C Silver mirror and an organic compound containing a ketone and a carboxylic acid

D Silver mirror and an organic compound containing a ketone and a carboxylic salt

24 The reaction between ammonia and ethanoyl chloride proceeds *via* the nucleophilic acyl substitution mechanism shown below.



Which of the statements is **incorrect** about the above mechanism?

A Ammonia behaves as a nucleophile.

B Arrow pushing in **step 2** has been shown correctly.

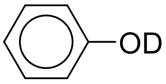
C Ethanoyl chloride behaves as an electrophile.

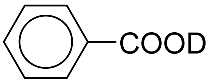
D Proton loss in **step 3** has been shown correctly.

25 Phenyl propanoate undergoes acid hydrolysis in the presence of water labelled with the deuterium ^2D isotope.

Which of the following products are formed?

1 CH_3CH_2COOD

2 

3 

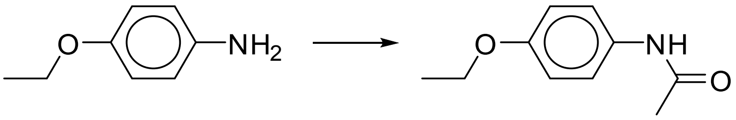
A Only **1**

B **1** and **2** only

C **1** and **3** only

D **1**, **2** and **3**

26 The synthesis of an aromatic amide from compound **X** is shown below.



What is the most suitable reagent to use in this synthesis?

A CH_3COCl

B CH_3COCH_3

C CH_3CONH_2

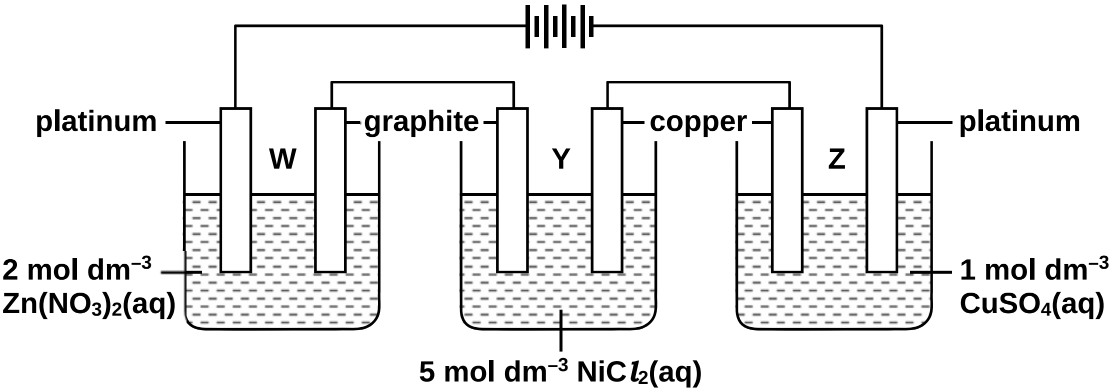
D CH_3COOH

27 Which of the following shows the nitrogen compounds arranged in order of increasing pK_b values?

A	NH_3	<	CH_3NH_2	<	$(CH_3)_2NH$
B	$CH_3CH_2NH_2$	<	NH_3	<	$C_6H_5NH_2$
C	$CH_3CH_2NH_2$	<	$(C_2H_5)_2NH$	<	$C_6H_5NH_2$
D	$C_6H_5NH_2$	<	NH_3	<	$CH_3CH_2NH_2$

28 *Use of the Data Booklet is relevant to this question.*

The following electrolytic cell is set up.

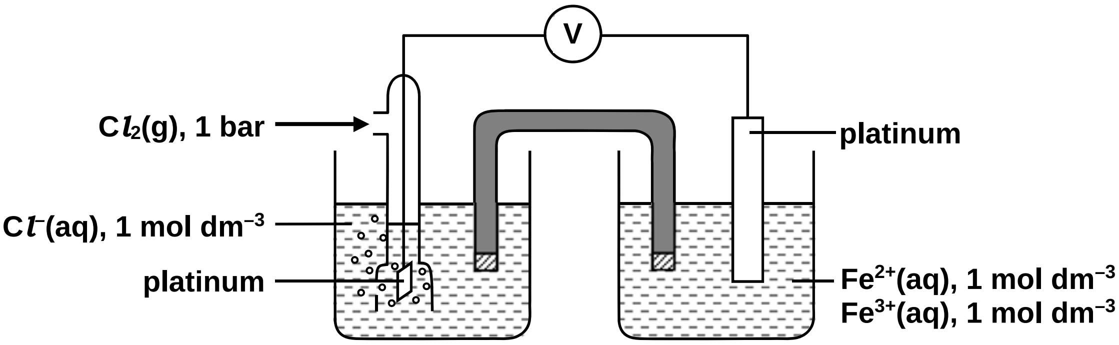


What is the ratio of the volume of gas formed at the anode in cell **W** : cell **Y** : cell **Z**?

A 1 : 1 : 1 **B** 1 : 2 : 1 **C** 1 : 1 : 0 **D** 1 : 2 : 0

29 *Use of the Data Booklet is relevant to this question.*

The cell shown below is set up.



Which statements are correct?

1 The voltmeter will register an initial reading of 0.59 V, which decreases gradually with time.

2 Addition of a few crystals of silver(I) nitrate to the left-hand-side half-cell will cause the voltmeter reading to increase.

3 Addition of excess solid sodium cyanide to the right-hand-side half-cell will cause the voltmeter reading to increase.

A **1** only is correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1**, **2** and **3** are correct

30 Which of the following processes is **not** involved in the following reaction between the two transition metal complexes in acidic medium?

$$\left[CoCl(NH_3)_5\right]^{2+} + \left[Cr(OH_2)_6\right]^{2+} + 5H_3O^+ \rightarrow \left[CrCl(OH_2)_5\right]^{2+} + \left[Co(OH_2)_6\right]^{2+} + 5NH_4^+$$

A electron transfer

B hydration

C ligand exchange

D neutralisation

Answer :

Question	Answer	Question	Answer
1	**C**	16	**B**
2	**D**	17	**A**
3	**B**	18	**C**
4	**A**	19	**A**
5	**B**	20	**D**
6	**B**	21	**C**
7	**A**	22	**C**
8	**C**	23	**B**
9	**B**	24	**D**
10	**A**	25	**B**
11	**C**	26	**A**
12	**D**	27	**B**
13	**C**	28	**D**
14	**C**	29	**D**
15	**D**	30	**B**

2018 JC2 Preliminary Examination
H2 Chemistry 9729
Paper 1 Worked Solution

1 The positive α particles either passes straight through the empty space or are occasionally repelled by the dense positive nucleus. They are not affected by the much smaller electrons and hence does not provide any information about the electrons.

⇒ **C**

2 [O] : $Am^{n+} \rightarrow Am^{2n+} + ne^-$

[R] : $nCu^{3+} + ne^- \rightarrow nCu^{2+}$

So, $Am^{n+} + nCu^{3+} \rightarrow Am^{2n+} + nCu^{2+}$

$$n_{Am^{n+}} = \frac{25.0}{1000} \times 0.0100 = 2.5 \times 10^{-4} \text{ mol}$$

$$n_{Cu^{3+}} = \frac{15.0}{1000} \times 0.0500 = 7.5 \times 10^{-4} \text{ mol}$$

$n_{Am^{n+}} : n_{Cu} = 1 : n = 1 : 3 \Rightarrow n = 3$

Am species formed has O.S. of +6 $\left(AmO_2^{2+}\right)$

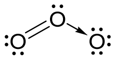
⇒ **D**

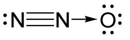
3 OF_2 : 2 b.p. + 2 l.p. ⇒ bent ⇒ 105º

CH_4 : 4 b.p. + 0 l.p. ⇒ tetrahedral ⇒ 109.5º

SF_6 : 6 b.p. + 0 l.p. ⇒ octahedral ⇒ 90º

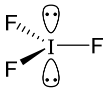
H_2O : 2 b.p. + 2 l.p. ⇒ bent ⇒ 105º

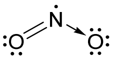
O_3 :  ⇒ bent ⇒ <120º

N_2O :  ⇒ linear ⇒ 180º

PF_3 : 3 b.p. + 1 l.p. ⇒ trig. pyr. ⇒ 107º

BF_3 : 3 b.p. + 0 l.p. ⇒ trig. planar ⇒ 120º

IF_3 :  ⇒ trig. planar ⇒ 120º

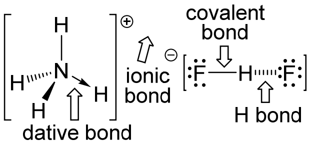
NO_2 :  ⇒ bent ⇒ >120º

SO_2 : 2 b.p. + 1 l.p. ⇒ bent ⇒ <120º

CO_2 : 2 b.p. + 0 1.p. ⇒ linear ⇒ 180º

⇒ **B**

4 Bonding in solid NH_4HF_2:



⇒ **A**

5 At low pressure, gas particles are far apart. IMF between particles causes force they impinge on wall to be smaller and thus pressure is lower than ideal gas ⇒ $pV_{real} < pV_{ideal}$

At higher pressure, gas particles are close together and the volume occupied by particles is significant compared to volume of container. Hence the gas occupies a larger volume than ideal gas ⇒ $pV_{real} > pV_{ideal}$

⇒ **B**

6 ✓Arrhenius acid: Produces H^+(aq) in water

✗ Brønsted-Lowry acid: H^+ donor; $B(OH)_3$ accepts a OH^- and does not donate H^+

✓Lewis acid: Lone pair acceptor; accepts a lone pair fron OH^-

✓Monobasic acid: each mole of $B(OH)_3$ reacts with one mole of OH^-

⇒ **B**

7 NaCl : no hydrolysis ⇒ pH = 7

$MgCl_2$: slight hydrolysis ⇒ pH ≈ 6.5

$MgCl_2 + H_2O \ldots Mg(OH)Cl + HCl$

$AlCl_3$: extensive hydrolysis ⇒ pH ≈ 3

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$

$SiCl_4$: complete hydrolysis ⇒ pH ≈ 1

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

PCl_5 : complete hydrolysis ⇒ pH ≈ 1

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

⇒ **A**

8 **A** ✗: Graph is for ionic radii

B ✗: Melting point of Si should be highest due to extensive strong Si–Si covalent bonds within giant molecular structure

C ✓: Nuclear charge increases across period while shielding effect is the same, hence ENC increases across the period resulting in increase in electronegativity

D ✗: Silicon being a metalloid should only have conductivity below that of the metals (Na, Mg, Al)

⇒ **C**

9
$$\begin{aligned}\Delta H_1^{\ominus} &= \sum \Delta H_f^{\ominus}(\text{products}) - \sum \Delta H_f^{\ominus}(\text{reactants}) \\ &= 2\Delta H_f^{\ominus}(NaOH(aq)) + \Delta H_f^{\ominus}(H_2(g)) - \\ &\quad 2\Delta H_f^{\ominus}(Na(s)) - 2\Delta H_f^{\ominus}(H_2O(l)) \\ &= 2\Delta H_f^{\ominus}(NaOH(aq)) + 0 - \\ &\quad 0 - 2\Delta H_f^{\ominus}(H_2O(l)) \\ &= 2\Delta H_f^{\ominus}(NaOH(aq)) - 2\Delta H_f^{\ominus}(H_2O(l))\end{aligned}$$

$\Delta H_f^{\ominus}(H_2O(l)) = \Delta H_c^{\ominus}(H_2(g))$ as both corresponds to the same reaction:

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

⇒ **B**

10 **B** ✗: At 298 K, C is a solid

C ✗: Hydrogen exists as H_2 under std state

D ✗: At 298 K, H_2O is a liquid

⇒ **A**

11 Units for rate is concentration per unit time, in this case, mol dm^{-3} s^{-1}

If k has units of mol^{-2} dm^6 s^{-1}, the reaction must be overall third order:

$$\text{mol dm}^{-3}\ \text{s}^{-1} = \left(\text{mol}^{-2}\ \text{dm}^3\ \text{s}^{-1}\right)\left(\text{mol dm}^{-3}\right)^3$$

⇒ **C**

12 Given $X_2(g) \rightarrow 2X(g)$,

rate $= k[X_2]$, $t_{\frac{1}{2}} = 20$ min

1 ✓: 12.5% X_2 is left after 3 $t_{\frac{1}{2}}$ (60 min).

i.e. 87.5% of X_2 had reacted

$$\underset{}{X_2} \xrightarrow{t_{\frac{1}{2}}} \underset{50\%\ X_2}{\tfrac{1}{2}X_2} \xrightarrow{t_{\frac{1}{2}}} \underset{25\%\ X_2}{\tfrac{1}{4}X_2} \xrightarrow{t_{\frac{1}{2}}} \underset{12.5\%\ X_2}{\tfrac{1}{8}X_2}$$

2 ✓: $n_X = 2n_{X_2\ \text{reacted}} = 2 \times \frac{87.5}{100} \times 1 = 1.75$ mol

3 ✓: $n_{gas} = n_{X_2} + n_X = \frac{12.5}{100} \times 1 + 1.75 = \frac{15}{8}$ mol

At constant temperature and volume,

$$\frac{p_1}{n_1} = \frac{p_2}{n_2} \Rightarrow p_2 = \frac{p_1}{n_1} \times n_2 = \frac{p}{1} \times \frac{15}{8} = \frac{15}{8}p$$

⇒ **D**

13 From the graph,

As pressure increases, % products decreases. Hence, there must be more gaseous particles on the product side, since backward reaction is favoured to decreases the pressure

As temperature increases, % products decreases. Hence the forward reaction must be exothermic, since backward reaction is favoured to absorb heat

⇒ **C**

14 **A** ✗: $n_{\mathbf{Q}} = n_{\mathbf{R}}$; $n_{\mathbf{L}} = n_{\mathbf{M}} = 1.0 - n_{\mathbf{R}}$

Since $n_{\mathbf{R}}$ at eqm can be read from the graph, the partial pressures of **L**, **M**, **Q** and **R** can be obtained. Hence K_p can be obtained.

B ✗: Since the amount of product **R** decreases when temperature is increased, the forward reaction must be exothermic since the backward reaction is favoured to absorb heat.

C ✓: The position of eqm does not provide information about the kinetics of the reaction

D ✗: From the graph, it can seen that it takes a shorter time to plateau at higher temperature, hence eqm is achieved at a faster rate

⇒ **C**

15 pH = 4 ⇒ $[H^+] = 10^{-pH} = 10^{-4}$ mol dm^{-3}

⇒ **X** is fully dissociated, *i.e.* strong acid

pH = 3 ⇒ $[H^+] = 10^{-pH} = 10^{-3}$ mol dm^{-3}

⇒ **Y** is not fully dissociated, *i.e.* weak acid

pH = 14 ⇒ $[OH^-] = 10^{-pOH} = 10^{-(14-pH)} = 10^0$

$= 1$ mol dm^{-3}

⇒ **Z** is a fully ionised, *i.e.* strong base

⇒ **D**

16 Let the solubility of Ag_3PO_4 be s mol dm^{-3}

$K_{sp} = [Ag^+]^3[PO_4^{3-}]$

A : $K_{sp} = (3s)^3(s) \Rightarrow 27s^4 = K_{sp}$

$$s = \sqrt[4]{\frac{K_{sp}}{27}} = 4.26 \times 10^{-5}$$

B : $K_{sp} = (3s + 0.10)^3(s) \approx 0.10^3 s$

$$s = \frac{K_{sp}}{0.10^3} = 8.89 \times 10^{-14}$$

C : $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$

Formation of complex increases solubility of Ag_3PO_4

D : $K_{sp} = (3s)^3(s + 0.10) \approx (3s)^3\,0.10$

$$s = \sqrt[3]{\frac{K_{sp}}{27 \times 0.10}} = 3.21 \times 10^{-6}$$

⇒ **B**

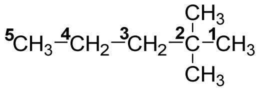
17 **B** ✗: No chiral centre

C ✗: $=CH_2$ ⇒ no *cis-trans* isomerism

D ✗: No chiral centre

⇒ **A**

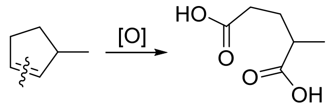
18 Structure of 2,2-dimethylpentane:



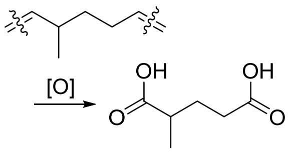
$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_3$$

⇒ **C**

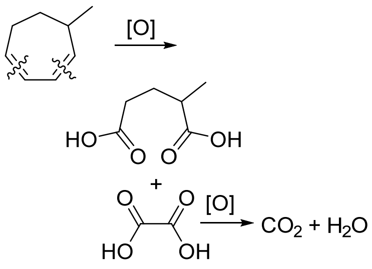
19 **1 ✓**:



2 ✓:

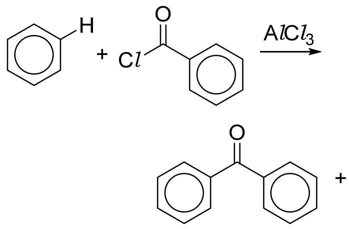


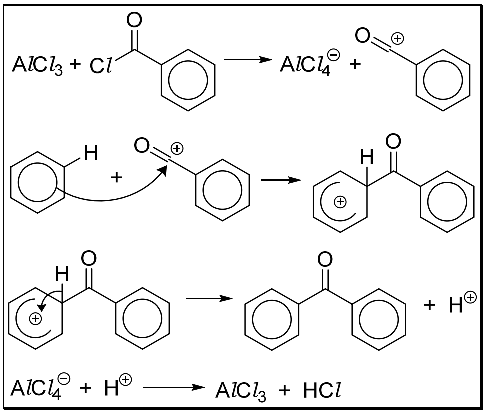
3 ✓:



⇒ **C**

20 Friedel-Crafts acylation, similar to Friedel-Crafts alkyation, using acyl chloride instead of alkyl chloride:





⇒ **D**

21 **A ×**: Second mechanism is **single-step** S_N2 involving only a **transition state**

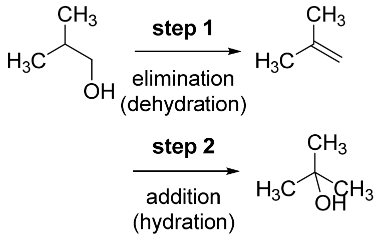
B ×: Second mechanism is a nucleophilic **substitution** reaction

C ✓: Since both mechanisms involves two reacting species in the rate determining step, both reactions are second order

D ×: The first mechanism involves addition of the CN^- to a trigonal planar C=O which can take place on both faces with equal chance, hence a racemic product will be obtained

⇒ **C**

22 The reaction involves



⇒ **C**

23 Tollens' reagent, $\left[Ag(NH_3)_2\right]^+OH^-$, only oxidises the –CHO into –COO⁻ (the salt is obtained and not $–CO_2H$ since Tollens' reagent is alkaline), while itself is reduced to silver metal. Alcohols are **not** oxidised.

⇒ **B**

24 **A ×**: NH_3 donates a pair of electrons to the electron-deficient acyl carbon, hence a nucleophile

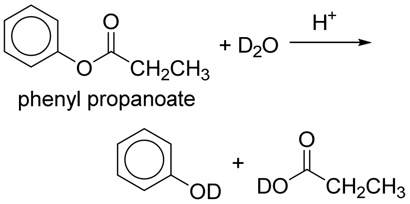
B ×: The arrow pushing is correct, leading to the regeneration of C=O and expulsion of the Cl^- leaving group

C ×: The acyl carbon is electron-deficient as it is bonded to two electronegative atoms, O and Cl, hence attracting the NH_3 nucleophile

D ✓: The arrow pushing is wrong as the pair of N–H electrons end up on the H, which will lead to formation of H^- and a doubly positive N instead

⇒ **D**

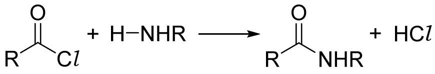
25



2 **1**

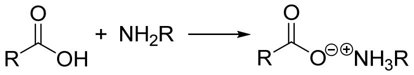
⇒ **B**

26 Amides are made from the reaction between an amine and an acyl chloride:



$$RCOCl + H–NHR \longrightarrow RCONHR + HCl$$

Amine and carboxylic acid gives an ammonium salt:



$$RCOOH + NH_2R \longrightarrow RCOO^{\ominus}\,{}^{\oplus}NH_3R$$

⇒ **A**

27 Basicity (availability of lone pair of electrons on N for donation to H^+) :

Generally $R_2NH > RNH_2 > NH_3 > ArNH_2$ as R groups exert electron-donating effect, rendering the lone pair more available for donation, while the lone pair is delocalised into the benzene ring of $ArNH_2$ rendering the lone pair less available for donation.

↓ing basicity ⇒ ↑ing pK_b

So pK_b : $R_2NH < RNH_2 < NH_3 < ArNH_2$

⇒ **B**

28 **W** : Nitrogen in NO_3^- is already in the maximum oxidation of +5 and cannot be further oxidised. Oxidation of H_2O

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Y : Due to the high concentration of chloride, oxidation of Cl^- occurs instead of H_2O

$$2Cl^- \rightarrow Cl_2 + 2e^- \left(4Cl^- \rightarrow 2Cl_2 + 4e^-\right)$$

Z : Oxidation of Cu instead of H_2O due to the less positive $E^\ominus$. **No gas** evolved

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad E^\ominus = +0.34\ V$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\ominus = +1.23\ V$$

Since the same amount of charge passes through all three cells, $V_{O_2} : V_{Cl_2} = 1:2$

⇒ **D**

29 **1 ✓**: $[R]: Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^\ominus = +1.36\ V$

$[O]: Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\ominus = +0.77\ V$

$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$$
$$= E^\ominus\left(Cl_2|Cl^-\right) - E^\ominus\left(Fe^{3+}|Fe^{2+}\right)$$
$$= +1.36 - (+0.77) = +0.59\ V$$

As reaction progresses, $[Cl_2]$ ↓es and $[Fe^{2+}]$ ↓es. So $E\left(Cl_2|Cl^-\right)$ ↓es, while $E\left(Fe^{3+}|Fe^{2+}\right)$ ↑es. Hence E_{cell} ↓es.

2 ✓: Addition of $AgNO_3$ causes AgCl to precipitate, hence $[Cl^-]$ ↓es. Thus $E\left(Cl_2|Cl^-\right)$ ↑es, causing E_{cell} to ↑.

3 ✓: Fe^{2+} and Fe^{3+} forms the respective hexacyano complex with CN^-:

$$\left[Fe(CN)_6\right]^{3-} + e^- \rightleftharpoons \left[Fe(CN)_6\right]^{4-} \qquad E^\ominus = +0.36\ V$$

Since $E^\ominus_{oxidation}$ ↓es , hence $E^\ominus_{cell}$ ↑es

⇒ **D**

30 **A ×**: Oxidations state of Co decreases from +3 in $\left[CoCl(NH_3)_5\right]^{2+}$ to +2 in $\left[Co(OH_2)_6\right]^{2+}$, while that of Cr increases from +2 in $\left[Cr(OH_2)_6\right]^{2+}$ to +3 in $\left[CrCl(OH_2)_5\right]^{2+}$. Hence electron is transferred from Cr to Co

B ✓: Hydration refers to the formation of the aqueous species from the gaseous species, which is not observed in the reaction

C ×: The Cl^- and NH_3 ligands around the Co ion is replaced by H_2O, while one of the H_2O ligand around the Cr ion is replaced by Cl^-. Hence ligand exchange has taken place

D ×: The ammonia ligands around Co^{3+} upon replacement by H_2O, reacted with H_3O^+ to give NH_4^+. Hence acid-base neutralisation had taken place

⇒ **B**

Answer Key

Qn	Ans	Qn	Ans	Qn	Ans
1	C	**11**	C	**21**	C
2	D	**12**	D	**22**	C
3	B	**13**	C	**23**	B
4	A	**14**	C	**24**	D
5	B	**15**	D	**25**	B
6	B	**16**	B	**26**	A
7	A	**17**	A	**27**	B
8	C	**18**	C	**28**	D
9	B	**19**	A	**29**	D
10	A	**20**	D	**30**	B

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME						
CIVICS GROUP	1	7	–			

INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
Total	

This document consists of **21** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 The table below shows the melting points of some oxides of Period 3 elements.

compound	**chemical formula**	**melting point / °C**
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) **(i)** Briefly relate the melting points of these oxides to their structure and bonding.

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.... [2]

(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

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.... [4]

(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

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.... [2]

(ii) Silicon tetrachloride, $SiCl_4$, hydrolyses in water while carbon tetrachloride, CCl_4, remains insoluble in water.

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.... [1]

(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5\,(g) \rightleftharpoons 4NO_2\,(g) + O_2\,(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

[1]

(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

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.... [2]

(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

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.... [2]

[Total: 15]

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

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.... [2]

(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

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.... [2]

(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

.... [1]

(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

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.... [2]

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, $MgCl$. Attempts to isolate $MgCl$ have not been successful. It is proposed that the $MgCl$ formed undergoes disproportionation to form $MgCl_2$ and Mg.

$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

(i) Define the standard enthalpy change of formation of $MgCl$.

....

.... [1]

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, $MgCl$.

Enthalpy change of atomisation of magnesium = $+148$ kJ mol^{-1}
First electron affinity of chlorine = -349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = -130 kJ mol^{-1}

[4]

(iii) The preferential formation of $MgCl_2$ can also be explained through the use of lattice energy of both $MgCl_2$ and $MgCl$ and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of $MgCl_2$ is -2526 kJ mol^{-1}, explain why $MgCl_2$ is formed preferentially and $MgCl$ is not.

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.... [1]

[Total: 15]

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) **(i)** Write an equation, including state symbols, for the Haber Process.

.... [1]

(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

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.... [2]

(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

(i) State **two** assumptions of the kinetic theory of gases.

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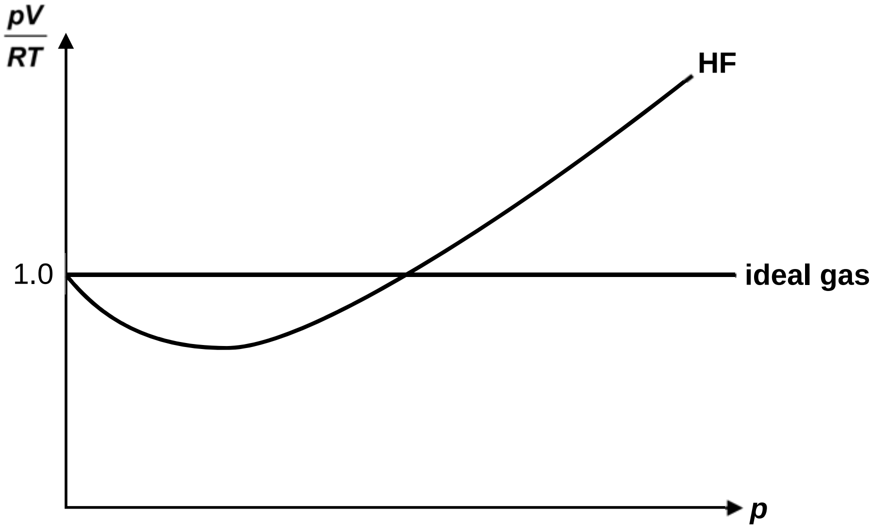
.... [2]

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

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.... [2]

(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

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.... [3]

[Total: 10]

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

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.... [2]

(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

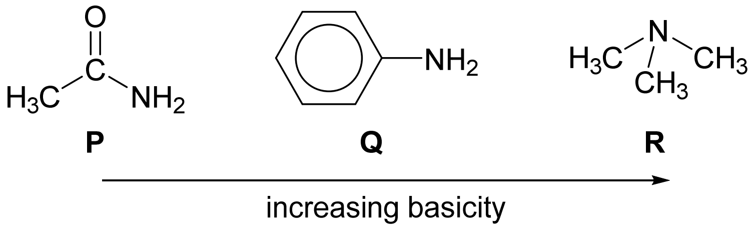
[2]

(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.

[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

Account for the trend in basicity as shown below.



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.... [3]

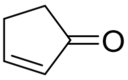
[Total: 10]

5 (a) This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion $\mathbf{R}^-$ on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone,  , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

[3]

(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

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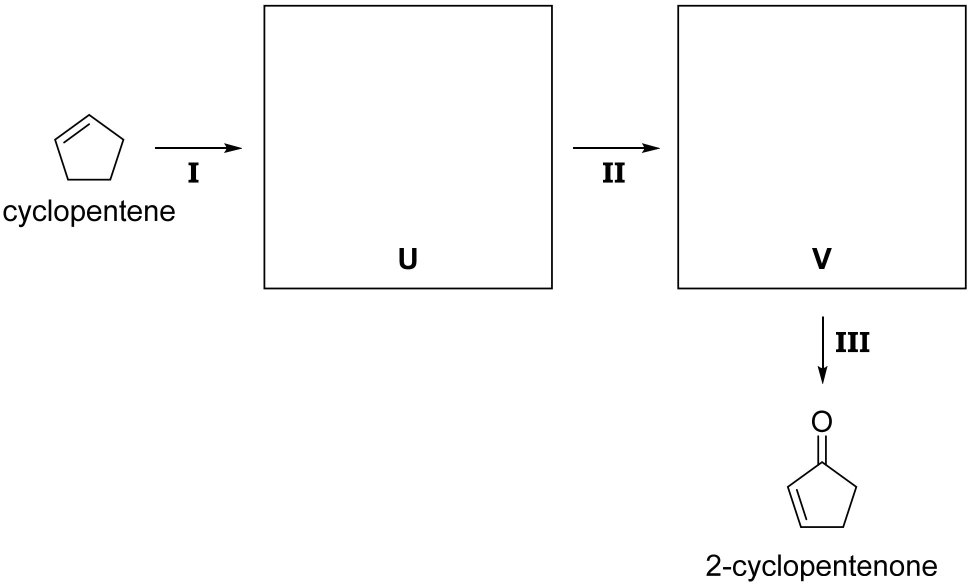
.... [1]

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: ....

Step II: ....

Step III: .... [3]

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[3]

[Total: 10]

6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

$$\text{rate} = k\,[\text{benzyl chloride}]$$

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

[2]

(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

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.... [1]

(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, CH_2=CHBr, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

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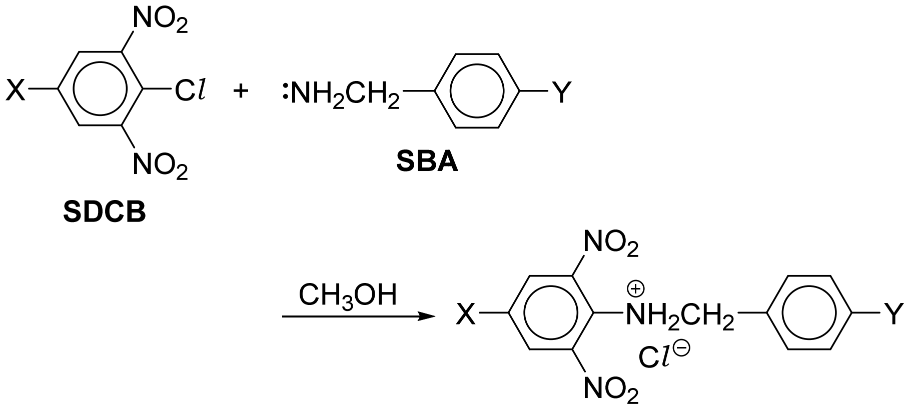
.... [1]

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

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.... [1]

(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

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.... [1]

The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k[\text{SDCB}][\text{SBA}]$$

The rate constant, *k* ($\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 °C is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-C*l***
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, *k*, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, *k*, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

[2]

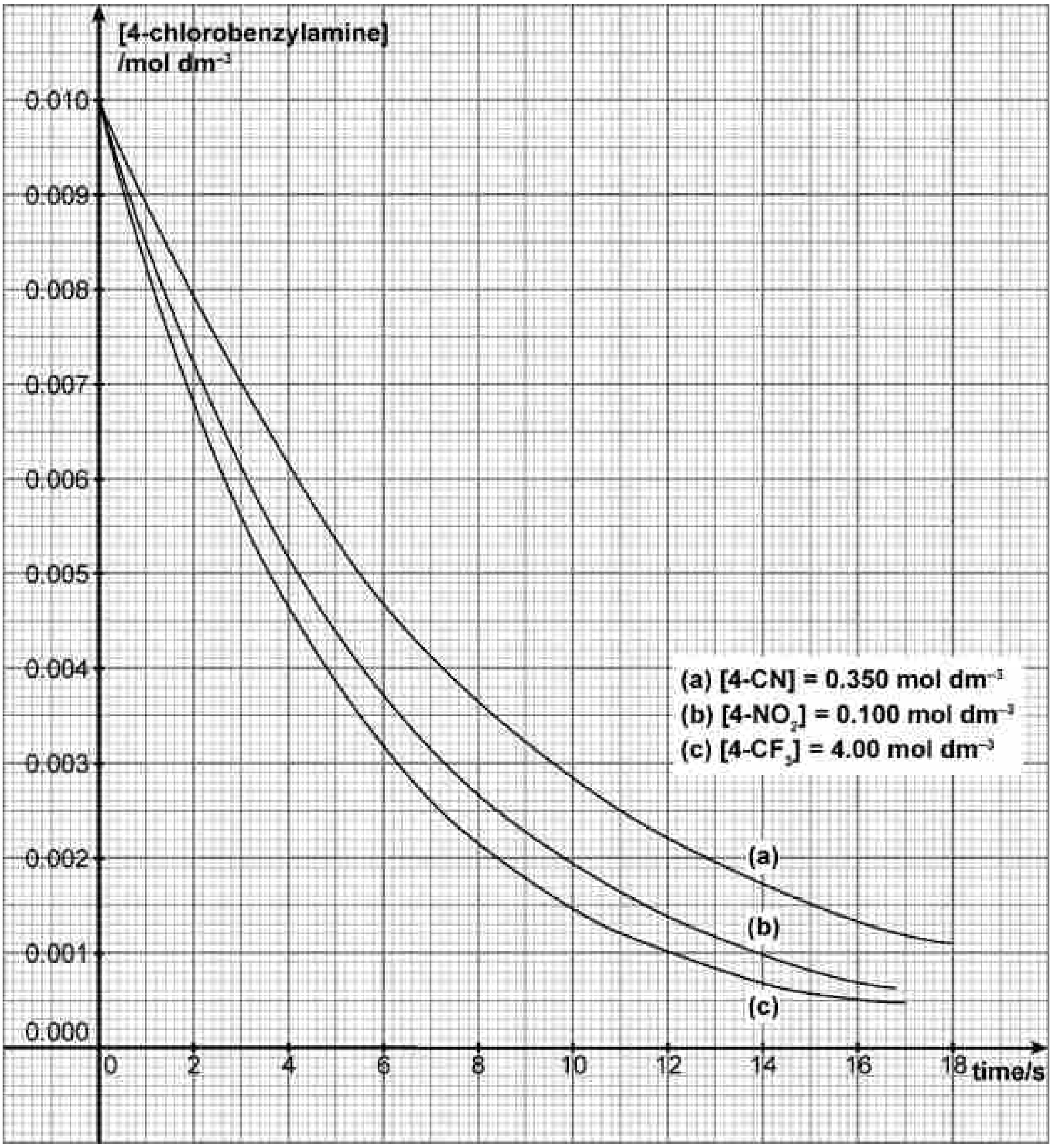
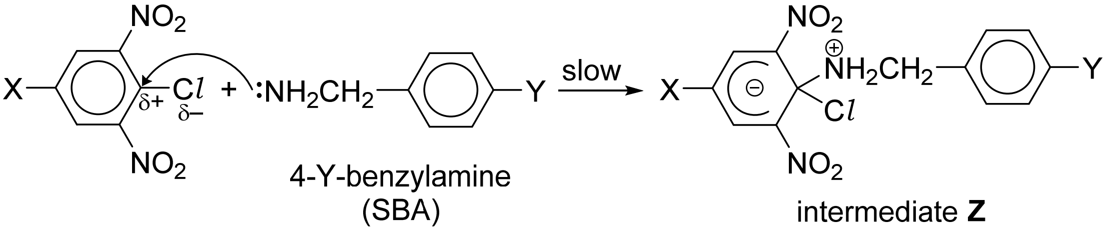
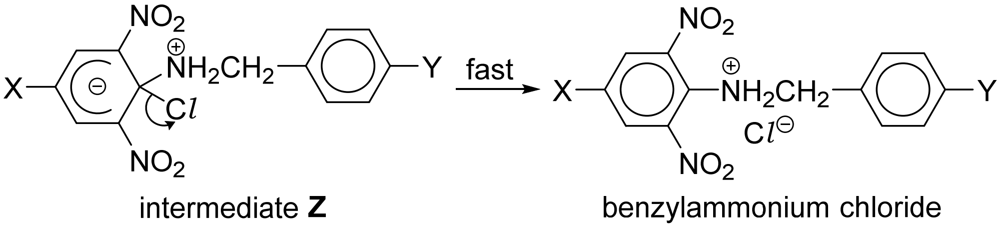

[4-chlorobenzylamine] /mol dm⁻³
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2
4
6
8
10
12
14
16
18
time/s
(a) [4-CN] = 0.350 mol dm⁻³
(b) [4-NO₂] = 0.100 mol dm⁻³
(c) [4-CF₃] = 4.00 mol dm⁻³
(a)
(b)
(c)

Figure 6.1

(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–C*l* carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:



Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

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.... [1]

(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

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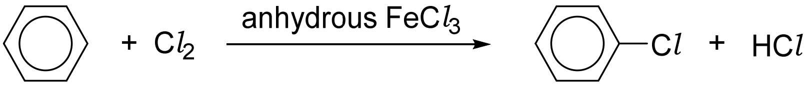
.... [1]

Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

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.... [1]

Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3{\cdot}6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) **(i)** Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

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.... [1]

(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

....

....

....

....

.... [1]

For Examiner's Use

(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$Fe(CO)_4I_2 + \tfrac{1}{2}I_2 \xrightarrow[\text{hexane}]{\text{uv light}} FeI_3 + 4CO$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

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.... [1]

A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

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.... [1]

[Total: 15]

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EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	7	–			INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
Total	

This document consists of **21** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 The table below shows the melting points of some oxides of Period 3 elements.

compound	**chemical formula**	**melting point / °C**
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) (i) Briefly relate the melting points of these oxides to their structure and bonding.

Both Al_2O_3 and Na_2O **are of giant ionic lattice structure**. During melting, a lot of energy is required to break **strong electrostatic forces of attraction between oppositely charged ions** **[both, 1m]** in these two compounds, resulting in their high melting points. Al_2O_3 has higher melting point than Na_2O as Al_2O_3 has a larger magnitude of lattice energy (since Al^{3+} ion has higher charge and is smaller in size compared to Na^+ ion).

SO_3 has **covalent simple molecular structure** that has **weak intermolecular instantaneous dipole-induced dipole (id-id) interactions** **[both, 1m]** between SO_3 molecules, **requiring little amount of energy to overcome** during melting. Thus, SO_3 has the lowest melting point. [2]

(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

Na_2O is an ionic oxide that reacts with water to form strongly alkaline solutions.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ **[1m]** (**pH ≈ 13–14**).

Al_2O_3 **does not dissolve in water** because its lattice energy is highly exothermic **[1m]**. (**pH = 7**)

SO_3 is an acidic oxide that react readily with water to form strongly acidic solutions.

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ **[1m]** (**pH ≈ 1–2**)

[all three pH's correct – 1m] [4]

(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

Al^{3+} has a **high charge density** and **further polarises** and **weakens the O–H bonds** of the water ligands **[1m]**. Hence $[Al(H_2O)_6]^{3+}$ undergoes **appreciable hydrolysis**, giving an acidic solution that reacts with sodium carbonate to give carbon dioxide.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$ **[both eqns – 1m]**

[2]

(ii) Silicon tetrachloride, $SiCl_4$, hydrolyses in water while carbon tetrachloride, CCl_4, remains insoluble in water.

Carbon in CCl_4, unlike silicon in $SiCl_4$, **does not have low-lying vacant orbitals** to accommodate the lone pair from water during hydrolysis.

In addition, **steric hindrance** from the 4 bulky chlorine atoms prevents approach/attack of water nucleophiles at the carbon atom in CCl_4.

[both, 1m]

[1]

(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

$$K_p = \frac{p_{O_2} \times (p_{NO_2})^4}{(p_{N_2O_5})^2}$$ **[1m]**

[1]

(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

$$K_p = \frac{p_{N_2O_5}}{\left(p_{O_2}\right)^{\frac{1}{2}} \times \left(p_{NO_2}\right)^2} = \left(\frac{1}{\dfrac{p_{O_2} \times \left(p_{NO_2}\right)^4}{\left(p_{N_2O_5}\right)^2}}\right)^{\frac{1}{2}}$$

$$= \left(\frac{1}{3.23 \times 10^3}\right)^{\frac{1}{2}} = \mathbf{1.76 \times 10^{-2}\ atm^{-\frac{3}{2}}}\ \mathbf{[1m]}$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

The enthalpy change will have a **positive value** **[1m]**.

The value of K_p for the dissociation **increases** with **increasing** temperature.

Therefore **the amounts of products (O_2 and NO_2) will increase while the amount of reactant (N_2O_5) will decrease** **[1m]** when temperature increases.

According to Le Chatelier's Principle, the forward reaction must be endothermic as it is favoured when temperature increases.

[2]

(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

Increasing the volume decreases the total pressure of the system.

This shifts the position of equilibrium to the **right** **[1m]** to **form more gaseous particles** to **increase pressure** as there are **more gaseous particles on the right** **[1m]**.

[2]

[Total: 15]

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

From chlorine to iodine,

- Valence electrons are **further away** from the nucleus.
- **Weaker electrostatic attraction** between nucleus and the valence electrons.
- **Less** energy is required to remove the valence electron. **[1m] for explanation**

Hence, first ionisation energy generally **decreases** down the group. **[1m]** [2]

(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

From HC*l* to HI,

- Covalent **bond length of H—X increases**
- Covalent **bond strength decreases** *or* **bond (dissociation) energy decreases**

[1m] for both

- **Thermal stability decreases [1m]** [2]

(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ **[1m] ss optional** [1]

(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V

As $E^\ominus(Br_2|Br^-)$ is **more positive** than $E^\ominus(I_2|I^-)$, **I_2 is the weaker oxidising agent [1m, with correct $E^\ominus$ values]** and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+2.5** in $S_4O_6^{2-}$. Bromine is the stronger oxidising agent and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+6** in SO_4^{2-}. **[1m]** [2]

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

Iodometric equation: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

$$n_{I_2} \text{ formed} = n_{I_2} \text{ reacted with } S_2O_3^{2-}$$
$$= \frac{1}{2}\times(0.0400\times0.10)$$
$$= \underline{\mathbf{2.00\times10^{-3}\ mol}}\ \textbf{[1m] ecf from eqn in (c)(i)}$$

$$\frac{n_{I_2}}{n_{BrO_4^{n-}}} = \frac{2.00\times10^{-3}}{5.0\times10^{-4}} = 4$$

Oxidation: $2I^- \rightarrow I_2 + 2e^-$

Mole ratio: $\mathbf{BrO_4^{n-} \equiv 4I_2 \equiv 8e^-}$

1 mole of BrO_4^{n-} gains 8 moles of electrons.

Oxidation number of Br in BrO_4^{n-} decreases by 8 to –1 in Br^-

Oxidation number of Br in BrO_4^{n-} = +7

$+7 + 4(-2) = n(-1)$

n = <u>1</u> **[1m] with logical working to deduce this**

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, $MgCl$. Attempts to isolate $MgCl$ have not been successful. It is proposed that the $MgCl$ formed undergoes disproportionation to form $MgCl_2$ and Mg.

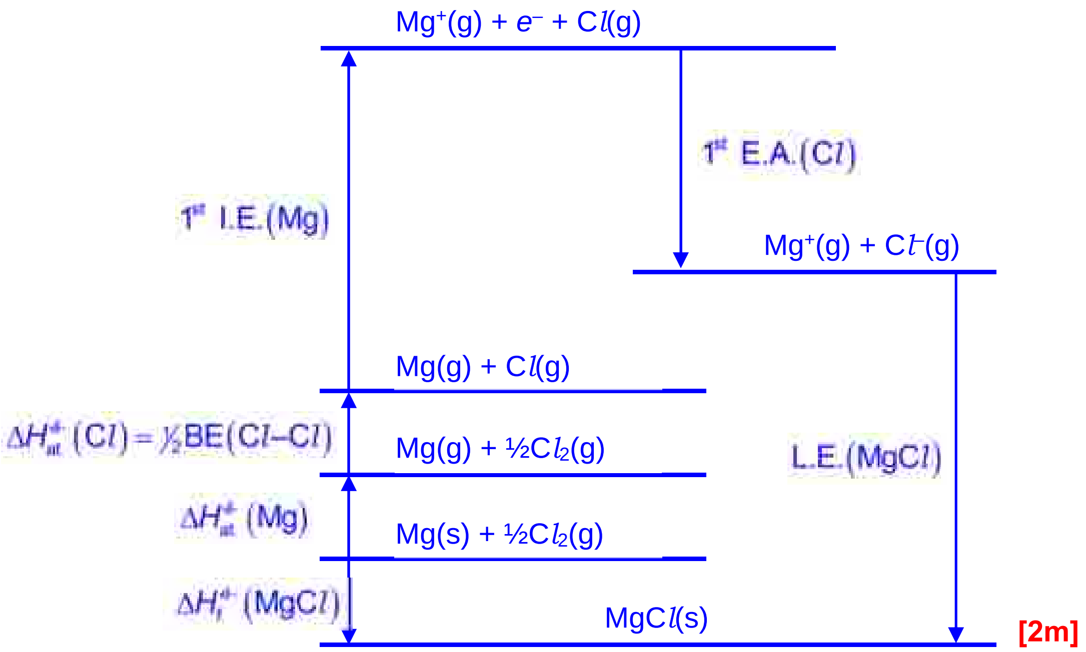
$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

(i) Define the standard enthalpy change of formation of $MgCl$.

The enthalpy change when **<u>1 mole of MgC*l*</u>** is formed from its **<u>constituent elements in their standard states</u>** at 298 K and 1 bar **[1m]** [1]

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, MgCl.

Enthalpy change of atomisation of magnesium = +148 kJ mol^{-1}
First electron affinity of chlorine = –349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = –130 kJ mol^{-1}



By Hess' Law,

$$\Delta H_{at}^{\ominus}(Mg) + \frac{1}{2}BE(Cl–Cl) + 1^{st}\ I.E.(Mg) + 1^{st}\ E.A.(Cl) + L.E.(MgCl) = \Delta H_f^{\ominus}(MgCl)$$

$$L.E.(MgCl) = -130 - (+148) - \frac{1}{2}(+244) - (+736) - (-349)$$ **[1m]**

$$= \underline{\mathbf{-787\ kJ\ mol^{-1}}}$$ **[1m]**

[4]

(iii) The preferential formation of MgCl_2 can also be explained through the use of lattice energy of both MgCl_2 and MgCl and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of MgCl_2 is –2526 kJ mol^{-1}, explain why MgCl_2 is formed preferentially and MgCl is not.

- The ionisation energy required to produce Mg^{2+} (1st IE(Mg) = +736 kJ mol^{-1} and 2nd IE(Mg) = +1450 kJ mol^{-1}) can be compensated reasonably well by the higher magnitude of lattice energy (higher amount of energy (–2526 kJ mol^{-1}) is released during the formation of MgCl_2). **[1m]**

  or
- Whereas the ionisation energy required to produce Mg^+ is only merely compensated by the formation of MgCl due to its lower lattice energy (–787 kJ mol^{-1}). **[1m]**

  Therefore MgCl_2 is formed preferentially. [1]

[Total: 15]

For Examiner's Use

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) **(i)** Write an equation, including state symbols, for the Haber Process.

N_2 (g) + $3H_2$ (g) $2NH_3$ (g) **[1m]** [1]

(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

In the reaction in **(a)(i)**, there is a **decrease in the number of gas molecules**, **reducing** the number of ways that the **particles and energy can be distributed**. **[1m] for gas molecules and particles/energy distributed**

Hence, there is a **decrease in entropy**. The sign of the entropy change should **be negative**. **[1m] for entropy and sign of entropy change**

[2]

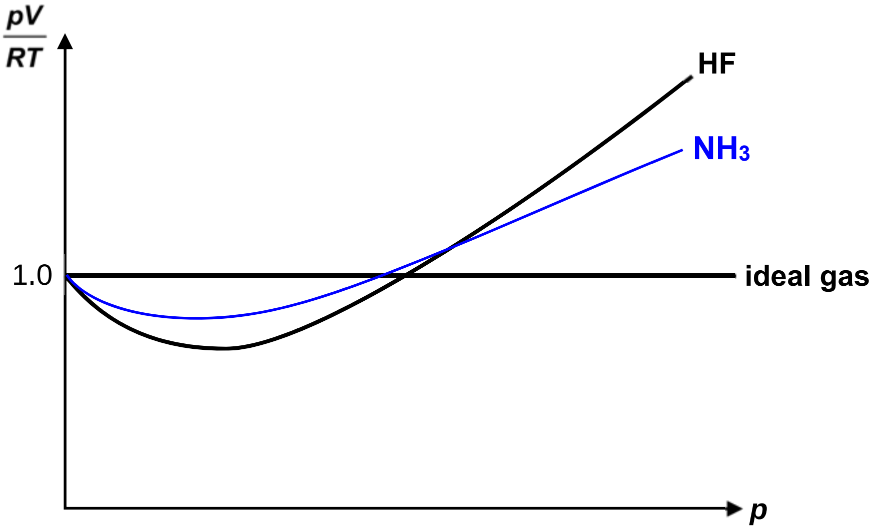
(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

(i) State **two** assumptions of the kinetic theory of gases.

- There are **no/negligible intermolecular forces of attraction** between the gas molecules.
- Gas molecules **does not occupy any volume**. (volume is negligible compared to the volume of container)
- Collisions between gas molecules are **"perfectly elastic"**.

[2m] any 2 [2]

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

The **hydrogen bonds** between NH_3 are **weaker** than that between HF molecules since **N–H bond is less polar than H–F bond**. **[1m] for concept of weaker hydrogen bonding between molecules**

Hence, NH_3 **deviates less** from ideal gas behaviour. **[1m] for correct sketching of line** [2]

(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

Under **low pressure and high temperature**. **[1m] for stating both conditions**

At lower pressure, NH_3 molecules are **far apart**, such that **volume of gas molecules becomes insignificant compared to the volume of the container** **[1m]** in which the gas is held.

At high temperature, NH_3 molecules **moves faster** (or have higher average kinetic energy). As such, **the intermolecular forces of attraction between the molecules become negligible** **[1m]**.

[3]

[Total: 10]

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

$$\text{Concentration of triethylamine} = \frac{2\times\left(\frac{16.00}{1000}\times 0.250\right)}{\frac{10.0}{1000}} = \underline{\mathbf{0.800\ mol\ dm^{-3}}}\ \mathbf{[1m]}$$

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

pOH = 14 – 11.85 = 2.15

$[OH^-(aq)] = 10^{-pOH} = 7.079\times10^{-3}$ mol dm^{-3} ≈ $\underline{\mathbf{7.08\times10^{-3}\ mol\ dm^{-3}}}$ **[1m]**

Since $[OH^-(aq)]$ is **less than** [trimethylamine (aq)], trimethylamine is **not fully ionised** in solution **[1m]** and hence is a weak base.

[2]

(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

$$K_b = \frac{\left[(CH_3)_3NH^+(aq)\right]\left[OH^-(aq)\right]}{\left[(CH_3)_3N\ (aq)\right]}\ \mathbf{[1m]}$$

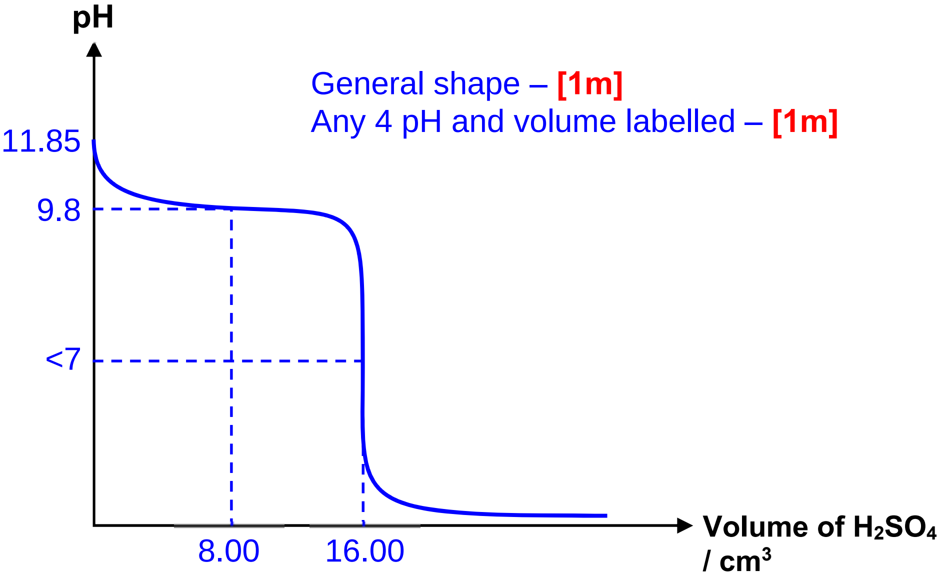
$$= \frac{\left(7.079\times10^{-3}\right)\left(7.079\times10^{-3}\right)}{\left(0.800 - 7.079\times10^{-3}\right)} = 6.321\times10^{-5}\ \text{mol}$$

pK_b = –log (6.321×10^{-5}) = 4.199 = $\underline{\mathbf{4.20}}$ (3 sf) **[1m]**

[If assuming the dissociation to be very small, and approximating $0.800 - 7.079\times10^{-3} \approx 0.800$, then p$K_b$ = **4.203** or **4.20** (3sf)]

[2]

(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.



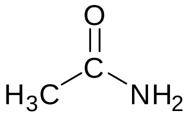
General shape – **[1m]**

Any 4 pH and volume labelled – **[1m]**

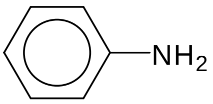
[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

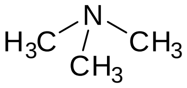
Account for the trend in basicity as shown below.



P



Q



R

increasing basicity →

amide P: lone pair of electrons on N is delocalised into the neighbouring carbonyl group with δ+ C and highly electronegative O due to overlap of p orbital of N with the π electron cloud of C=O

⇒ not readily available for donation **[1m]**

aryl amine Q: lone pair of electron delocalised into the benzene ring

⇒ less readily available for donation **[1m]**

tertiary amine R: alkyl groups are electron donating, increases the electron density around N

⇒ lone pair of electrons more easily donated, increased basic strength **[1m]**

[3]

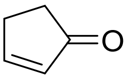
[Total: 10]

5 (a) This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

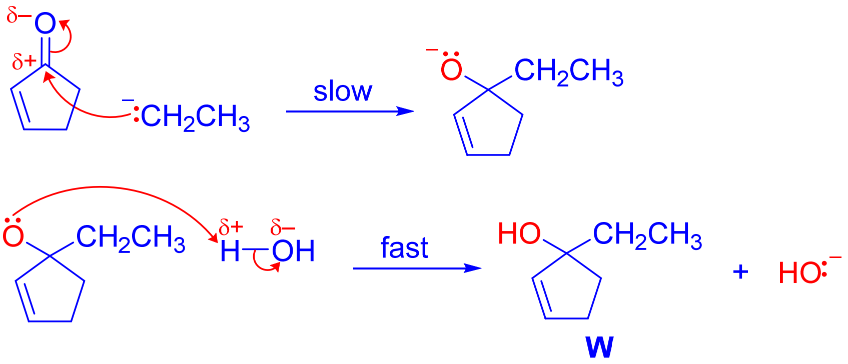
The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion **R**$^-$ on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone,  , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

Nucleophilic addition **[1m]**



[1m] curly arrows, partial charges, lone pair
[1m] intermediate and slow step products

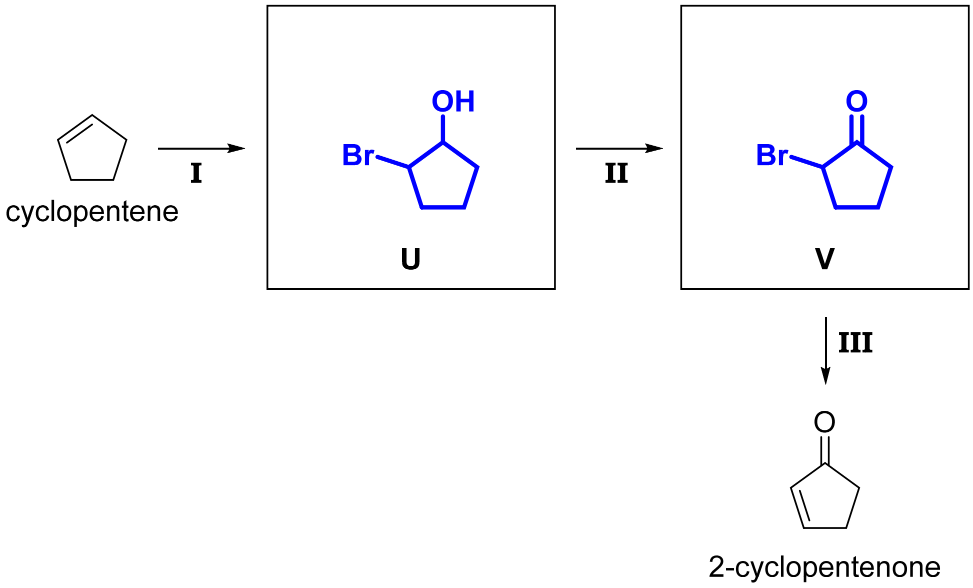
[3]

(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

No. There is no *cis-trans* isomerism as the C=C is in a small cyclic ring, so only the *cis* isomer is present due to **ring strain**. **[1m]**

[1]

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: Br_2 (aq), room temperature

Step II: $KMnO_4$(aq) or $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat

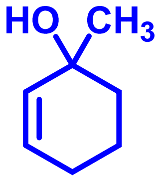
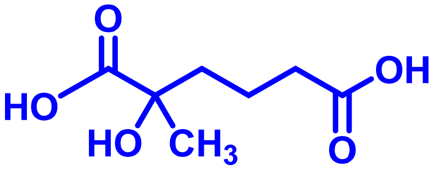
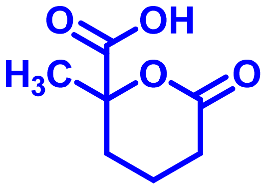
Step III: ethanolic KOH, heat [3]

[1m] for each step and intermediate

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

For Examiner's Use

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[1m] for each compound

[3]

[Total: 10]

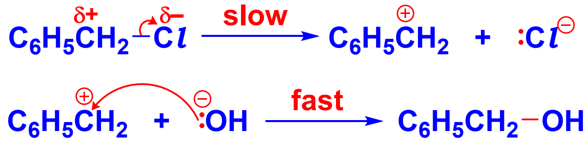
6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

$$\text{rate} = k\,[\text{benzyl chloride}]$$

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

S_N1 Nucleophilic substitution



$$C_6H_5\overset{\delta+}{C}H_2-\overset{\delta-}{Cl} \xrightarrow{\text{slow}} C_6H_5\overset{\oplus}{C}H_2 + :Cl^{\ominus}$$

$$C_6H_5\overset{\oplus}{C}H_2 + :\overset{\ominus}{O}H \xrightarrow{\text{fast}} C_6H_5CH_2-OH$$

[1m] curly arrows, partial charges, lone pair

[1m] benzyl cation intermediate and slow step products

[2]

(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

The benzyl cation, **$C_6H_5CH_2^+$, intermediate** formed although is a primary cation, is **stabilised by delocalisation of the electrons from the benzene ring** **[1m]** onto the carbocationic carbon, hence favouring the S_N1 mechanism instead of S_N2 mechanism.

[1]

(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, $CH_2{=}CHBr$, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

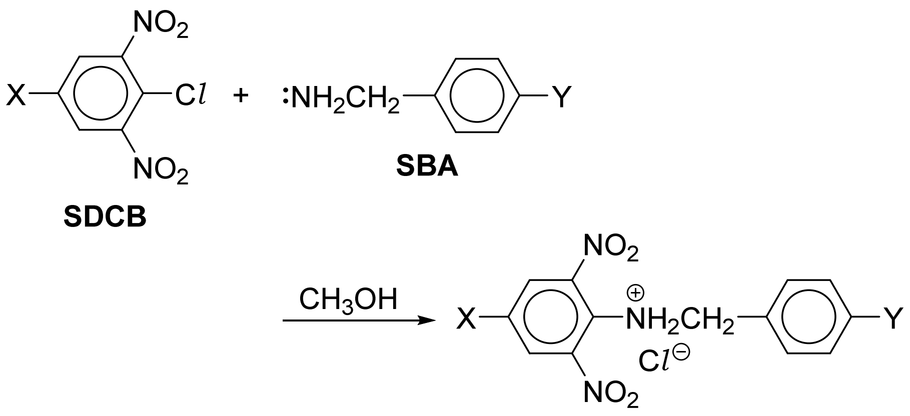
The **lone pair of electrons on Br is delocalised into the C=C**, imparting **partial double bond character** to the C–Br, and **strengthening the C–Br bond**, hence rendering cleavage of the C–Br bond difficult. **[1m]** In addition, this lowers the electron-deficiency of the α-carbon, making vinyl bromide less susceptible to nucleophilic attack.

[1]

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



SDCB

SBA

benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

Addition of **aqueous silver nitrate** to the reaction mixture will produce an **immediate white precipitate of AgC*l*** if the substitution reaction had taken place. Otherwise, no precipitate will be observed. **[1m] for both reagent and immediate ppt** [1]

(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

Since the reaction **produces an ionic product** from electrically neutral reactants, the **electrical conductivity** **[1m]** of the mixture will increase with the amount of the product formed, allowing the progress of the reaction to be followed.

[1]

The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k[\text{SDCB}][\text{SBA}]$$

The rate constant, *k* ($\text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 °C is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-C*l***
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	**0.357**
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, *k*, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, *k*, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

From the graph,

$$\text{initial rate} = \left|\frac{0.010-0}{0-8}\right| = 1.25\times10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}\ \textbf{[1m]}$$

$$\text{Hence, } k = \frac{\text{rate}}{[\text{SDCB}][\text{SBA}]} = \frac{1.25\times10^{-3}}{0.350\times0.010} = 0.3571 \approx \underline{\mathbf{0.357}}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}\ \textbf{[1m]}$$

[2]

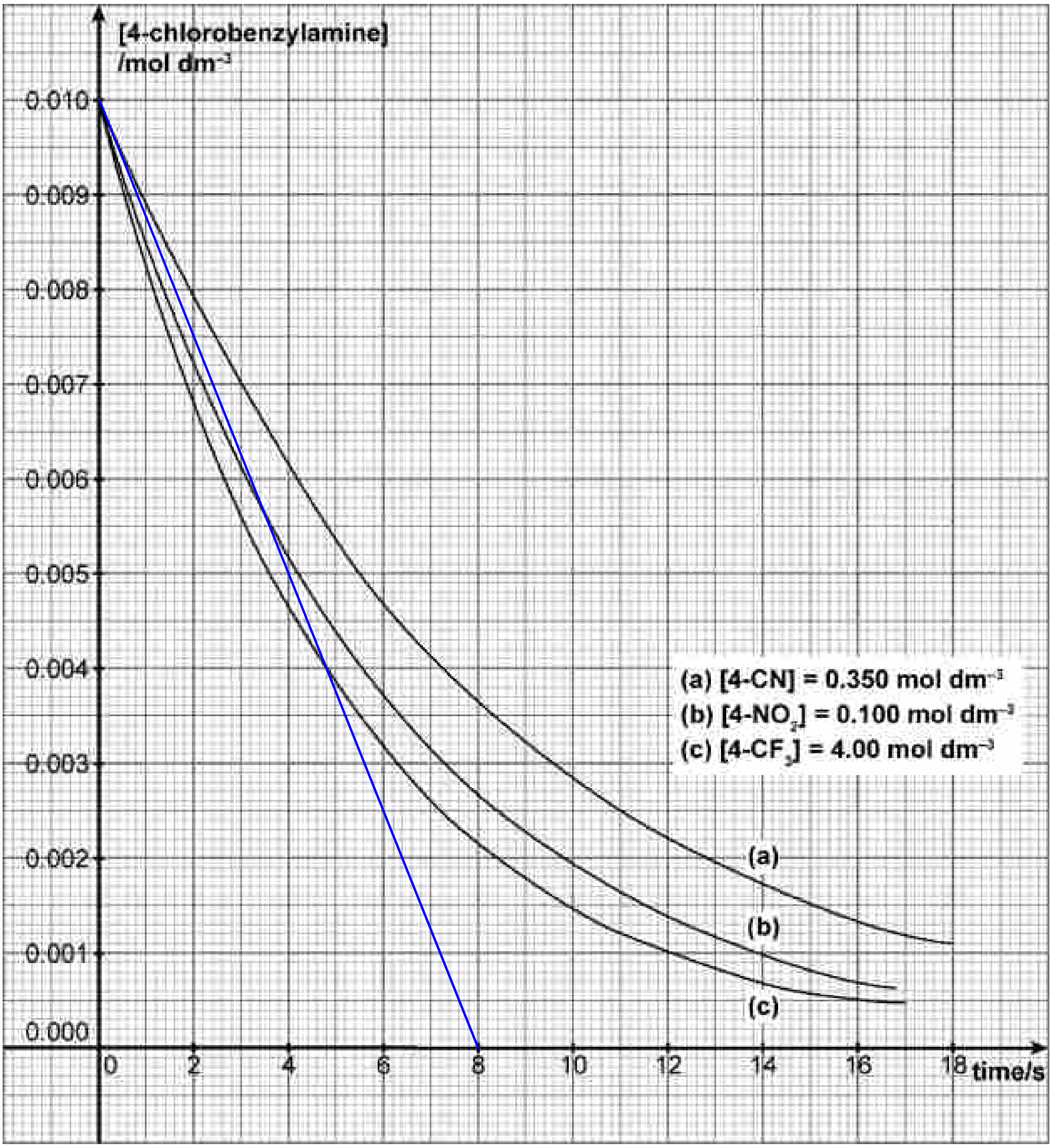
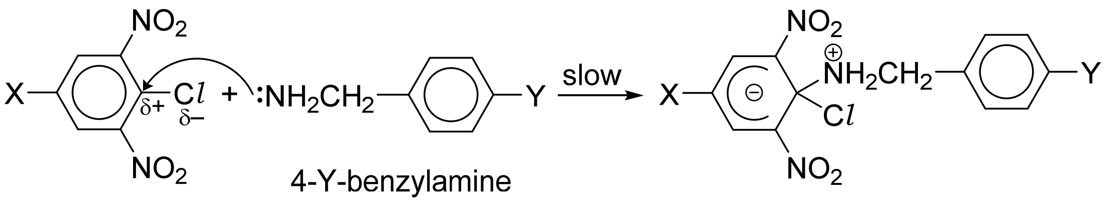

[4-chlorobenzylamine]
/mol dm⁻³
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2
4
6
8
10
12
14
16
18
time/s
(a) [4-CN] = 0.350 mol dm⁻³
(b) [4-NO₂] = 0.100 mol dm⁻³
(c) [4-CF₃] = 4.00 mol dm⁻³
(a)
(b)
(c)

Figure 6.1

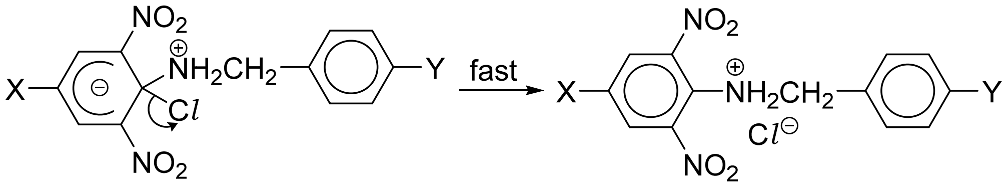
(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–C*l* carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:



4-Y-benzylamine (SBA)

intermediate **Z**

Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



intermediate **Z**

benzylammonium chloride

This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

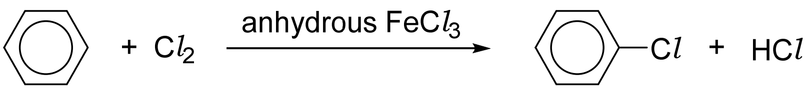
From the mechanism, since the slow step involves the formation of intermediate **Z**, the **more stable Z** is, the **faster** the reaction will be. The **negative charge** of intermediate **Z** will be **stabilised** by the presence of **electron-withdrawing substituents**. Since the reaction is fastest (largest *k*) with X = NO_2, **NO_2** must be the strongest electron-withdrawing group. **[1m]** [1]

(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

From the mechanism, since the **slow step** involves the **nucleophilic attack** of the 4-Y-benzylamine at the electrophilic carbon of the benzene ring, the **more nucleophilic** the 4-Y-benzylamine, the **lower** will be the **activation energy**, and hence **larger** the **rate constant** *k*. **[1m] for nucleophilic attack being slow step and lower activation energy** [1]

Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

The role of anhydrous $FeCl_3$ is to serve as a halogen carrier to **generate the strong electrophile**, the chlorine cation, from chlorine:

$$Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$$

[1m] for strong electrophile and equation [1]

Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3{\cdot}6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) **(i)** Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

Despite containing iron(III), the two complexes possesses **different ligands** and hence, the 3d orbitals of iron(III) is **split** into two different energy levels by **different extent**, resulting in **different energy gaps** between the two levels. **[1m]**

[1]

(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

Due to the high charge density of the Fe^{3+} ion, $[Fe(H_2O)_6]^{3+}$ undergoes **hydrolysis** readily: $[Fe(H_2O)_6]^{3+}(aq) \quad [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

Hence, a **high concentration of $H^+(aq)$** is needed to **suppress the hydrolysis**, to stabilise the $[Fe(H_2O)_6]^{3+}$ ion. **[1m]**

[1]

(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$\mathrm{Fe(CO)_4I_2} + \tfrac{1}{2}\mathrm{I_2} \xrightarrow[\text{hexane}]{\text{uv light}} \mathrm{FeI_3} + 4\mathrm{CO}$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

Redox reaction. The oxidation state of iron in $Fe(CO)_4I_2$ is +2, which is increased to +3 in FeI_3, while the oxidation state of iodine in I_2 is 0 which is decreased to –1 in FeI_3 **[1m] with correct explanation**

[1]

A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

Since $E^{\ominus}(Fe^{3+}|Fe^{2+}) = +0.77\text{ V} > E^{\ominus}(I_2|I^-) = +0.54\text{ V}$, Fe^{3+} is capable of oxidising I^- to I_2, while itself reduced to Fe^{2+}:

$$FeI_3 \rightarrow FeI_2 + \tfrac{1}{2}I_2$$

The possible products are **FeI_2** and **I_2**. **[1m] for both products** [1]

[Total: 15]

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EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME					
CIVICS GROUP	1	7	–		

INDEX NUMBER		

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

---

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

Shift
Laboratory

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **19** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 Analysis of a solution containing both sodium hydroxide and sodium carbonate by Warder titration (double indicator method)

Aqueous sodium hydroxide easily reacts with atmospheric carbon dioxide. This results in the sodium hydroxide being contaminated with sodium carbonate Na_2CO_3.

The Warder titration (double indicator method) can be used to analyse a mixture containing both sodium hydroxide and sodium carbonate.

FA 1 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 2 is an aqueous solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.

(a) Titration of FA 2 against FA 1 using methyl orange or screened methyl orange indicator

In this titration, **FA 1** is run from the burette into the conical flask containing **FA 2** with methyl orange or screened methyl orange indicator.

The end-point is reached when the yellow colour changes to orange for methyl orange, or the green colour changes to grey for screened methyl orange.

(i) 1. Fill the burette with **FA 1**.

2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a conical flask.

3. Add a few drops of methyl orange or screened methyl orange indicator.

4. Run **FA 1** from the burette into the conical flask until the colour of the solution changes.

5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.

6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

[5]

For Examiner's Use

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 1** = ... [1]

(b) Titration of FA 2 against FA 1 using thymolphthalein indicator

When the titration in **(a)** was repeated using thymolphthalein as the indicator, 25.0 cm^3 of **FA 2** required 23.35 cm^3 of **FA 1**.

The following explains why different results were obtained using two different indicators.

- When **thymolphthalein** is used as the indicator, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

- When **methyl orange** is used as the indicator in **(a)**, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
  3. $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 1** calculated in **(a)(ii)**.

amount of HC*l* in volume in **(a)(ii)** = ... [1]

(ii) Calculate the amount of hydrochloric acid in 23.35 cm^3 of **FA 1**.

amount of HC*l* in 23.35 cm^3 of **FA 1** = ... [1]

(iii) Using your answer to **(b)(i)** and **(b)(ii)**, calculate the amount of hydrochloric acid that reacts with the Na_2CO_3 in the titration using thymolphthalein indicator.

amount of HC*l* that react with Na_2CO_3 = ... [1]

(iv) Hence, calculate the mass of sodium carbonate present in 25.0 cm^3 of **FA 2**.

[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = ... [1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HC*l* when methyl orange is used as indicator is given below.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of HC*l* that reacted with the Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 2**.

amount of HC*l* = ... [1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of sodium hydroxide in 25.0 cm^3 of **FA 2**.

[A_r: H, 1.0; O, 16.0; Na, 23.0]

mass of NaOH = ... [1]

(vii) Calculate the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in **FA 2**.

percentage by mass of Na_2CO_3 in **FA 2** = ... [1]

(c) The error (uncertainty) associated with **each reading** is given as follows:

50.00 cm^3 burette: ±0.05 cm^3

25.0 cm^3 pipette: ±0.04 cm^3

Using the above data, calculate the percentage error (uncertainty) when a

(I) 50.00 cm^3 burette

(II) 25.0 cm^3 pipette

is used to measure 25 cm^3 of **FA 2** into the conical flask.

Hence state whether a 50.00 cm^3 burette or 25.0 cm^3 pipette will be more suitable to measure 25.0 cm^3 of **FA 2** accurately.

....

....

....

....

....

....

.... [2]

[Total: 15]

2 To determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on gravimetric method

Sodium hydrogencarbonate decomposes on heating to give sodium carbonate, carbon dioxide and water vapour.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Sodium chloride on the other hand is unaffected by heat.

FA 3 is a mixture of anhydrous sodium hydrogencarbonate, $NaHCO_3$, and sodium chloride, $NaCl$.

In this question, you will heat to decompose the sodium hydrogencarbonate in **FA 3** and determine the mass of carbon dioxide and water lost. The data will be used to determine

- the mass of $NaHCO_3$ in **FA 3**,
- the percentage composition by mass of $NaHCO_3$ in **FA 3**.

(a) Thermal decomposition of $NaHCO_3$

In this experiment, solid **FA 3** is heated strongly in a boiling tube, over a non-luminous Bunsen flame, until there is no further change in the mass.

1. Weigh accurately about 4.5 g of **FA 3** in the boiling tube provided. Record your weighings in the space provided below.

2. Heat the tube gently first, then strongly.

3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

> You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.

5. Repeat points **2** to **4** as necessary until a constant mass is obtained.

6. **Turn off your Bunsen burner**.

(i) In an appropriate format in the space below, record all weighings measurements.

[3]

(ii) Using your results, calculate the mass of carbon dioxide and water vapour evolved.

mass of CO_2 and H_2O evolved = ... [1]

(iii) Using your answer to **(a)(ii)**, calculate the amount of carbon dioxide evolved.

[A_r: H, 1.0; C, 12.0; O, 16.0]

amount of CO_2 evolved = ... [1]

(iv) Calculate the mass of sodium hydrogencarbonate in the sample of **FA 3**.

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

mass of $NaHCO_3$ in sample of **FA 3** = ... [1]

(v) Determine the percentage by mass of sodium hydrogencarbonate in **FA 3**.

percentage by mass of $NaHCO_3$ in **FA 3** = ... [1]

(b) Suggest one possible source of error in this experiment. How would this error affect the calculated results in **(a)(iv)**?

....

....

....

....

.... [2]

(c) **Planning**

Plan an experiment to determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on volumetric analysis method.

In this experiment, you will titrate a **solution of FA 3** against **FA 1**, using a suitable indicator.

You can assume you are provided with the following reagent:

FA 4 is a solution containing 30.00 g dm^{-3} of **FA 3**.

In your plan, you should include details of

- the amount of reagents you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- appropriate calculations to show how the percentage by mass of sodium hydrogencarbonate in **FA 3** can be determined, assuming the average titre is ***y*** cm^3.

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For Examiner's Use

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.... [6]

[Total : 15]

3 Investigation of the kinetics of the reaction between calcium carbonate and hydrochloric acid

Calcium carbonate that reacts with hydrochloric acid in an acid-carbonate reaction as shown below.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

FA 5 is powdered $CaCO_3$.

In this question, you will measure the volume of CO_2 gas produced at timed intervals until the reaction is complete, using an excess of dilute hydrochloric acid.

You will need access to **FA 1** solution you used earlier.

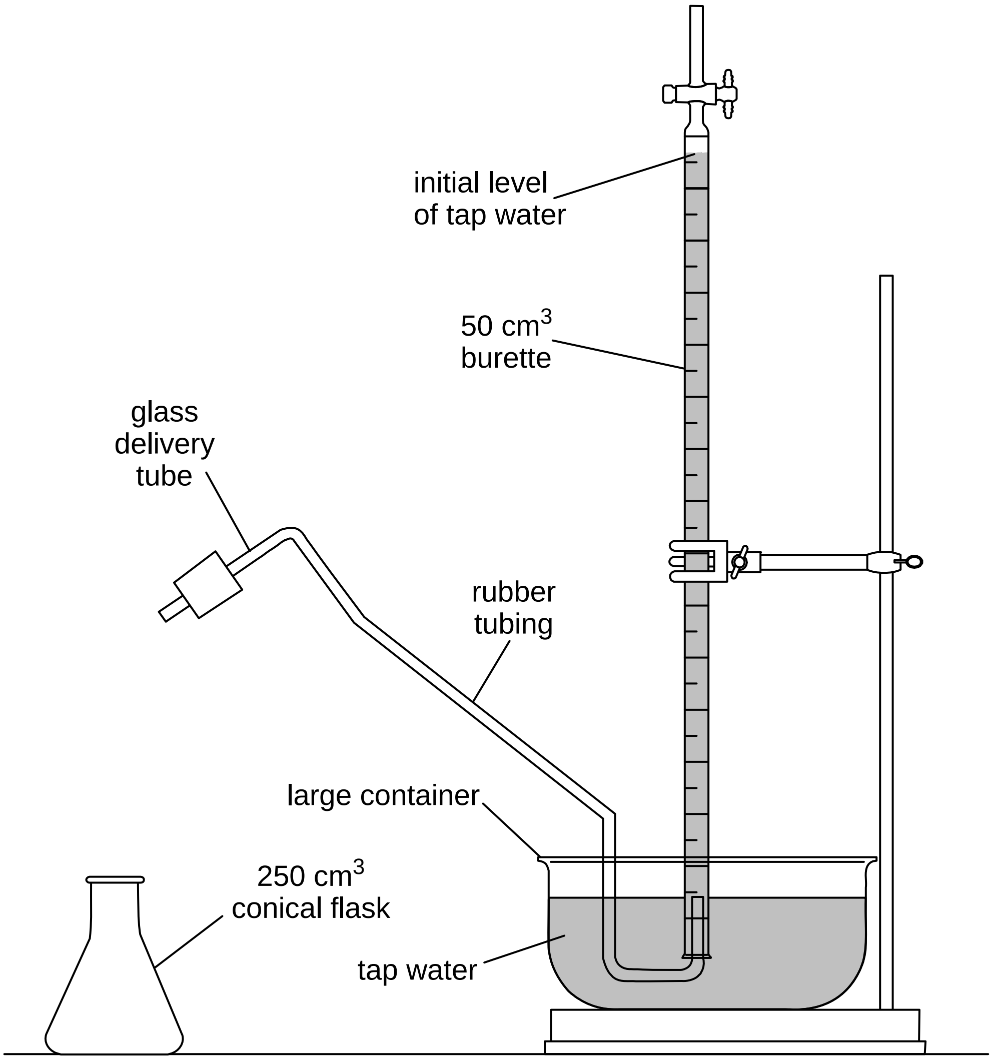

Fig 3.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page **11**, prepare a table in which you may record each burette reading and the time it was taken. The time taken should be recorded to one decimal place.

In addition, your table will need to show the volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in the Fig. 3.1. You should insert the rubber tubing to a sufficient depth in the burette so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.

3. Transfer all the solid **FA 5** provided in the weighing bottle into a dry and clean 250 cm^3 conical flask.

4. Use an appropriate measuring cylinder, measure 40 cm^3 of **FA 1**.

5. Transfer the **FA 1** into the conical flask containing **FA 5** and insert the bung into the conical flask.

6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.

   Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until the reaction is complete.

7. Check that the rubber tubing is securely positioned in the burette.

8. Hold the flask by its neck and **gently swirl** it continuously.

9. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.

10. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

[3]

For Examiner's Use

(ii) Plot on the grid below, a graph of the volume of CO_2 on the *y*-axis, against time, *t*, on the x-axis.

Draw the most appropriate best-fit curve, taking into account all of your points.

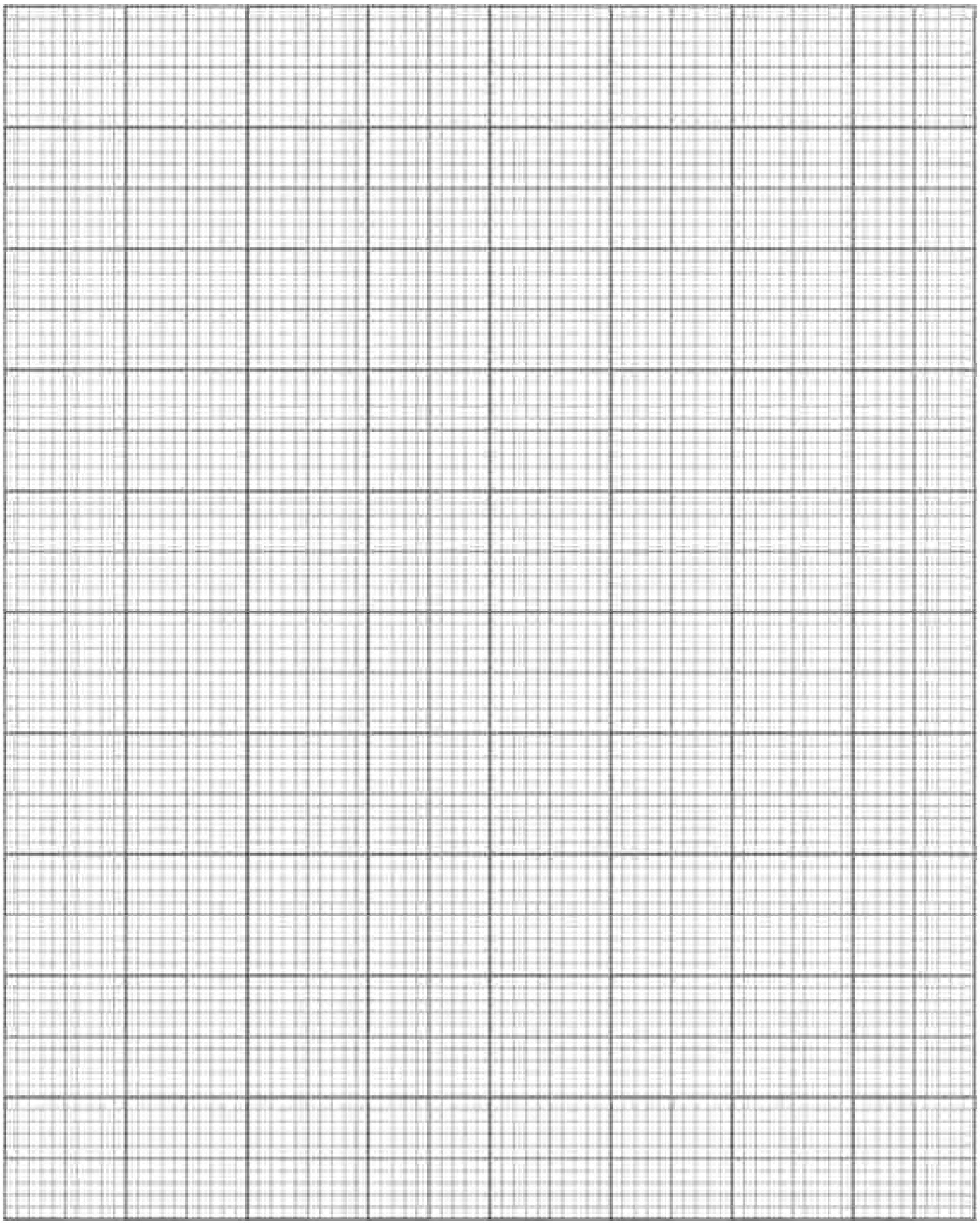

Fig. 3.2

[3]

(iii) It has been claimed that the reaction between calcium carbonate and hydrochloric acid is pseudo-first order with respect to calcium carbonate.

State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 3.2 to support your answer.

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.... [2]

(b) Planning

Besides using the continuous measurement method in **3(a)** to determine the order of reaction of a reactant, the initial rates method can also be used.

Plan an investigation, which **does not** involve graph plotting, to determine the order of reaction with respect to hydrochloric acid, HC*l*, using the initial rates method.

You are provided the following chemicals and apparatus:
- same apparatus used in the experimental setup in **3(a)**,
- 2.00 mol dm^{-3} HC*l* solution
- **FA 5** powdered $CaCO_3$
- stopwatch

In your plan, you should include details of:
- the different concentrations of the reactants used and the conditions of the experiment,
- the procedure you would follow, including the end-point of the experiment
- the measurements you would take,
- an outline of how you would use your results to determine the order of reaction with respect to HC*l*.

You may use the space below to draw a table indicating the headers of the measurements and calculations you would be performing.

For Examiner's Use

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.... [6]

[Total: 14]

4 Carry out the following experiments with **FA 6**.

In all tests the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

Observations should include:

(i) descriptions of colour changes and precipitates;

(ii) names of gases evolved and details of the test used to identify each one.

You should indicate clearly at which stage in a test a change occurs, writing any deductions that you make alongside the observations upon which they are based.

Marks will be given *only* for the prescribed tests and will *not* be given for chemical equations.

TEST	OBSERVATION	CONCLUSION
Tests of FA 6 **(a)** Heat **FA 6** in a test-tube until no further change is observed. **Allow the residue to cool** and retain it for **(b)**. You may wish to proceed with the tests in **4(c)** while waiting for the residue to cool.		
(b) Dissolve the residue from test **(a)** in deionised water and use separate portions of the solution for tests **(i)** to **(iii)**		
(i) Add aqueous silver nitrate to a portion of the solution. Then add aqueous ammonia.		

For Examiner's Use

TEST	OBSERVATION	CONCLUSION
(ii) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.		
(iii) Add a few crystals of **FA 6**, shake to dissolve and then add dilute sulfuric acid.		
(c) Dissolve **FA 6** in water and use separate portions of the solution for tests **(i)** and **(ii)**.		
(i) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.		
(ii) Add aqueous potassium bromide followed by dilute sulfuric acid. Add hexane and shake the mixture.		

You are *not* required to identify **FA 6**. [7]

(d) **(i)** **FA 6** and the residue from **(a)** contains element **X** in two different oxidation states. Using your observations from the tests in **(b)** and **(c)**, explain which compound, **FA 6** or the residue, contains **X** in the higher oxidation state.

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.... [2]

(ii) The reaction in test **(b)(iii)** is said to be a **comproportionation** reaction. In light of your observations to test **(b)(i)** and **(b)(iii)**, together with your answer to **(d)(i)**, suggest what the term comproportionation may refer to.

....

....

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....

.... [2]

[Total: 11]

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Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	7	–			INDEX NUMBER		

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 19 and 20.

Shift
Laboratory

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
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Total	

This document consists of **19** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

For Examiner's Use

1 Analysis of a solution containing both sodium hydroxide and sodium carbonate by Warder titration (double indicator method)

Aqueous sodium hydroxide easily reacts with atmospheric carbon dioxide. This results in the sodium hydroxide being contaminated with sodium carbonate Na_2CO_3.

The Warder titration (double indicator method) can be used to analyse a mixture containing both sodium hydroxide and sodium carbonate.

FA 1 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 2 is an aqueous solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.

(a) Titration of FA 2 against FA 1 using methyl orange or screened methyl orange indicator

In this titration, **FA 1** is run from the burette into the conical flask containing **FA 2** with methyl orange or screened methyl orange indicator.

The end-point is reached when the yellow colour changes to orange for methyl orange, or the green colour changes to grey for screened methyl orange.

(i) 1. Fill the burette with **FA 1**.

2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a conical flask.

3. Add a few drops of methyl orange or screened methyl orange indicator.

4. Run **FA 1** from the burette into the conical flask until the colour of the solution changes.

5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.

6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

Titration number	1	2
Final burette reading / cm^3	33.70	35.80
Initial burette reading / cm^3	0.00	2.00
Volume of **FA 1** used / cm^3	33.70	33.80
	✓	✓

[1] **table with correct headings *('burette' must be stated)* and units.** ***(Do not award if any final and initial burette readings are inverted/ if 50 is used as initial burette reading/ burette reading is >50)***
[1] **All burette readings recorded to the nearest 0.05 cm^3 + correct computation of titres**
[1] **Has two uncorrected titres for end-point within 0.10 cm^3 + place ✓ under two selected titres within 0.10 cm^3.** ***(Do not award if additional titration is performed after consistent titres are obtained.)***
[2] **Accuracy (Teacher's reading ±0.20 cm^3: 2m; ±0.40 cm^3: 1m)**

[5]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Average volume of **FA 1** $= \frac{33.70 + 33.80}{2}$

$= 33.75 \text{ cm}^3$

- **state correct term "Average volume"**
- **quote the selected titres in the average working**
- **give correct final value to 2 d.p.**

Volume of **FA 1** = ...**33.75 cm^3**........ [1]

(b) **Titration of FA 2 against FA 1 using thymolphthalein indicator**

When the titration in **(a)** was repeated using thymolphthalein as the indicator, 25.0 cm^3 of **FA 2** required 23.35 cm^3 of **FA 1**.

The following explains why different results were obtained using two different indicators.

- When **thymolphthalein** is used as the indicator, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

- When **methyl orange** is used as the indicator in **(a)**, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
  3. $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 1** calculated in **(a)(ii)**.

Amount of HC*l* in 33.75 cm^3 of **FA 1** $= 0.125 \times \frac{33.75}{1000}$ = **0.00422** mol

amount of HC*l* in volume in **(a)(ii)** = ...**0.00422 mol**........ [1]

(ii) Calculate the amount of hydrochloric acid in 23.35 cm^3 of **FA 1**.

Amount of HC*l* in 23.35 cm^3 of **FA 1** $= 0.125 \times \frac{23.35}{1000}$ = **0.00292** mol

amount of HC*l* in 23.35 cm^3 of **FA 1** = ...**0.00292 mol**........ [1]

(iii) Using your answer to **(b)(i)** and **(b)(ii)**, calculate the amount of hydrochloric acid that reacts with the Na_2CO_3 in the titration using thymolphthalein indicator.

Amount of HC*l* that react with Na_2CO_3 = 0.00422 – 0.00292 = **0.00130** mol

amount of HC*l* that react with Na_2CO_3 = ...**0.00130 mol**........ [1]

(iv) Hence, calculate the mass of sodium carbonate present in 25.0 cm^3 of **FA 2**.

[A_r: C, 12.0; O, 16.0; Na, 23.0]

Mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = 0.00130 × 106.0 = **0.138** g

mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = ...**0.138 g**........ [1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HC*l* when methyl orange is used as indicator is given below.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of HC*l* that reacted with the Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 2**.

Amount of HC*l* that react with Na_2CO_3 = 2 × 0.00130 = **0.00260** mol

amount of HC*l* = ...**0.00260 mol**........ [1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of sodium hydroxide in 25.0 cm^3 of **FA 2**.

[A_r: H, 1.0; O, 16.0; Na, 23.0]

Mass of NaOH in 25.0 cm^3 of **FA 2** = (0.00422 – 0.00260) × 40.0 = **0.0648** g

mass of NaOH = ...**0.0648 g**........ [1]

(vii) Calculate the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in **FA 2**.

$$\% \text{ by mass of } Na_2CO_3 \text{ in } \mathbf{FA\ 2} = \frac{0.138}{0.138 + 0.0648} \times 100 = \underline{\mathbf{68.0\%}}$$

percentage by mass of Na_2CO_3 in **FA 2** = **68.0%** [1]

(c) The error (uncertainty) associated with **each reading** is given as follows:

50.00 cm^3 burette: ±0.05 cm^3

25.0 cm^3 pipette: ±0.04 cm^3

Using the above data, calculate the percentage error (uncertainty) when a

(I) 50.00 cm^3 burette

(II) 25.0 cm^3 pipette

is used to measure 25 cm^3 of **FA 2** into the conical flask.

Hence state whether a 50.00 cm^3 burette or 25.0 cm^3 pipette will be more suitable to measure 25.0 cm^3 of **FA 2** accurately.

Error when burette is used = 2 × ±0.05 = ±0.10 cm^3

Note: This is because when using the burette, 2 readings are made- initial and final; hence the error has to be added up.

% error when using burette = 0.10/25 × 100% = **<u>0.4%</u>**

[1]

Error when 25 cm^3 pipette is used = ±0.04 cm^3

% error when using 25 cm^3 pipette = 0.04/25 × 100% = **<u>0.16%</u>**

The use of a burette to measure 25 cm^3 of **FA 2** will result in greater % error.

Hence a **25.0 cm^3 pipette is more suitable** to measure 25 cm^3 of **FA 2**. **[1]**

(from correct % calculations, allow ecf from % error)

[2]

[Total: 15]

2 To determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on gravimetric method

Sodium hydrogencarbonate decomposes on heating to give sodium carbonate, carbon dioxide and water vapour.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Sodium chloride on the other hand is unaffected by heat.

FA 3 is a mixture of anhydrous sodium hydrogencarbonate, $NaHCO_3$, and sodium chloride, $NaCl$.

In this question, you will heat to decompose the sodium hydrogencarbonate in **FA 3** and determine the mass of carbon dioxide and water lost. The data will be used to determine

- the mass of $NaHCO_3$ in **FA 3**,
- the percentage composition by mass of $NaHCO_3$ in **FA 3**.

(a) Thermal decomposition of $NaHCO_3$

In this experiment, solid **FA 3** is heated strongly in a boiling tube, over a non-luminous Bunsen flame, until there is no further change in the mass.

1. Weigh accurately about 4.5 g of **FA 3** in the boiling tube provided. Record your weighings in the space provided below.
2. Heat the tube gently first, then strongly.
3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

> You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.
5. Repeat points **2** to **4** as necessary until a constant mass is obtained.
6. **Turn off your Bunsen burner**.

(i) In an appropriate format in the space below, record all weighing measurements.

Mass of empty boiling tube / g	29.410
Mass of boiling tube and **FA 3** / g	33.891
Mass of **FA 3** used / g	4.481
Mass of boiling tube and residue after first heating /g	33.218
Mass of boiling tube and residue after second heating /g	33.065
Mass of boiling tube and residue after third heating /g	33.065

[1] Record "total mass of boiling tube + FA 3" + "mass of boiling tube + residue after 1st heating" + "mass of boiling tube + residue after 2nd heating"
[1] Record two constant masses (within 0.01g) of boiling tube + residue after heating
[1] All mass readings are recorded to 3 d.p. and mass of FA 3 used is within ±0.05 g, with appropriate units stated

[3]

(ii) Using your results, calculate the mass of carbon dioxide and water vapour evolved.

Mass of CO_2 and H_2O evolved = 4.481 g – 3.655 g = 0.826 g

mass of CO_2 and H_2O evolved = ...**0.826 g**........ [1]

(iii) Using your answer to **(a)(ii)**, calculate the amount of carbon dioxide evolved.

[A_r: H, 1.0; C, 12.0; O, 16.0]

Let the amount of carbon dioxide evolved by *x* mol.

$n_{CO_2} = n_{H_2O} = x$ mol

$$x(44.0) + x(18.0) = 0.826$$

$$x = \frac{0.826}{44.0 + 18.0} = 0.01332$$

amount of CO_2 evolved = ...**0.0133 mol**........ [1]

(iv) Calculate the mass of sodium hydrogencarbonate in the sample of **FA 3**.

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

$$n_{NaHCO_3} = 2n_{CO_2} = 2 \times 0.01332 = 0.02665 \text{ mol}$$

$$\begin{aligned}\text{Mass of NaHCO}_3 &= 0.02665 \times (23.0 + 1.0 + 12.0 + 3 \times 16.0) \\ &= 0.02665 \times 84.0 \\ &= 2.238 \text{ g} \approx 2.24 \text{ g}\end{aligned}$$

mass of $NaHCO_3$ in sample of **FA 3** = ...**2.24 g**........ [1]

(v) Determine the percentage by mass of sodium hydrogencarbonate in **FA 3**.

$$\%\text{ by mass of NaHCO}_3\text{ in FA1} = \frac{2.238}{4.481} \times 100\% = 49.9\%$$

percentage by mass of $NaHCO_3$ in **FA 3** = ...**49.9%**........ [1]

For Examiner's Use

(b) Suggest one possible source of error in this experiment. How would this error affect the calculated results in **(a)(iii)**?

Incomplete decomposition **[1]** may occur and therefore the mass lost recorded or mass of CO_2 and H_2O evolved is lower than actual. The calculated mass of $NaHCO_3$ is lower than actual. **[1]**

[2]

(c) Planning

Plan an experiment to determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on volumetric analysis method.

In this experiment, you will titrate a **solution of FA 3** against **FA 1**, using a suitable indicator.

You can assume you are provided with the following reagent:

FA 4 is a solution containing 30.00 g dm^{-3} of **FA 3**.

In your plan, you should include details of

- the amount of reagents you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- appropriate calculations to show how the percentage by mass of sodium hydrogencarbonate in **FA 3** can be determined, assuming the average titre is ***y*** cm^3.

Procedure

Step 1: Pipette 25.0 cm^3 of **FA 4** into a 250 cm^3 conical flask and add 1–2 drops of methyl orange indicator.

Step 2: Fill a burette with **FA 1**.

Step 3: Titrate the contents of the conical flask with **FA 4** from the burette until the solution changes from yellow to orange at the end point.

Step 4: Tabulate your titration values in the table below.

Titration number	Accurate		
	1	2	
Final burette reading / cm^3			
Initial burette reading / cm^3			
Volume of **FA 1** used / cm^3			

Step 5: Obtain from your titration results a suitable average titre. Show clearly the titres you used in calculating this average.

- Suitable volume of reagents used, apparatus used **[1]**
- Suitable indicator and colour change at the end point **[1]**
- Logical flow of procedure and Data collection **[1]**

Calculations

Average titre = y cm^3

Calculate the mass of $NaHCO_3$ per dm^3 of **FA 4**

$$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$$

n_{HCl} used in titration = $\frac{\boldsymbol{y} \times 0.200}{1000} = 2\boldsymbol{y} \times 10^{-4}$ mol $= n_{NaHCO_3}$ in 25.0 cm^3 of **FA 4** **[1]**

n_{NaHCO_3} per dm^3 = $\frac{2\boldsymbol{y} \times 10^{-4} \times 1000}{25} = 8\boldsymbol{y} \times 10^{-3}$ mol

mass of $NaHCO_3$ per dm^3 = $8\boldsymbol{y} \times 10^{-3} \times 84.0 = 0.672\boldsymbol{y}$ g **[1]**

% mass of $NaHCO_3$ in **FA 3** = $\frac{0.672\boldsymbol{y}}{30.0} \times 100\% = 2.24\boldsymbol{y}$ % **[1]**

[6]

[Total : 15]

3 Investigation of the kinetics of the reaction between calcium carbonate and hydrochloric acid

Calcium carbonate that reacts with hydrochloric acid in an acid-carbonate reaction as shown below.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

FA 5 is powdered $CaCO_3$.

In this question, you will measure the volume of CO_2 gas produced at timed intervals until the reaction is complete, using an excess of dilute hydrochloric acid.

You will need access to **FA 1** solution you used earlier.

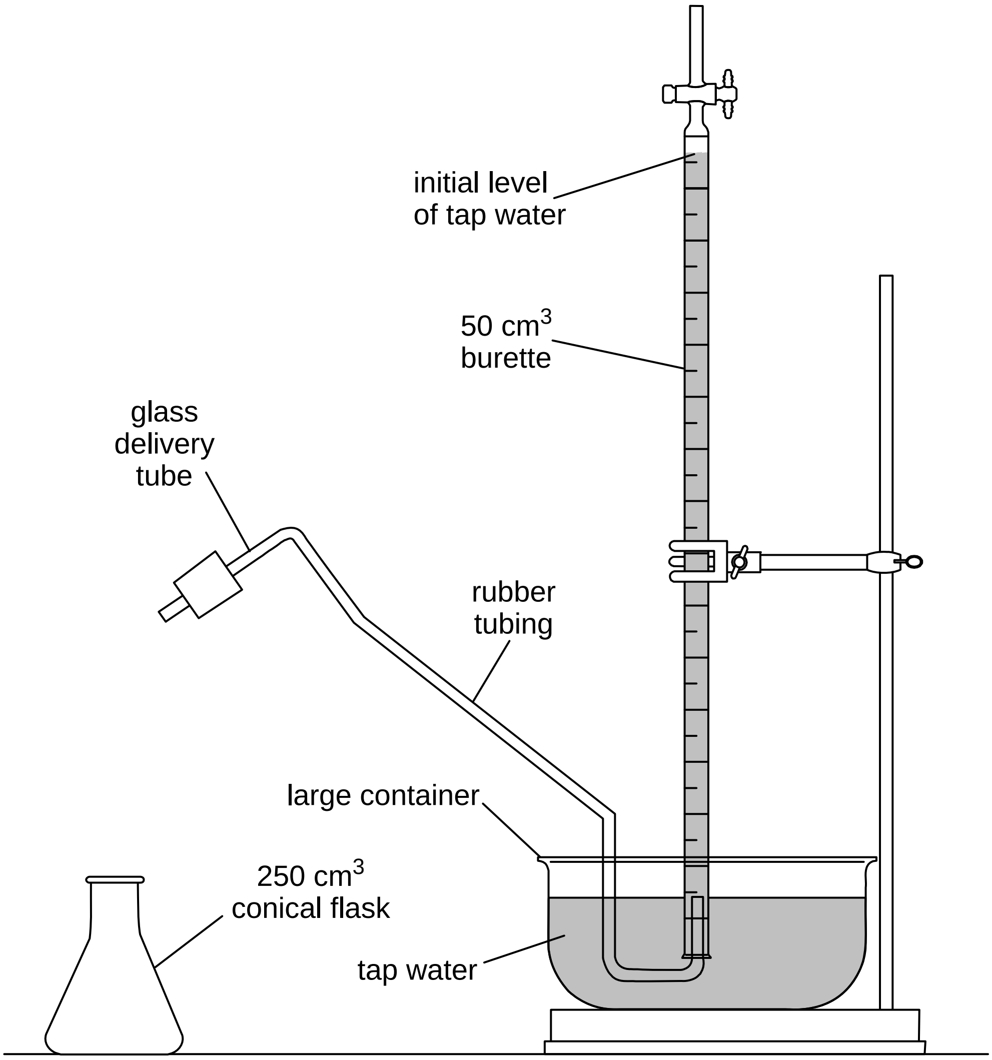

Fig 3.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page **11**, prepare a table in which you may record each burette reading and the time it was taken. The time taken should be recorded to one decimal place.

In addition, your table will need to show the volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in the Fig. 3.1. You should insert the plastic/rubber tubing to a sufficient depth in the burette so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.

3. Transfer all the solid **FA 5** provided in the weighing bottle into a dry and clean 250 cm^3 conical flask.

4. Use an appropriate measuring cylinder, measure 40 cm^3 of **FA 1**.

5. Transfer the **FA 1** into the conical flask containing **FA 5** and insert the bung into the conical flask.

6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.

   Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until the reaction is complete.

7. Check that the plastic/rubber tubing is securely positioned in the burette.

8. Hold the flask by its neck and **gently swirl** it continuously.

9. At *t* = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.

10. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

Time / min	**Burette Reading / cm^3**	**Volume of CO_2 / cm^3**
0.0	48.0	0.0
0.5		
1.0		

[1] Tabulates burette readings at t = 0 until the end of the experiment, time/min and volume of CO_2/cm^3.
Tables have correct headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table
[1] All burette readings and CO_2 volumes to 0.1 cm^3, and times to 0.5 min.
[1] Full set of results with final readings that have at least 3 values that are the same

[3]

For
Examiner's
Use

(ii) Plot on the grid below, a graph of the volume of CO_2 on the *y*-axis, against time, *t*, on the x-axis.

Draw the most appropriate best-fit curve, taking into account all of your points.

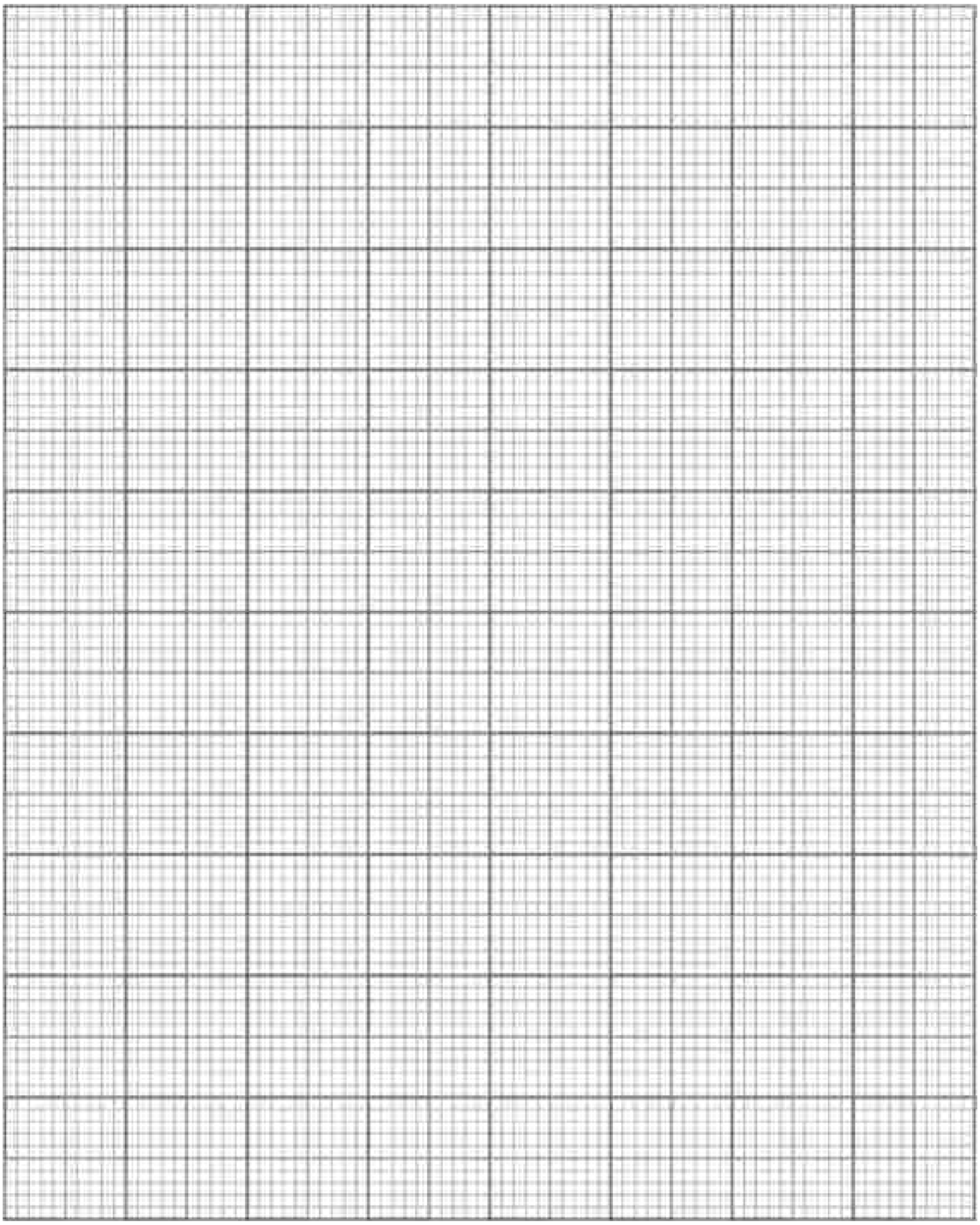

Fig. 3.2

[3]

[1] Axes correct way round + correct labels + units + scale
Sensible linear scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions

[1] All points correctly plotted to within ±½ small square. Check all points and put ticks if correct

[1] Graph line must be best-fit line (*Do not allow mark if clearly anomalous points are included*)

(iii) It has been claimed that the reaction between calcium carbonate and hydrochloric acid is pseudo-first order with respect to calcium carbonate.

State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 3.2 to support your answer.

[1] Determine at least 2 half-lives

[1] Conclude correctly on claim based on half-lives obtained

....

....

....

.... [2]

(b) Planning

Besides using the continuous measurement method in **3(a)** to determine the order of reaction of a reactant, the initial rates method can also be used.

Plan an investigation, which **does not** involve graph plotting, to determine the order of reaction with respect to hydrochloric acid, HC*l*, using the initial rates method.

You are provided the following chemicals and apparatus:

- same apparatus used in the experimental setup in **3(a)**,
- 2.00 mol dm^{-3} HC*l* solution
- **FA 5** powdered $CaCO_3$
- stopwatch

In your plan, you should include details of:

- the different concentrations of the reactants used and the conditions of the experiment,
- the procedure you would follow, including the end-point of the experiment
- the measurements you would take,
- an outline of how you would use your results to determine the order of reaction with respect to HC*l*.

You may use the space below to draw a table indicating the headers of the measurements and calculations you would be performing.

[1] Controls concentrations, volumes and total volume to be used for the experiment. States that temperature should be done at constant T (room temperature)

[2] Describe a suitable "stop-time"; *i.e.* the time required to produce at most 10% of the expected total volume of CO_2

[3] Propose to use the same procedure as 3(a) but modified to include the collection of CO_2 for two different concentrations of HC*l* that can be used to determine order of reaction.

[4] Describe the appropriate measurements needed to be taken and describing the calculations of 1/*t*

[5] Describe the use of 1/*t* as the initial rate of the experiment.

[6] Using inspection method or mathematically, describe how the deduction of the order of reaction of HC*l* can be done.

[6]

[Total: 14]

4 Carry out the following experiments with **FA 6**.

In all tests the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

Observations should include:

(i) descriptions of colour changes and precipitates;

(ii) names of gases evolved and details of the test used to identify each one.

You should indicate clearly at which stage in a test a change occurs, writing any deductions that you make alongside the observations upon which they are based.

Marks will be given *only* for the prescribed tests and will *not* be given for chemical equations.

TEST	OBSERVATION	CONCLUSION
Tests of FA 6 **(a)** Heat **FA 6** in a test-tube until no further change is observed. **Allow the residue to cool** and retain it for **(b)**. You may wish to proceed with the tests in **4(c)** while waiting for the residue to cool.	- Violet gas evolved which bleaches litmus. **[1] with identity of gas** - Colourless gas evolved which relights glowing splint. **[1] with identity of gas** - White residue, same colour as original	- Gas is I_2 - Gas is O_2 - IO_3^- present - K^+, Na^+, Ca^{2+}, Ba^{2+} or Mg^{2+} may be present
(b) Dissolve the residue from test **(a)** in deionised water and use separate portions of the solution for tests **(i)** to **(iii)**	- Colourless solution	
(i) Add aqueous silver nitrate to a portion of the solution.	- Yellow ppt	
Then add aqueous ammonia.	- Ppt insoluble in aqueous ammonia **[1] for both**	- I^- present in residue **[1]**

TEST	OBSERVATION	CONCLUSION
(ii) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.	- Brown solution / black ppt **[1]** - Purple $KMnO_4$ decolourised	- I_2 produced **[1]** - I^- present in residue - Reducing agent present **[1]**
(iii) Add a few crystals of **FA 6**, shake to dissolve and then add dilute sulfuric acid.	- Brown solution obtained **[1]** **with identification of I_2**	- I_2 produced - **FA 6** is an oxidising agent **[1]** - I^- present in residue
(c) Dissolve **FA 6** in water and use separate portions of the solution for tests **(i)** and **(ii)**.	- Colourless solution	
(i) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.	- Purple colour of $KMnO_4$ remains **[1]**	- Reducing agent absent **[1]**
(ii) Add aqueous potassium bromide followed by dilute sulfuric acid.	- Orange solution formed	**[1] either**
Add hexane and shake the mixture.	- Dark red top organic layer and yellow/orange bottom aqueous layer	- Br_2 produced **[1]** - Oxidising agent present **[1]**

You are *not* required to identify **FA 6**. **[14 max 7]** [7]

(d) **(i)** **FA 6** and the residue from **(a)** contains element **X** in two different oxidation states. Using your observations from the tests in **(b)** and **(c)**, explain which compound, **FA 6** or the residue, contains **X** in the higher oxidation state.

FA 6 **[1, with correct reasoning]** contains **X** in the higher oxidation state. From test **(c)(i)**, **FA 6** does not react with the strong oxidising agent, $KMnO_4$, whereas in test **(b)(ii)**, the residue decolourises $KMnO_4$. [1] Hence, **FA 6** cannot be oxidised, while the residue can be oxidised, meaning that **FA 6** must have contained **X** in the higher oxidation state

[2]

(ii) The reaction in test **(b)(iii)** is said to be a **comproportionation** reaction. In light of your observations to test **(b)(i)** and **(b)(iii)**, together with your answer to **(d)(i)**, suggest what the term comproportionation may refer to.

Test **(b)(i)** confirms the presence of I^- in the residue, which is oxidised to I_2 by **FA 6**, which contains I (**X**) in a higher oxidation state, in test **(b)(iii)**. [1]

Comproportionation refers to a reaction in which **two reactants**, each containing the **same element** but with a **different oxidation state**, form **a product** in which the element involved has the **same intermediate oxidation state**. [1]

[2]

[Total: 11]

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Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	17S
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

21 September 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

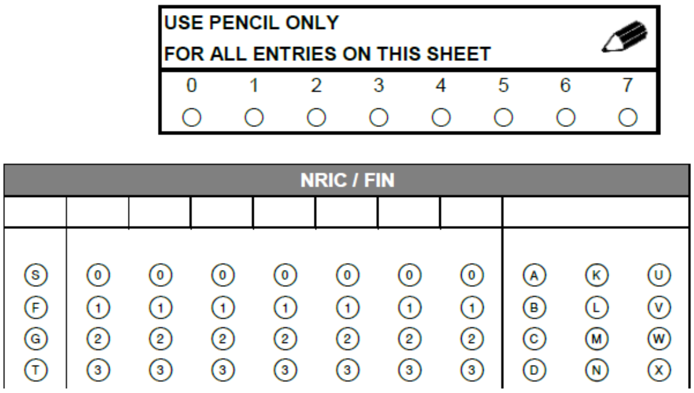
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Complete the information on the Answer Sheet as shown below.

1. Enter your **NAME** (as in NRIC). ______________
2. Enter the **PAPER NUMBER.** ______________
3. Enter your **CT GROUP.** ______________
4. Enter your **NRIC NUMBER** or **FIN Number**
5. Now **SHADE** the corresponding circles in the grid for **EACH DIGIT** or **LETTER**



There are **30** questions on this paper. Answer **all** questions. For each question, there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

This document consists of **14** printed pages.

1 The successive ionisation energies, in kJ mol^{-1}, of an element **X** are given below.

870 1800 3000 3600 5800 7000 13200

What can be inferred from the data provided?

A **X** has a half-filled p-subshell.

B **X** has a giant covalent structure.

C **X** is likely to form a compound with the formula BeX_2 when reacted with beryllium.

D **X** has a lower first ionisation energy than the element preceding it in the Periodic Table.

2 In which pair does the first species have a larger bond angle than the second?

A CF_4 and BF_3

B SO_2 and CO_2

C ClO_3^- and H_2S

D PO_4^{3-} and NO_3^-

3 Silicon has a giant covalent structure similar to that of diamond. At room temperature, it is a very poor conductor. However, when heated to higher temperatures, its electrical conductivity increases.

What is the best explanation for the increase in electrical conductivity at higher temperatures?

A Heating ionises silicon to give Si^{4+} ions.

B Heating increases the frequency of vibration of silicon atoms.

C Heating breaks some of the Si−Si bonds, allowing silicon particles to move.

D Heating excites some of the valence electrons to higher energy levels such that they can be delocalised.

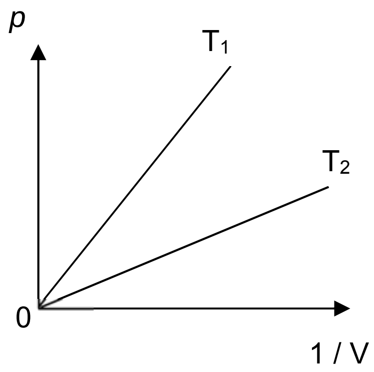
4 Measured values of the pressure, volume and temperature of a known mass of a gaseous compound are to be substituted into the ideal gas equation to calculate the relative molecular mass, M_r, of the compound.

Which conditions of pressure and temperature would give the most accurate value of M_r?

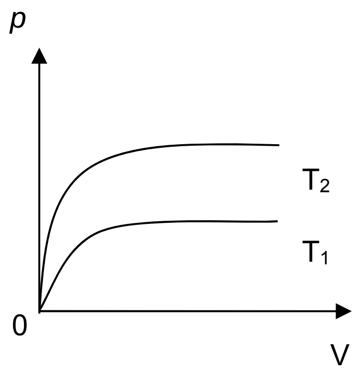
	pressure	temperature
A	low	low
B	low	high
C	high	high
D	high	low

5 Which graph shows the behaviour of a fixed mass of an ideal gas at two constant temperatures, T_1 and T_2, where $T_2 > T_1$?

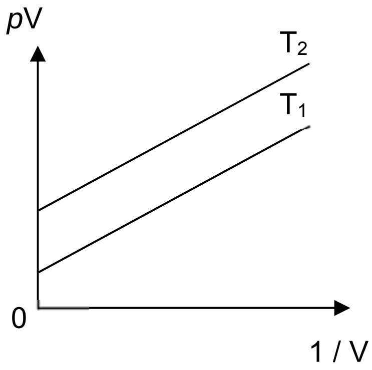
A



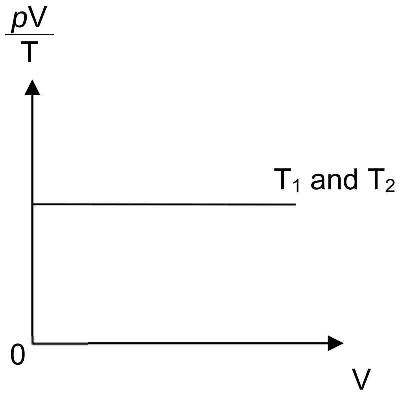
B



C



D



6 When hydrogen chloride gas reacts with ammonia gas, ammonium chloride is produced which is seen as white fumes.

Which statement about this reaction is **incorrect**?

A Ammonia is a Brønsted-Lowry base because it accepts a proton from hydrogen chloride.

B Ammonia is a Lewis base because it donates its lone pair of electrons to a proton in hydrogen chloride.

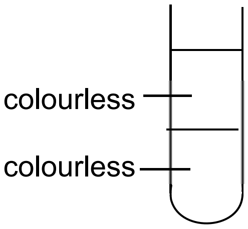
C Hydrogen chloride is an Arrhenius acid because it dissociates to give H^+ ion.

D Hydrogen chloride is a Lewis acid because it accepts a lone pair of electrons from ammonia.

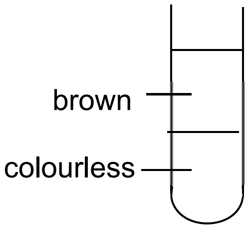
7 Aqueous chlorine is added to aqueous sodium iodide and the mixture was shaken with an equal volume of trichloromethane.

Given that the density of trichloromethane is 1.48 g cm^{-3}, which observation can be seen?

A



B



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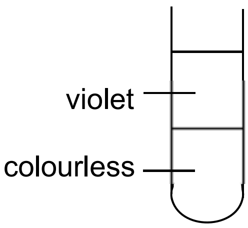
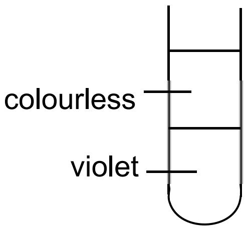


D



8 *Use of the Data Booklet is relevant to this question.*

FeO_4^{2-} is a strong oxidising agent. It is produced by warming $Fe(OH)_3$ with ClO^- in alkaline medium.

$$2Fe(OH)_3 + 3ClO^- + 4OH^- \rightarrow 2FeO_4^{2-} + 5H_2O + 3Cl^-$$

The FeO_4^{2-} produced is typically precipitated out as $BaFeO_4$ (M_r = 257.1) and it is kept in dark bottles for future usage.

What can be deduced from the above information?

1 0.25 mol of $Fe(OH)_3$ and 0.40 mol of $NaClO$ dissolved in excess NaOH solution can produce a maximum of 64.3 g of $BaFeO_4$.

2 $E^\ominus(FeO_4^{2-}/ Fe(OH)_3)$ is likely to be less than +0.81 V.

3 $BaFeO_4$ is likely to be sensitive to light.

A 1, 2 and 3 **B** 1 and 3 only **C** 2 and 3 only **D** 1 only

9 When water freezes, 6.0 kJ mol^{-1} of heat enthalpy is evolved.

What is the entropy change when 54 g of water freezes at 0 C?

A -66 J K^{-1} **B** -22 J K^{-1} **C** 22 J K^{-1} **D** 66 J K^{-1}

10 The initial rate of the slow reaction between peroxodisulfate(VI) and iodide ions can be studied by the "clock" method, using sodium thiosulfate.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \qquad \text{reaction } \mathbf{I}$$
$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6 \qquad \text{reaction } \mathbf{II}$$

When sodium thiosulfate is added to the reaction mixture, the iodine produced by reaction **I** will immediately react in reaction **II** until all the sodium thiosulfate has been used up. At that point, there will be a sudden appearance of a deep blue colour if starch is present.

A series of experiments are carried out and the results are shown below.

experiment	volume of 0.200 mol dm^{-3} $S_2O_8^{2-}$ /cm^3	volume of 2.00 mol dm^{-3} I^- /cm^3	volume of 0.050 mol dm^{-3} $Na_2S_2O_3$ /cm^3	volume of starch solution /cm^3	volume of water /cm^3	time *t* /s	Relative rate /s^{-1}
1	10	20	2	4	14	56	0.0179
2	10	30	2	4	4	37	0.0270
3	10	10	1	2	2	28	0.0357

Which statements about the above reaction are correct?

1 The rate equation for this reaction is rate = $k[S_2O_8^{2-}][I^-]$.

2 The rate of formation of iodine in experiment 1 is 1.79×10^{-5} mol dm^{-3} s^{-1}.

3 Both Fe^{2+} and Fe^{3+} can be catalysts for this reaction.

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

11 The numerical values of the equilibrium constant, K_p, for the reaction

$$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

are 3.20×10^{-3} and 1.50 at 298 K and 500 K respectively. Which statement is correct?

A The backward reaction is endothermic.

B The yield of carbon dioxide increases with temperature.

C The value of K_p depends on the amount of Ag_2CO_3 used.

D The yield of carbon dioxide will increase when Ag_2O is removed.

12 At 500 K, an equilibrium exists for the dissociation of Al_2Cl_6.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

A sample of Al_2Cl_6 at a pressure of 0.72 atm was placed in an empty container and allowed to reach equilibrium at 500 K. The total pressure at equilibrium was 1.20 atm.

Which statements are correct?

1 The degree of dissociation, α, is 0.67.

2 When volume of the container is halved, the position of equilibrium will shift to the left.

3 Both the rate constant and equilibrium constant would increase with temperature.

A 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

13 Human plasma is buffered mainly by dissolved CO_2 which has reacted to form carbonic acid, H_2CO_3.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Given that the pH of human plasma is 7.4 and the acid dissociation constant, K_a, of carbonic acid is 7.90×10^{-7} mol dm^{-3}, which statement is correct?

A The ratio of $[HCO_3^-]$ to $[H_2CO_3]$ in human plasma is 1 : 20.

B The ratio of $[HCO_3^-]$ to $[H_2CO_3]$ in human plasma is 10 : 1.

C This buffer system is more efficient in removing acid than base.

D This buffer system can be prepared by mixing suitable amounts of sodium hydrogencarbonate and sodium hydroxide.

14 Which statement explains the observations that magnesium hydroxide dissolves in ammonium chloride, but not in aqueous sodium chloride?

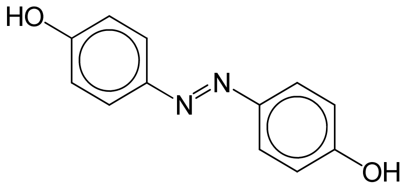
A The ammonium ion acts as an acid.

B The ammonium ion changes the solubility product of $Mg(OH)_2$.

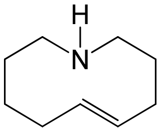
C Ammonium hydroxide is first formed, and then acts through a common ion effect.

D A complex is formed when magnesium hydroxide is added to ammonium chloride.

15



X



Y

Which bonds are present in compounds **X** and **Y** above?

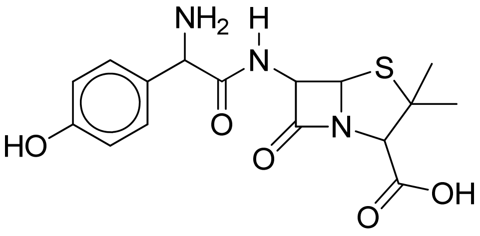
1 a σ bond formed by $2sp^2$-$2sp^2$ overlap between two N atoms in **X**

2 a σ bond formed by $2sp^3$-$2sp^2$ overlap between two C atoms in **Y**

3 a π bond formed by $2sp^2$-$2sp^2$ overlap between two C atoms in **Y**

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

16 The structure of amoxicillin, an antibiotic useful for the treatment of a number of bacterial infections, is shown below.



amoxicillin

What is the total number of chiral carbons in this molecule?

A 3 **B** 4 **C** 5 **D** 6

17 Deuterium (D or ^{2}H) is a heavy isotope of hydrogen. A deuterated hydrocarbon has the formula shown below.

$$CDH{=}CH{-}CH{=}CHC_3H_7$$

What is the total number of isomers with the above formula?

A 4 **B** 6 **C** 8 **D** 10

18 The equation for the complete combustion of an alkane, C_nH_{2n+2}, is given below.

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \rightarrow nCO_2 + (n+1)H_2O$$

Which statement is **incorrect**?

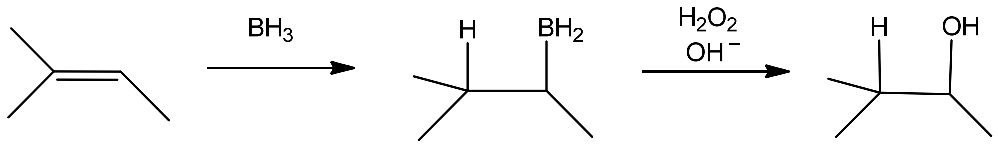
A The volume of oxygen required is directly proportional to the number of carbon atoms present in the alkane.

B At 120 °C, the volume of steam produced per mole of alkane is more than the volume of carbon dioxide produced.

C More oxygen is needed for the complete combustion of 1 mole of alkane as compared to 1 mole of an alkene with the same number of carbon atoms.

D The volume of carbon dioxide produced at 25 °C is the same for the complete combustion of 1 mole of an alkane or 1 mole of an alkene with the same number of carbon atoms.

19 Hydroboration is a two-step reaction for the preparation of alcohols from alkenes, as shown in the scheme below for compound **X**.



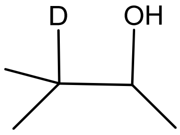
compound **X**

Which statement is **not** true for this reaction?

A H_2O_2 acts as a reducing agent in the second step.

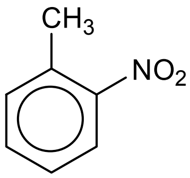
B The type of reaction involved in the first step is electrophilic addition.

C In the first step, the boron atom of BH_3 adds to the less substituted carbon of the C=C group.

D 

would be formed if BD_3 was used instead of BH_3 in the hydroboration above. (D = $^{2}_{1}H$)

20 2-methylnitrobenzene is a pale yellow oil and it is often used to make dyes.



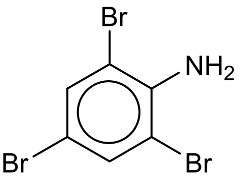
2-methylnitrobenzene

2-methylnitrobenzene is subjected to the following reactions:

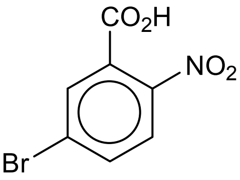
- heat with tin in concentrated HC*l* followed by careful addition of cold NaOH(aq)
- dropwise addition of aqueous bromine

What is the product obtained after the above reactions?

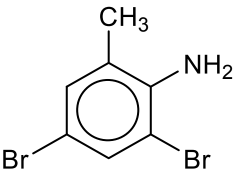
A



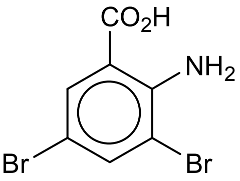
B



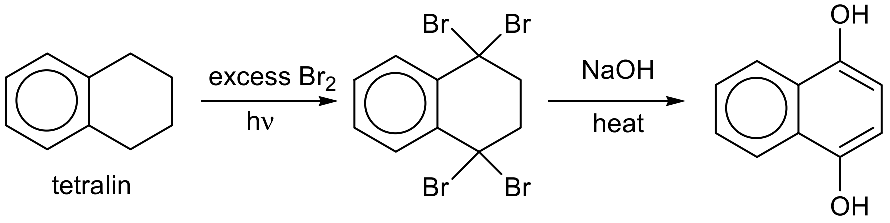
C



D



21 Naphthalene-1,4-diol could be made from tetralin via the following synthetic scheme.



tetralin

naphthalene-1,4-diol

What are the types of reactions involved in the above scheme?

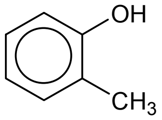
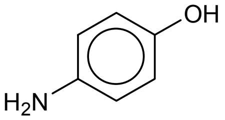
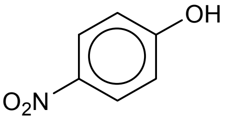
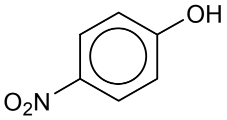
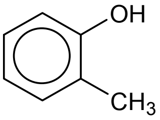
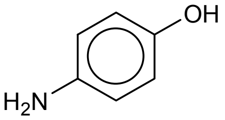
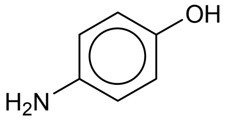
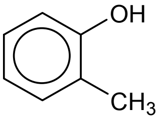
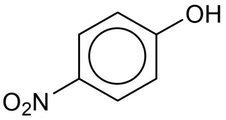
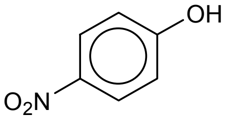
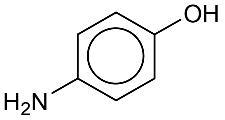
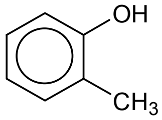
1 free radical substitution

2 nucleophilic substitution

3 dehydration

A	1 and 2 only	**B**	1 and 3 only	**C**	2 and 3 only	**D**	1, 2 and 3

22 Which row is correct?

	least acidic	⟶	most acidic
A			
B			
C			
D			

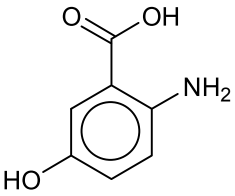
23 A contest for graduate students requires them to synthesise a molecule with the following features.

- It is cyclic.
- It contains two chiral centres.
- It does not decolourise aqueous bromine.
- It gives a silver mirror with Tollens' reagent.
- It gives yellow precipitate when warmed with aqueous alkaline iodine.

What is the minimum number of carbon atoms the synthesised molecule could have in order to satisfy the above features?

A 5 **B** 6 **C** 7 **D** 8

24 5-hydroxyanthranillic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.

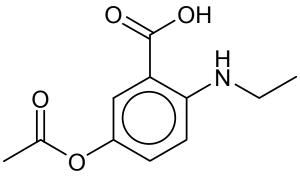


5-HAA

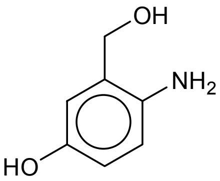
When 5-HAA was subjected to ethanoyl chloride followed by lithium aluminium hydride in dry ether, the product was found to give a purple colouration with neutral $FeCl_3$(aq).

Which is a likely product?

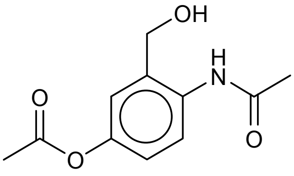
A



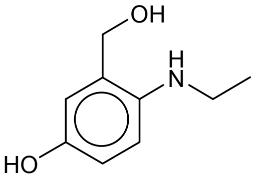
B



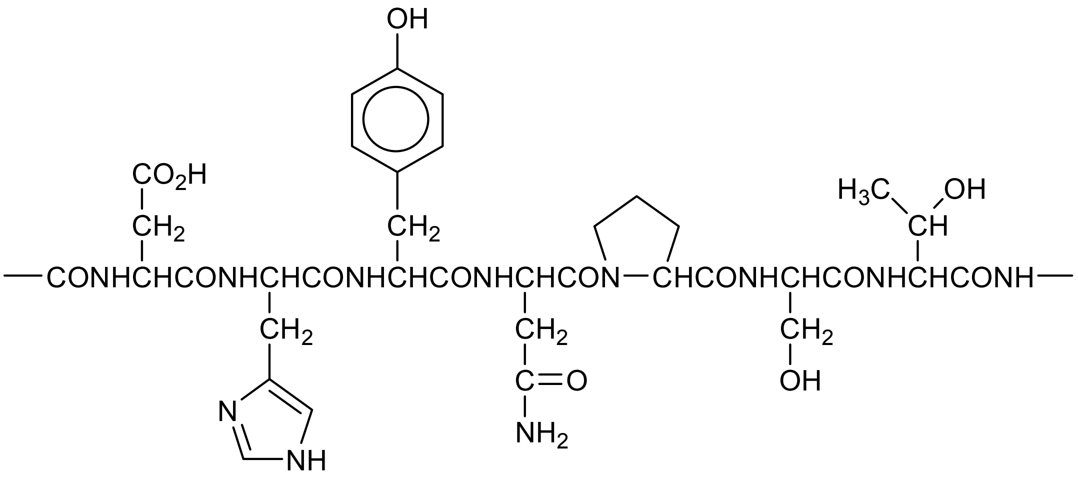
C



D

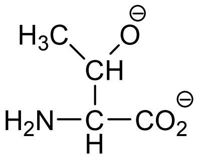


25 Part of the chain of a protein is shown.

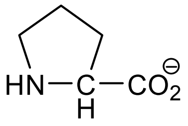


What can be the products obtained when this protein is hydrolysed by 6 mol dm^{-3} NaOH?

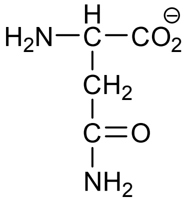
1



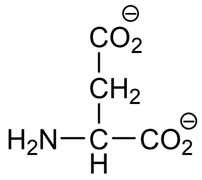
2



3



4



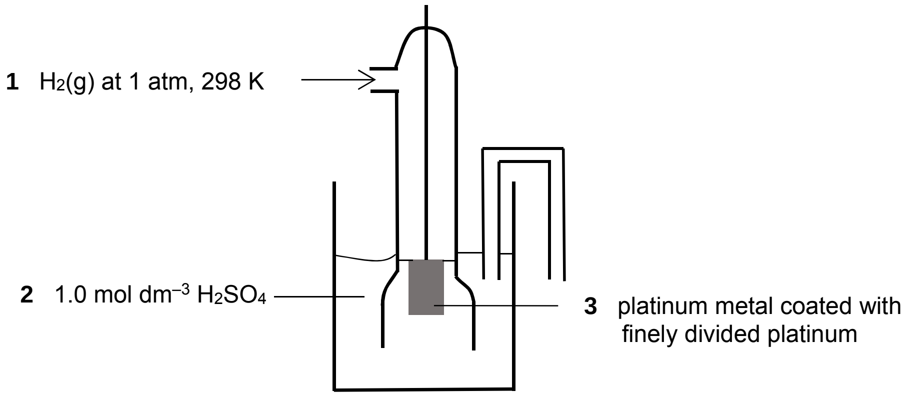
A 2 and 4 only

B 1, 2 and 3 only

C 2, 3 and 4 only

D 1, 3 and 4 only

26 In the diagram of the standard hydrogen electrode below, which labels are correct?



A 3 only

B 1 and 2 only

C 2 and 3 only

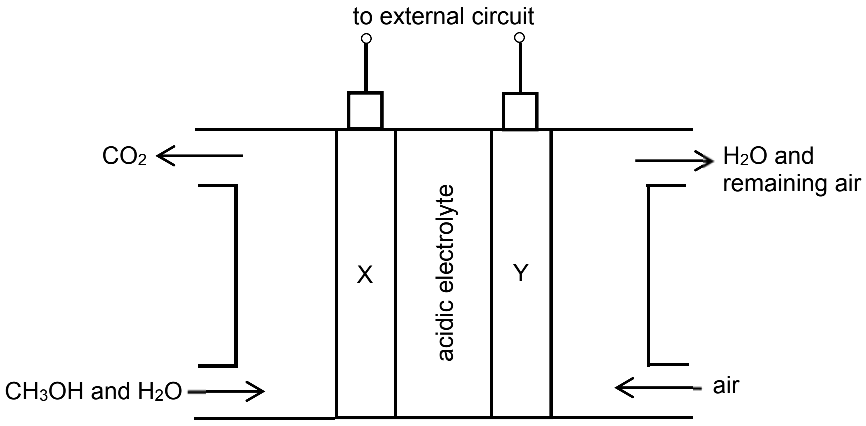
D 1, 2 and 3

27 Which factors determine the amount of oxygen produced at the anode during the electrolysis of molten aluminium oxide?

	mass of Al_2O_3 used	current	time
A	✓	✓	✗
B	✓	✗	✗
C	✗	✓	✓
D	✗	✗	✓

28 *Use of the Data Booklet is relevant to this question.*

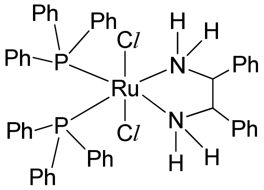
A contemporary direct methanol fuel cell is shown below.



In which direction do the electrons flow in the external circuit and which $E^\ominus$ value should be used for electrode Y?

	direction of electron flow	$E^\ominus$ of electrode Y / V
A	X to Y	+0.40
B	X to Y	+1.23
C	Y to X	+0.40
D	Y to X	+1.23

29 Ruthenium based organometallic catalysts are powerful tools for preparing organic compounds from previously unavailable routes. One of such complexes is shown.



Ph = C_6H_5

The electronic configuration of ruthenium metal in the ground state is [Kr]$4d^7 5s^1$.

What is the electronic configuration of ruthenium in the complex above?

A [Kr]$4d^7 5s^1$ **B** [Kr]$4d^7$ **C** [Kr]$4d^6$ **D** [Kr]$4d^5 5s^1$

30 Which set of data correctly illustrates copper as a typical transition element and calcium as an *s*-block element?

	property	copper	calcium
1	density / g cm^{-3}	8.92	1.54
2	melting point/ °C	1085	842
3	electrical conductivity/ $\mu S m^{-1}$	9.6	85

A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

END OF PAPER

1	2	3	4	5	6	7	8	9	10
D	**C**	**D**	**B**	**D**	**C**	**D**	**A**	**A**	**D**
11	12	13	14	15	16	17	18	19	20
B	**D**	**C**	**A**	**B**	**B**	**C**	**A**	**A**	**C**
21	22	23	24	25	26	27	28	29	30
D	**C**	**B**	**D**	**A**	**A**	**C**	**B**	**C**	**B**

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	17S
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

12 September 2018

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided in the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/ 19
2	/ 11
3	/ 11
4	/ 11
5	/ 15
6	/8
Deductions	
Total	/ 75

Calculator Model:

1 **(a)** Describe and explain the trend in thermal stability of Group 17 hydrides, HF to HI, by referring to relevant bond energies from the *Data Booklet*.

....

....

....

....[2]

(b) The very low acid strength of HF was frequently explained by the same reasoning in **(a)**. However, the dissociation of HF in aqueous solution

$$HF(aq) \rightarrow H^+(aq) + F^-(aq) \qquad \Delta H_{dissociation}$$

involves a cycle of steps. Hence, a whole series of enthalpy changes should be considered, one of which is the enthalpy change of hydration.

(i) Explain, with the aid of an equation, what is meant by *standard enthalpy change of hydration for* F^- *ion*.

....

....

....[2]

(ii) Fig. 1.1 shows an incomplete energy level diagram to represent the cycle of steps involved in the dissociation of HF.

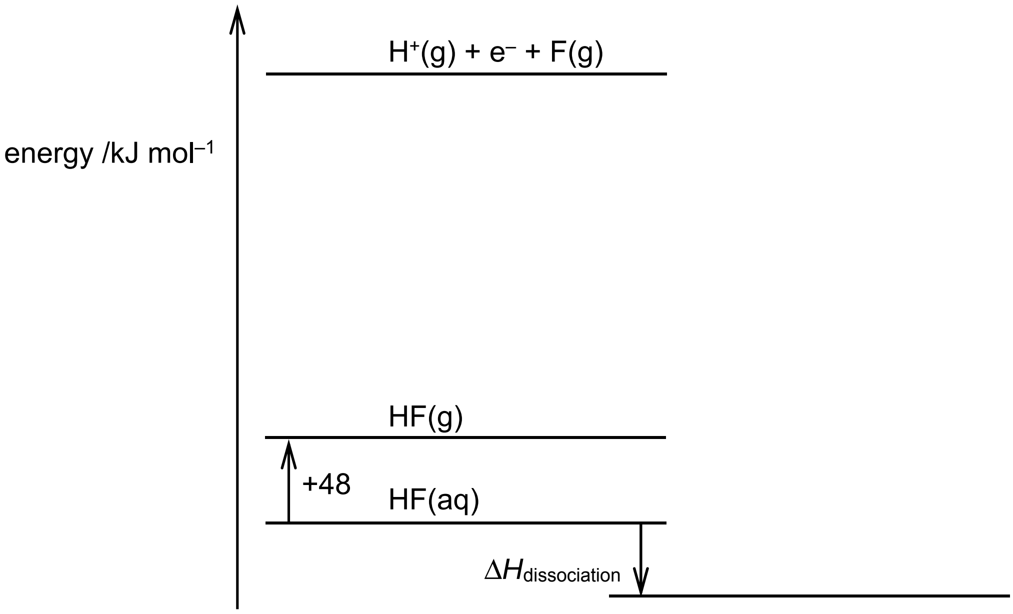


Fig. 1.1

Complete Fig. 1.1 by incorporating the following data and relevant data from the *Data Booklet*. Draw arrows and label each level with the appropriate formulae.

electron affinity for F(g)	= –328 kJ mol^{-1}
enthalpy change of hydration for $H^+(g)$	= –1091 kJ mol^{-1}
enthalpy change of hydration for $F^-(g)$	= –515 kJ mol^{-1}

[3]

(iii) Use your completed energy level diagram to calculate $\Delta H_{dissociation}$ for HF.

[1]

(c) **(i)** Explain why two HF molecules can form a hydrogen bond between them.

....

....

....

....

....[2]

(ii) When we measure the distance between a hydrogen nucleus and a fluorine nucleus in solid HF, two H to F 'bond distances' are found: 0.092 nm and 0.163 nm.

Draw a diagram containing two HF molecules, showing why there are two different 'bond distances'. Name and label which bond has 'bond distance' 0.092 nm, which has 'bond distance' 0.163 nm.

[2]

(d) Nitrogen also forms hydrides, such as hydrogen azide, HN_3, and ammonia, NH_3.

HN_3 has two bond angles: 104.5° and 180°.

Suggest a dot-and-cross diagram for HN_3.

[1]

(e) NH_3 is produced from N_2 and H_2 in the presence of a catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State and explain how the entropy will change when N_2 and H_2 react.

....

....

....

.... [2]

(ii) Write an expression for K_p for the above equilibrium.

[1]

(iii) In an experiment, N_2 and H_2 are placed in a sealed reactor in the molar ratio 1:3. The reactor is maintained at a temperature of 750 K. At equilibrium, 20% of N_2 is converted to NH_3, and the total pressure is 20.0 Mpa.

Calculate a value for K_p for the equilibrium, stating its units. (1 MPa = 10^6 Pa)

[3]

[Total: 19]

2 In addition to carbon and hydrogen, organic compounds commonly contain other elements covalently bonded in their molecules.

A strategy to identify these other elements in the compounds is to convert them to ionic forms so that these can be detected subsequently by qualitative tests.

(a) State the *type of reaction* that a chloroalkane can be subjected to so as to convert the chlorine present to chloride ions. Give the reagents and conditions for the reaction.

type of reaction: ………………………………………………...

reagents and conditions: …...……………………………………………………………[1]

"Sodium fusion" is an approach which uses the above strategy for the detection of other elements, in particular, halogens, nitrogen and/or sulfur, in organic compounds. The procedure is outlined below.

1. A sample of sodium metal is gently heated in a small boiling tube until molten.
2. The organic compound is added to the boiling tube a little at a time. Effervescence of hydrogen is observed immediately if the organic compound contains "active hydrogen".
3. The boiling tube is heated gently at first, then strongly while the "fusion reaction" between sodium and the organic compound occurs. During this process, other elements in the organic compound are converted to ions such as those in Table 2.1 and ionic sodium compounds are formed.
4. The contents of the hot boiling tube are completely emptied into a beaker of water. The "fusion reaction" is quenched because any excess sodium reacts with the water.
5. The contents of the beaker are filtered.
6. The filtrate is tested for relevant ions qualitatively.

Table 2.1

element(s) other than carbon and hydrogen in organic compound	ion after "fusion reaction"
chlorine	chloride, Cl^-
bromine	bromide, Br^-
both nitrogen and sulfur	thiocyanate, SCN^-
nitrogen in the absence of sulfur	cyanide, CN^-
sulfur in the absence of nitrogen	sulfide, S^{2-}

(b) **(i)** Suggest two different functional groups which may be present in organic compounds containing "active hydrogen", leading to effervescence in step 2.

……………………………………………………………………………………………[1]

(ii) One reason that sodium is used is that the sodium ion in the filtrate does not interfere with the tests in step 6.

Using **relevant** data from Table 2.2 about sodium, suggest another **two** reasons why sodium is used for the "fusion reaction".

Table 2.2

density	0.97 g cm^{-3}
melting point	98 C
standard redox potential, $E^{\ominus}(Na^+/Na)$	−2.71 V

....

....

....

....

....

....[2]

(c) In step 6, to test for the sulfide ion, the reagent sodium nitroprusside is added to the filtrate. A positive test is indicated by the appearance of a violet colouration owing to the formation of compound **A**, which contains an octahedral complex ion containing Fe^{2+}.

(i) Explain why compound **A** is coloured.

....

....

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....[3]

(ii) Compound **A** contains the following composition by mass.

element	Na	Fe	C	N	O	S
percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4

Determine the empirical formula of compound **A**.

[2]

(iii) The complex ion in compound **A** contains two different ligands, one of which is found in Table 2.1.

Suggest the formula of the **other** ligand, given that this ligand forms only one bond with the central Fe^{2+} ion. Information from other parts of **(c)** may be relevant.

....[1]

(d) **B** (M_r = 77.1) is an optically active organic compound. In addition to carbon and hydrogen, **B** contains only element(s) in Table 2.1. **B** underwent "sodium fusion" and its filtrate gave a blood-red complex on addition of aqueous Fe^{3+}.

Suggest the structure of compound **B**, given that it is non-cyclic and contains only single bonds. Assume that all elements show their usual valencies.

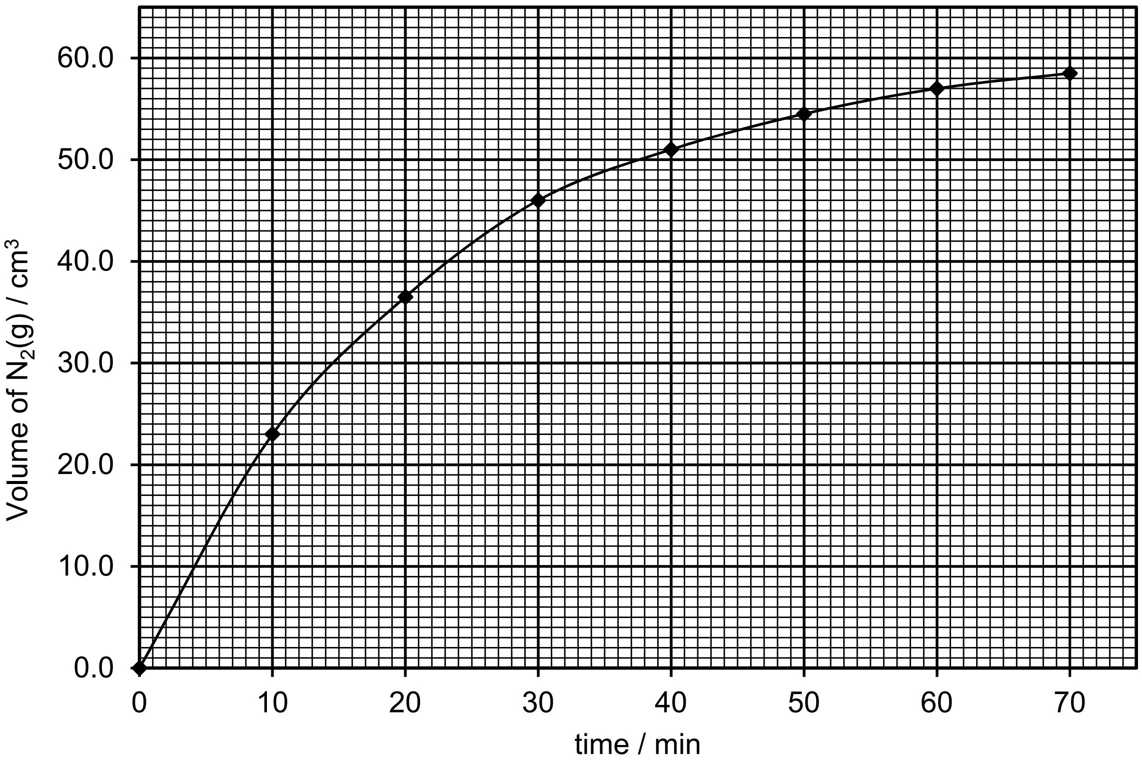
[1]

[Total: 11]

3 (a) Ethyl diazoethanoate, **D**, reacts with water to give compound **E,** and nitrogen.

$$\underset{\textbf{D}}{N_2CHCO_2CH_2CH_3(aq)} + H_2O(l) \rightarrow \underset{\textbf{E}}{HOCH_2CO_2CH_2CH_3(aq)} + N_2(g)$$

When 2.50×10^{-3} mol of **D** was added into water, the volume of nitrogen gas evolved at intervals of time after the start of the reaction were measured at 293 K, 1 atm. The experiment results were plotted in the graph below.



(i) State the *type of reaction* for the above reaction.

………………………………………………………………………………………… [1]

(ii) Use the information given and the graph above to show that the order of reaction with respect to **D** is 1.

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…………………………………………………………………………………………

…………………………………………………………………………………………[3]

(iii) Calculate the rate constant for this reaction at 293 K, stating its units.

[2]

(b) The rate of this reaction, using 1.00 mol dm^{-3} of solution **D**, was measured at 293 K in the presence of nitric acid. The results for a series of pH values are shown in Table 3.1.

Table 3.1

experiment	pH	initial rate / mol dm^{-3} min^{-1}
1	2.0	2.69×10^{-2}
2	2.3	1.35×10^{-2}
3	2.4	1.07×10^{-2}

(i) Using the information in Table 3.1, deduce the order of reaction with respect to H$^+$(aq), and hence write the rate equation for this reaction.

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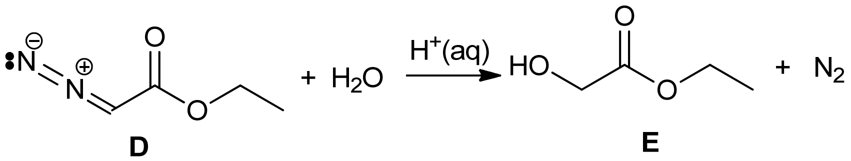
………………………………………………………………………………………………[2]

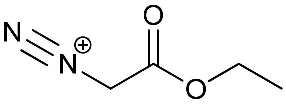
(ii) The overall reaction between **D** and water is shown below:



D **E**

This reaction occurs via a three-step mechanism in the presence of H^+(aq).

- In the first step, the lone pair of electrons on the negatively charged nitrogen forms a new π bond with the positively charge nitrogen and simultaneously, the C=N π bond attacks H^+(aq) to form a new σ bond to give intermediate **F**.



F

- In the second step, water reacts with **F**, giving the protonated form of **E** and N_2.
- In the third step, H^+(aq) is lost to give **E**.

Illustrate the mechanism for this reaction, showing any relevant lone pairs, dipoles and charges, and indicating the movement of electron pairs with curly arrows. Label the slow step in your mechanism.

[3]

[Total: 11]

4 **(a)** **(i)** The pK_a values for the two successive dissociation of $H_2C_2O_4$ at 25 °C are: pK_{a1} = 1.23; pK_{a2} = 4.19.

A small quantity of $H_2C_2O_4$ is usually found in fabrics as dye fixatives, a substance used to set dyes on fabrics. A dye having a density of 1.50 g cm^{-3} contains x % by mass of $H_2C_2O_4$.

The pH of the dye is found to be 1.27. Ignoring the second dissociation for $H_2C_2O_4$ and assuming that the acidity of the dye arises only from $H_2C_2O_4$, determine the value of x.

[2]

(ii) When 25.0 cm^3 of the dye is titrated with 0.100 mol dm^{-3} NaOH(aq), the pH at the second equivalence point is greater than 7.

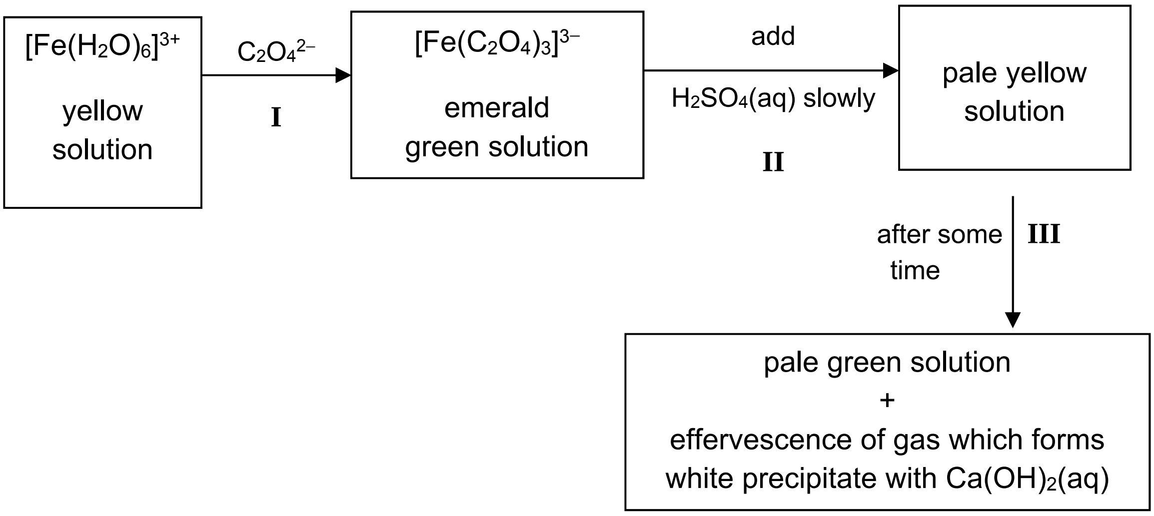
With the aid of a relevant equation, explain this observation.

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

(b) The following scheme illustrates a series of reactions involving $Fe^{3+}(aq)$.



(i) State the *type of reaction* which occurred in reaction **I** and write an equation for the reaction.

type of reaction: ……………………………………………..

equation: ……………………………………………………………………………………

[2]

(ii) In reaction **II**, when dilute H_2SO_4 is added slowly to the emerald green solution, a pale yellow solution is formed.

Given that $C_2O_4^{2-}$ can act as a base, and considering your answer in **(b)(i)**, account for this observation.

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…………………………………………………………………………………………… [2]

(iii) Use the following data and relevant data from the *Data Booklet* to account for the observations in reaction **III**. Write an equation for the reaction which occurred.

$$2CO_2 + 2H^+ + 2e^- \rightleftharpoons H_2C_2O_4 \qquad E^\ominus = -0.49V$$

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [3]

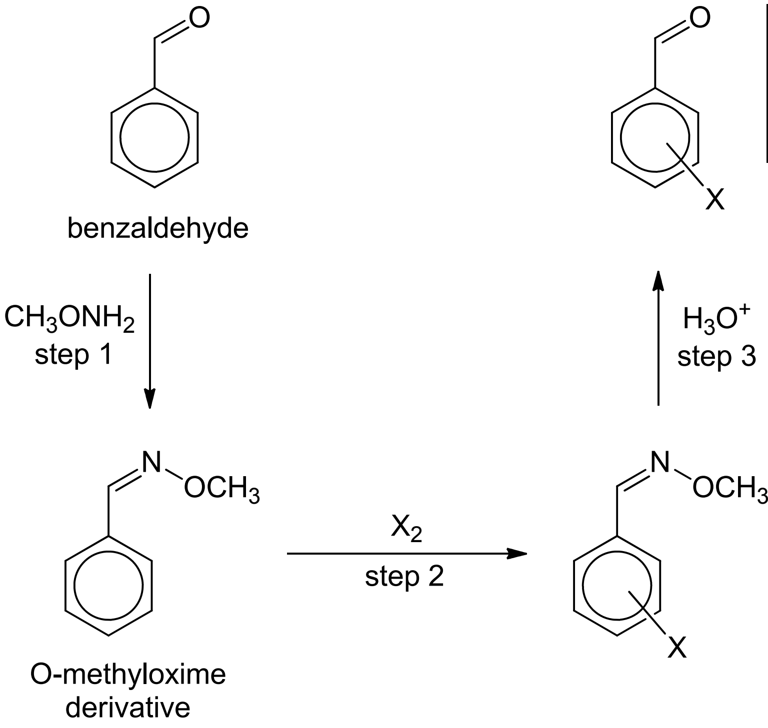
[Total: 11]

5 Substituted benzaldehydes serve as important intermediates in the production of medicines, agricultural chemicals, and functional polymers.

(a) Describe the mechanism for the nitration of benzaldehyde, showing clearly how the **major** mono-substituted product is formed. Include curly arrows showing the movement of electrons, charges and any relevant lone pairs.

[3]

(b) In 1994, H. Goda et. al. reported a method for the synthesis of some halo-substituted benzaldehydes from benzaldehyde. The synthetic scheme showing the relative position of the halogen, X, to the group already on the benzene ring, is shown in Fig. 5.1.



X	Position of X relative to group already on benzene ring
C*l*	2- or 4-
Br	4-

Fig. 5.1

(i) Using your knowledge of the orientating effect of groups in aromatic substitution reactions, explain the significance of the author's work.

....

....[1]

(ii) The O-methyloxime derivative formed in step 1 is able to exhibit cis-trans isomerism.

Explain why this is so.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………[2]

(c) Fig. 5.2 shows a possible reaction sequence with 2-chlorobenzaldehyde as the starting material.

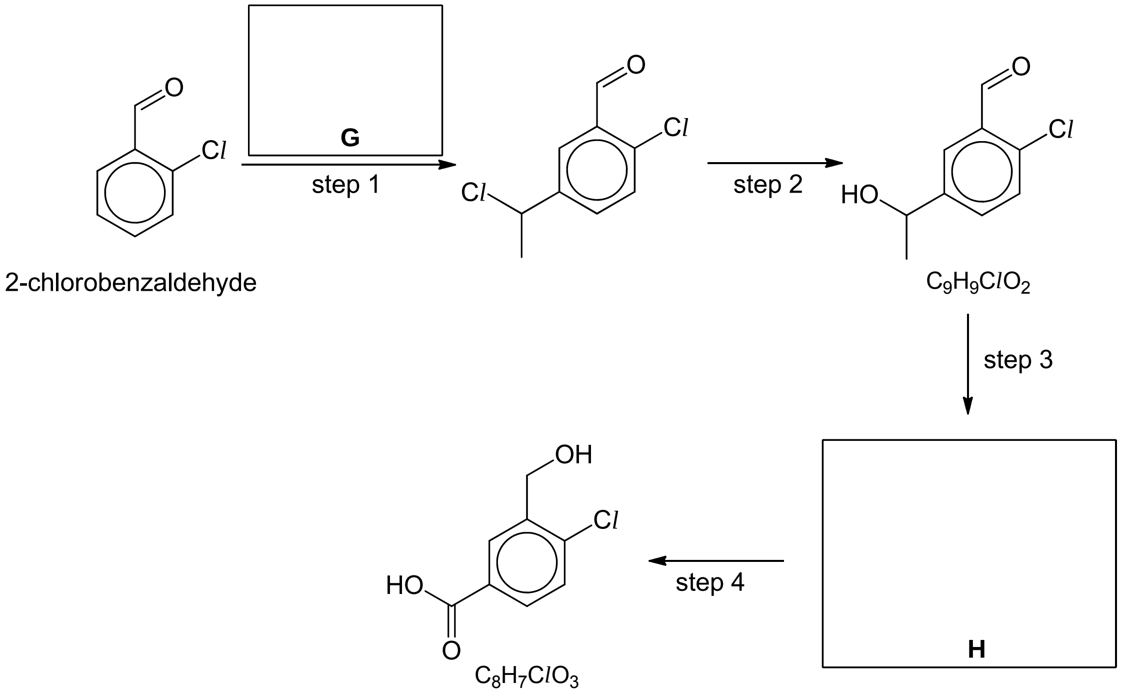


Fig. 5.2

(i) In the box above, draw the structure of the organic compound **G** needed for step 1. [1]

(ii) Suggest the reagents and conditions for step 1.

……………………………………………………………………………………… [1]

(iii) In the box above, draw the structure of the organic compound **H**. Propose the reagents and conditions for steps 3 and 4.

step 3: ……………………………………………………………………………………

step 4: …………………………………………………………………………………… [2]

(d) Tollens' reagent which consists of the diamminesilver(I) complex, $[Ag(NH_3)_2]^+$, is a commonly used reagent to test for the presence of aliphatic aldehydes and benzaldehydes.

With the aid of half-equations, write a balanced equation for the reaction of benzaldehyde, C_6H_5CHO, and $[Ag(NH_3)_2]^+$.

In this reaction, the oxidation number of the carbonyl carbon in benzaldhyde changes from +1 to +3.

Oxidation half-equation: ……………………………………………..………………………..

Reduction half-equation: …………………………………………..……………………….

Overall equation: …………………………………….………………………..……………….

[2]

(e) In linear complexes such as the $[Ag(NH_3)_2]^+$ complex, the ligands approach the central metal ion **along the z-axis**. This causes the d-orbitals of the central metal ion to split into three energy levels as shown in Fig. 5.3.

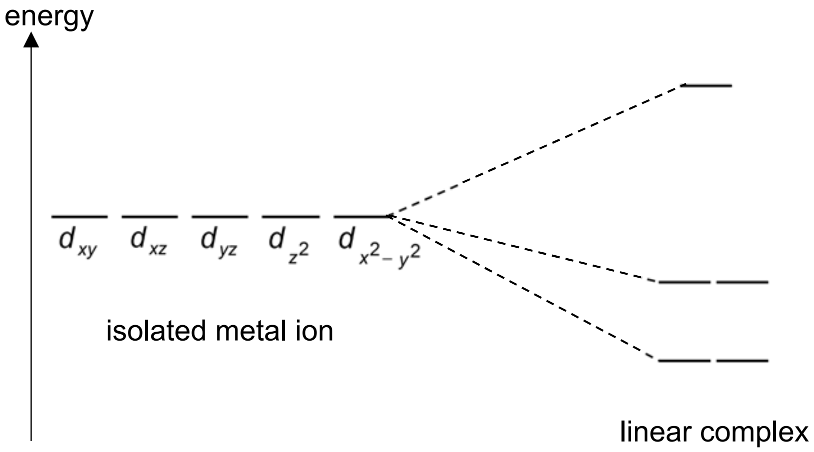


Fig. 5.3

(i) Draw the shapes of the $d_{x^2-y^2}$ and d_{yz} orbitals. Label your drawings clearly.

[2]

(ii) By considering the shape and orientation of the *d*-orbitals, suggest the identities of the highest and lowest energy *d*-orbitals in a linear complex.

Highest energy *d*-orbital: ……………………

Lowest energy *d*-orbitals: …………………… and ……………………

[1]

[Total: 15]

6 Glucose, $C_6H_{12}O_6$, is the most abundant monosaccharide in nature and has great potential for application in fuel cell. Glucose alkaline fuel cell is a promising power source for portable electronic equipment. The set-up is illustrated in Fig. 6.1.

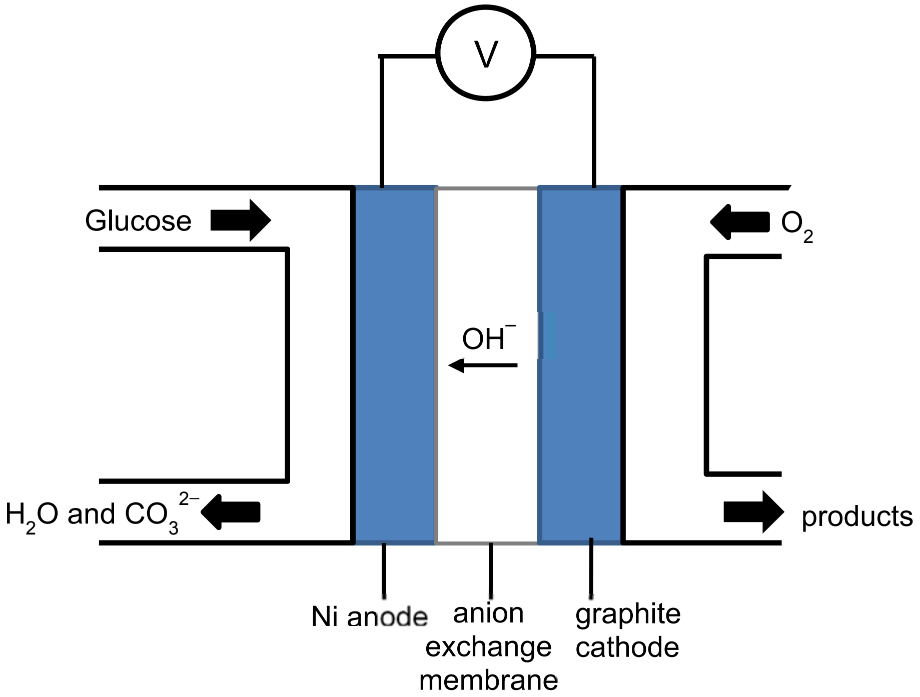


Fig. 6.1

At the anode, glucose is oxidised to carbonate ions, CO_3^{2-}, in an alkaline medium while at the cathode, oxygen gas is reduced. The value of $E^\ominus_{cell}$ is +0.85 V. The overall reaction occurring in the fuel cell is given below:

$$C_6H_{12}O_6 + 6O_2 + 12OH^- \rightarrow 6CO_3^{2-} + 12H_2O$$

(a) **(i)** Deduce the number of moles of electrons exchanged per mole of glucose in the fuel cell.

No. of moles of electrons exchanged per mole of glucose: …………..………. [1]

(ii) Hence, calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the overall reaction.

[1]

(iii) Determine the value for the $E^\ominus$ of the CO_3^{2-}/ $C_6H_{12}O_6$ electrode reaction.

[1]

(iv) Using your answer in **(a)(ii)** and the following data, calculate $\Delta H^\ominus$ and $\Delta S^\ominus$ for the overall reaction.

Table 6.1

Compound	**$\Delta H^\ominus_f$ / kJ mol^{-1}**
$C_6H_{12}O_6$	–1270
OH^-	–230
CO_3^{2-}	–670
H_2O	–286

[2]

(b) In the fuel cell, glucose molecules are adsorbed on the nickel anode surface prior to oxidation to carbonate ions. Fig. 6.2 shows how E_{cell} varies with the concentration of glucose.

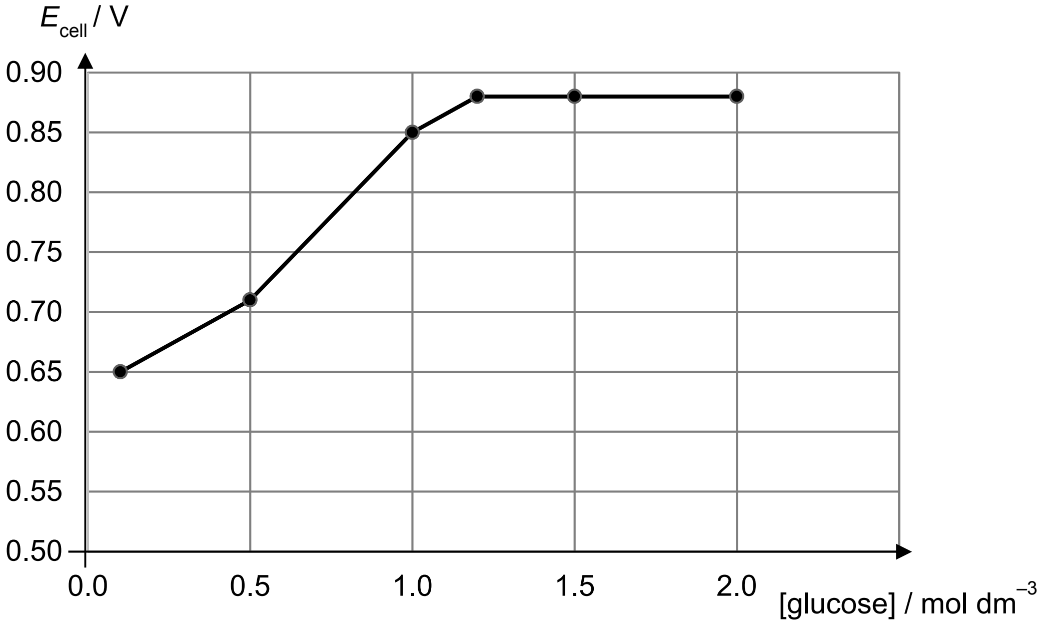


Fig. 6.2

Explain the shape of the graph.

....

....

....

....

....[2]

(c) Suggest a possible advantage of using the glucose fuel cell compared to a hydrogen fuel cell.

....

.... [1]

[Total: 8]

END OF PAPER

HWA CHONG INSTITUTION
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

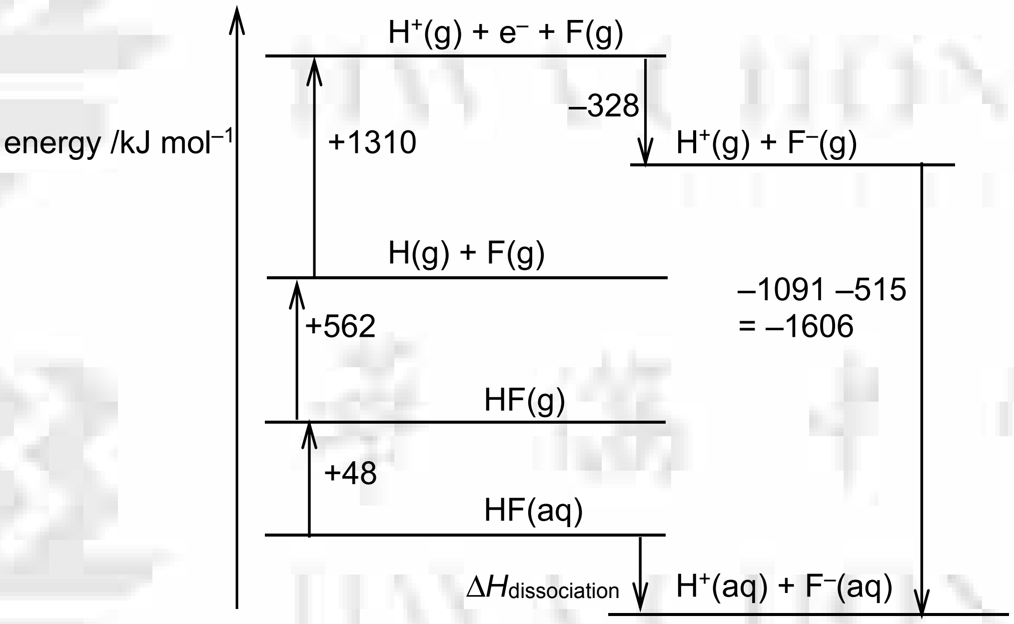
Paper 2

1 (a)

1. Thermal stability decreases from H–F to H–I **[1]**
2. Quote bond energy data:H–F +562 > H–C*l* +431 > H–Br +366 > H–I +299 kJ mol^{-1} and state that this H–X bond is broken during thermal decomposition. **[1]**

(b) (i) It is the heat released when 1 mol of gaseous F^- is dissolved in an infinite volume of water (or completely dissolved in water) at 298 K and 1 bar. **[1]**
$F^-(g) \rightarrow F^-(aq)$ **[1]**

(ii)



The steps to be drawn are:

1. +562	linking $HF(g) \rightarrow H(g) + F(g)$
2. +1310	linking $H(g) + F(g) \rightarrow H^+(g) + e^- + F(g)$
3. –328	linking $H^+(g) + e^- + F(g) \rightarrow H^+(g) + F^-(g)$
4. –1091 –515	linking $H^+(g) + F^-(g) \rightarrow H^+(aq) + F^-(aq)$

1 link correct	⇒ 1 mark
2-3 links correct	⇒ 2 marks
4 links correct	⇒ 3 marks

(iii) $\Delta H_{\text{dissociation}}$ = +48 + 562 + 1310 – 328 – 1606 = –14 kJ mol^{-1}

[1] allow ecf from **(a)(ii)**

(c) **(i)** The hydrogen bond is formed because:

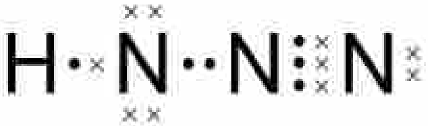
1. there is a H atom bonded to the highly electronegative F atom of one HF molecule **[1]**
2. and there is a lone pair on the F atom of another HF molecule **[1]**

(ii)

1. label δ+ δ– for the HF molecule that provides the protonic H
2. hydrogen bond link $H^{\delta+}$ atom of one HF molecule to lone pair on F atom of the second HF molecule
3. label H–F covalent bond 0.092 nm
4. label hydrogen bond 0.163 nm

[½] each

(d)



[1]

(e) **(i)**

1. Reaction between N_2 and H_2 gives fewer number of moles of gases (from 4 mol of gases to 2 mol) or fewer gas molecules **[1]**
2. Number of ways to distribute particles and/or energy decreases, disorder decreases. Hence entropy decreases **[1]**

(ii)

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$ **[1]**

(iii)

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$	
initial mol	1	3		0	
change	–0.2	–0.2×3		+0.2×2	
eqm mol	0.8	2.4		0.4	Sum=3.6
eqm partial pressure	0.8/3.6 ×20 = 4.44	2.4/3.6 ×20 = 13.33		0.4/3.6 ×20 = 2.22	

$$K_p = \frac{(2.22)^2}{4.44(13.33)^3} = 4.69 \times 10^{-4}\ \text{MPa}^{-2}$$

[1] for all three equilibrium partial pressures
[1] for K_p value (allow ecf from partial pressures)
[1] for K_p units

Alternative working:

	$N_2(g)$	$+ 3H_2(g)$	$=$	$2NH_3(g)$	
initial MPa	x	$3x$		0	
change	$-0.2x$	$-0.6x$		$+0.4x$	
eqm MPa	$0.8x$	$2.4x$		$0.4x$	Sum=$3.6x$

$3.6x = 20$ MPa $\Rightarrow x = 5.556$

$K_p = \frac{(0.4x)^2}{(0.8x)(2.4x)^3} = 4.69 \times 10^{-4}$ MPa^{-2}

2 **(a)** Nucleophilic substitution
NaOH(aq), heat OR ethanolic KCN, heat OR ethanolic concentrated NH_3, heat (in sealed tube) **[1]**

Accept Elimination, ethanolic NaOH, heat
Accept (alkaline) Hydrolysis, NaOH(aq), heat

(b) **(i)** alcohol, phenol, carboxylic acid (any 2) **[1]**

(ii) The melting point of sodium, 98°C, is relatively low so it can easily be melted to react with the organic compound in the molten form. **[1]**

The standard reduction potential $E^\ominus(Na^+/Na) = -2.71$ V is very negative, which shows that sodium is a strong reducing agent / Na can easily be oxidised to Na^+, so sodium can react with / reduce the organic compound in the fusion reaction. **[1]**

(c) **(i)** In the presence of ligands, the partially filled degenerate 3d orbitals of Fe^{2+} split into two different energy levels. The difference in the two energy levels, ΔE, is small, and falls within the visible region of the electromagnetic spectrum. There are vacancies in the higher energy d orbitals. An electron in a lower energy d orbital can absorb radiation in the visible spectrum and be promoted to the higher energy d orbital. This d-d electron transition gives rise to the colour. The violet colour seen is the complement of the absorbed colour which is yellow. **[3]**

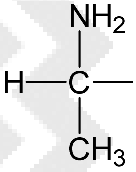
(ii)

Element	Na	Fe	C	N	O	S
Percentage by mass	27.1	16.4	17.7	24.7	4.7	9.4
A_r	23.0	55.8	12.0	14.0	16.0	32.1
Molar ratio **[1]**	1.178	0.294	1.475	1.764	0.294	0.293
Simplest ratio	4	1	5	6	1	1

Compound **A**: $Na_4FeC_5N_6OS$ **[1]**

(iii) NOS^- **[1]**

(d)



$$H-\overset{\overset{NH_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-SH$$

[1]

3 (a) (i) Hydrolysis **[1]**

(ii) No. of moles of N_2 formed = 2.50×10^{-3} mol
Max vol. of N_2 gas formed = $2.50 \times 10^{-3} \times 24.0 \times 10^{3} = 60$ cm^3 **[1]**

[1] for finding and annotating the two half-lives in graph

[1] explanation: from the graph, <u>$t_{1/2}$ is constant to about 14.5 min</u> hence reaction is first order with respect to **D**.

(iii) $k = \ln 2 / t_{1/2} = \ln 2 / 14.5 = \underline{0.0478\ min^{-1}}$ **[1m ans ; 1m unit]**

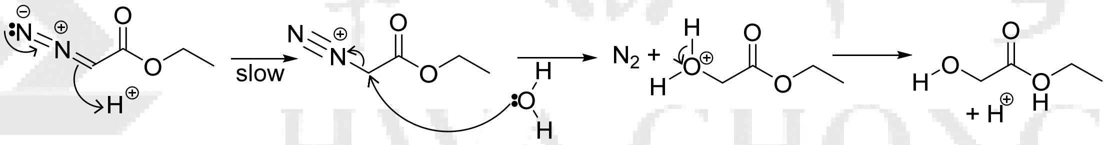
(b) (i)

expt	pH	Rate / mol dm^{-3} s^{-1}	$[H^+]$ / mol dm^{-3}
1	2.0	2.69×10^{-2}	0.0100
2	2.3	1.35×10^{-2}	0.00500
3	2.4	1.07×10^{-2}	0.00398

[1]: correct order of H^+ with justification, e.g. comparing expt 1 and 2, when $[H^+]$ increases by 0.01/0.005 = 2 times, rate increased by $2.69 \times 10^{-2}/1.35 \times 10^{-2}$ = 2 times. Reaction is first order with respect to H^+.

[1] Rate = k $[H^+]$[**D**] ecf from order of H^+

(ii)



[3] total

4 (a) (i) pH = 1.27
$[H^+] = 0.0537$ mol dm^{-3}
Let a = $[H_2C_2O_4]$ used
$K_a = (0.0537)^2 / a - 0.0537$
a = 0.1027 mol dm^{-3} **[1]**

$$\frac{x}{100} \times \frac{1.50}{90.0} \times 1000 = 0.1027$$

x = <u>0.616%</u> **[1]** with ecf

(ii) $C_2O_4^{2-} + H_2O = HC_2O_4^{-} + OH^{-}$ **[1]**

[1] Explanation:
$C_2O_4^{2-}$ undergoes <u>hydrolysis to form OH^-</u>
$[OH^-] > [H^+]$ indicates pH is more than 7

(b) **(i)** ligand exchange reaction **[1]**
$[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightarrow [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$ **[1]**

(ii) $H_2C_2O_4$ formed / neutralization / acid-base reaction when H_2SO_4 is added. The decrease in $[C_2O_4^{2-}]$ causes the position of equilibrium in equilibrium $[Fe(H_2O)_6]^{3+} + 3\ C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-} + 6\ H_2O$ to shift to the left **.**Hence, the presence of $[Fe(H_2O)_6]^{3+}$ gives rise to a pale yellow solution .

[1] mention $H_2C_2O_4$ formed/ neutralization / acid-base reaction occur <u>and</u> decrease in $[C_2O_4^{2-}]$
[1] equilibrium shift left, forming yellow $[Fe(H_2O)_6]^{3+}$

(iii) $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V
$2CO_2 + 2H^+ + 2e \rightleftharpoons H_2C_2O_4$ $E^\ominus = -0.49$ V

$2Fe^{3+} + H_2C_2O_4 \rightarrow 2Fe^{2+} + 2CO_2 + 2H^+$ **[1]**

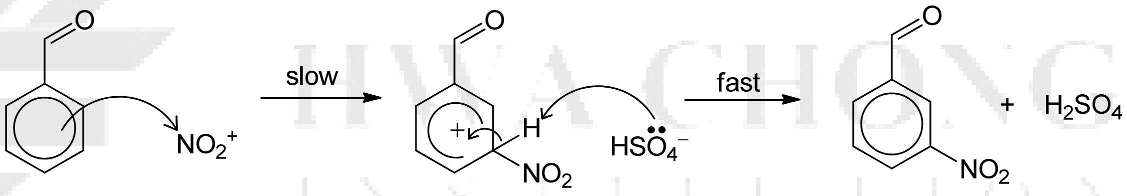
$E^o_{cell} = +1.26V > 0$ (spontaneous) **[1]**

The Fe^{3+}(aq) formed oxidises $H_2C_2O_4$ to form CO_2 while itself is reduced to green Fe^{2+}(aq) **[1]**.

5 **(a)** Electrophilic substitution **[1]**

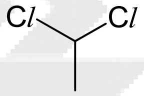
[2] mechanism

$$2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$



(b) **(i)** **[1]** Idea along the lines of "2- or 4- chloro/bromobenzaldehydes can be formed despite –CHO being 3-directing"

(ii)
- restricted rotation about C=N bond **[1]**
- two different groups on C and on N on each end of the C=N double bond **[1]**

(c) **(i)** 

[1]

(ii) **G**, $AlCl_3$ (or $FeCl_3$), heat **[1]**

(iii)

H: **[0.5]**

Step 3: I_2(aq), NaOH(aq), heat/warm **[0.5]** followed by dilute H_2SO_4 **[0.5]**

Step 4: $NaBH_4$ in methanol (or H_2, Ni, high pressure) **[0.5]**

OR

H: **[0.5]**

Step 3: $NaBH_4$ in methanol or $LiAlH_4$ in dry ether (or H_2, Ni, high pressure) **[0.5]**

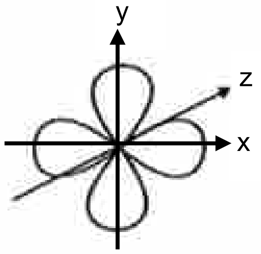
Step 4: 1) I_2(aq), NaOH(aq), heat/warm **[0.5]** followed by dilute H_2SO_4 **[0.5]**

(d) Oxidation half-equation: $C_6H_5CHO + 3OH^- \rightarrow C_6H_5CO_2^- + 2e^- + 2H_2O$ **[0.5]**

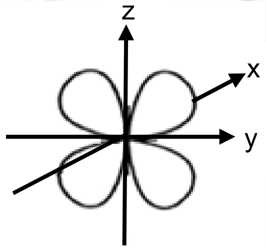
Reduction half-equation: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ **[0.5]**

Overall equation: $C_6H_5CHO + 3OH^- + 2[Ag(NH_3)_2]^+ \rightarrow C_6H_5CO_2^- + 2H_2O + 2Ag + 4NH_3$ **[1]**

(e) **(i)**



$d_{x^2-y^2}$ **[1]**



d_{yz} **[1]**

(ii) Highest energy d-orbital: d_{z^2} **[0.5]**

Lowest energy d-orbitals: d_{xy} and $d_{x^2-y^2}$ **[0.5]**

6 **(a)** **(i)** 24 **[1]**

(ii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -(24)(96500)(0.85) = -1\ 968\ 600$ J mol^{-1} ≈ –1970 kJ mol^{-1} **[1]** allow ecf from **(a)(i)**

(iii) $E^{\ominus}_{cell} = +0.40 - E^{\ominus}(CO_3^{2-}/C_6H_{12}O_6) = +0.85$
$E^{\ominus}(CO_3^{2-}/C_6H_{12}O_6) = 0.40 - 0.85 = -0.45$ V **[1]**

(iv) $\Delta H^{\ominus} = 6(-670) + 12(-286) - [-1270 + 12(-230)] = -3422$ kJ mol^{-1} **[1]**

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
$\Delta S^{\ominus} = [-3422 - (-1969)]/298 = -4.88$ kJ mol^{-1} K^{-1} **[1]** allow ecf

(b) As concentration of glucose increases, $E(CO_3^{2-}/C_6H_{12}O_6)$ becomes **<u>more negative</u>** as **<u>position of equilibrium</u>** for the $CO_3^{2-}/C_6H_{12}O_6$ electrode reaction **<u>shifts left</u>** to **<u>offset the increase in concentration of glucose</u>**, this results in the initial increase of E_{cell}. **[1]**

Beyond an optimum glucose concentration, the **<u>active sites</u>** on the **<u>surface</u>** of nickel anode becomes **<u>saturated</u>** and further increase in glucose concentration will not lead to a decrease in the value of $E(CO_3^{2-}/C_6H_{12}O_6)$. Hence, value of E_{cell} remains constant. **[1]**

(c) **[1]** Glucose is a solid or used in aqueous form (liquid) while H_2 is a gas. Hence glucose will occupy a smaller volume for the same mass.

OR There is a risk of explosion for hydrogen gas as it is highly flammable while glucose is not as flammable.

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**17S**
CENTRE NUMBER	☐☐☐☐	**INDEX NUMBER**	☐☐☐☐

CHEMISTRY

9729/03

Paper 3 Free Response

18 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a **new sheet of writing paper**.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Circle the question number for the question that you have attempted for Section B on the cover page provided.

Section A

Answer **all** the questions in this section.

1 (a) Aluminium is a major component used in the manufacture of various parts of airplanes.

With the aid of a labelled diagram, describe the structure and bonding in aluminium. [3]

(b) Pure aluminium is too soft to be used directly for aircraft applications. An alloy of aluminium is used instead to improve its tensile strength and corrosion resistance. One such alloy is aluminium bronze, which contains aluminium, copper and iron.

To determine the percentage by mass of copper in the alloy, an experiment is performed with the following procedure:

step 1: Concentrated HNO_3 is added to a 1.20 g sample of the alloy. The mixture is then heated until all the solid dissolves. The resulting solution, which contains Cu^{2+}, Fe^{2+} and Al^{3+} ions, is cooled and diluted.

step 2: H_2O_2(aq) is added dropwise until no further change is observed.

step 3: Excess concentrated NH_3 is added to the solution. The resulting mixture is filtered and a dark blue solution is obtained as filtrate.

step 4: HNO_3(aq) is added to the filtrate until no more traces of precipitate is observed in the solution.

step 5: Excess KI(aq) is added to the resulting solution. The reaction produces brown iodine and a white precipitate of copper(I) iodide, CuI.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow I_2(aq) + 2CuI(s)$$

A filtration is performed again, and the filtrate is made up to 250 cm^3 in a volumetric flask.

step 6: 25.0 cm^3 of this solution is titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$(aq), in the presence of starch indicator.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

(i) State the chemical role of H_2O_2(aq) in step 2. [1]

(ii) It is found that 17.50 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$(aq) is required for complete reaction in step 6.

Calculate the percentage by mass of copper in the alloy. [3]

(iii) Suggest how the volume of $Na_2S_2O_3$(aq) needed in step 6 would be affected if step 3 was not carried out in the procedure. Explain your answer. [2]

(c) When an airplane flies at very high altitude, the atmospheric pressure outside the airplane becomes very low. For the comfort of passengers, the airplane cabin is typically pressurised to 81.0 kPa and the temperature is maintained at 23.0 °C at cruising altitude.

(i) A passenger brought a balloon filled with 1500 cm^3 of carbon dioxide gas on board the airplane at sea level, which has an atmospheric pressure of 101 kPa, and a temperature of 30.0 °C.

Assuming that carbon dioxide gas behaves ideally, calculate the final volume of the balloon when the airplane is at cruising altitude. [1]

(ii) Would the actual volume of the balloon at cruising altitude be larger or smaller than the volume you calculated in **(c)(i)**? Justify your answer. [1]

(d) Swift Enterprises, a chemical company, has proposed 2-methylbutane as a fuel for light airplanes. Its structure is shown in Fig. 1.1.

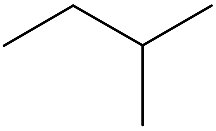


Fig. 1.1

2-methylbutane can react with chlorine in the presence of UV light to give substitution products. The following table shows the relative reactivity of different types of hydrogen for this reaction.

Table 1.1

types of hydrogen	relative reactivity
primary	1
secondary	3.5
tertiary	5

(i) Draw the structures of all the monochlorinated products for 2-methylbutane (ignoring stereoisomers), and give the relative proportions of all the products obtained using the data in Table 1.1. [3]

(ii) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction between 2-methylbutane and chlorine. [3]

(iii) The monochlorinated products serve as raw materials in the manufacture of chlorofluoroalkanes (CFCs), which have been banned in a number of countries due to their effect on the ozone layer in the upper atmosphere.

Explain how CFCs destroy ozone. [1]

[Total: 18]

2 Olympicene, first synthesised to celebrate the 2012 London Olympics, is made up of five rings like the Olympic logo.

The scheme in Fig. 2.1 shows a synthesis of olympicene.

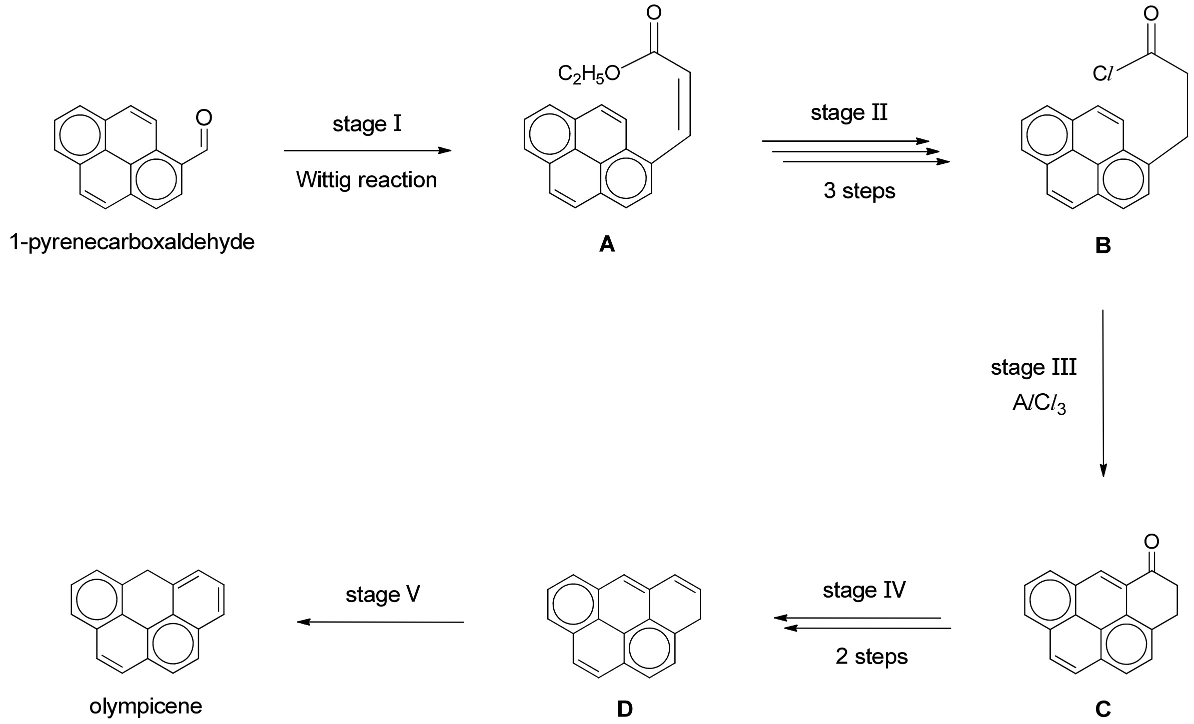


Fig. 2.1

(a) In stage I, **A** is formed from 1-pyrenecarboxaldehyde via a Wittig reaction. In a Wittig reaction, an aldehyde or ketone reacts with a triphenyl phosphonium ylide to give an alkene and triphenylphosphine oxide, as shown in Fig. 2.2.

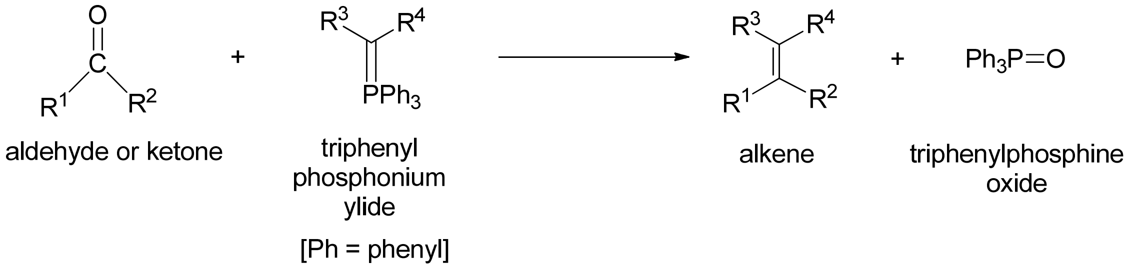


Fig. 2.2

(i) Suggest a reason why Wittig reaction is useful in organic synthesis. [1]

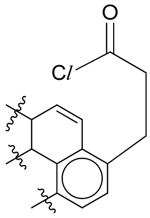
(ii) By considering the structure of **A**, suggest the structure of the triphenyl phosphonium ylide used in stage I. [1]

(b) State the *types of reaction* that occur during each of the three steps in stage II. [3]

(c) The formation of **C** from **B** in stage III follows a three-step mechanism:

1. C*l* on **B** is first abstracted by A*l*C*l*$_3$ catalyst to form a carbocation and [A*l*C*l*$_4$]$^-$.
2. Electrons from a neighbouring π bond attack the carbocation to form a second carbocation which has five rings.
3. [A*l*C*l*$_4$]$^-$ deprotonates the second carbocation, producing **C** and a by-product, and regenerating the catalyst.

Outline this mechanism, showing clearly any intermediates that are formed and use curly arrows to indicate the movement of electron pairs. You may represent **B** as shown below.



B

[3]

(d) Draw the structure of the organic product formed when **C** reacts with 2,4-dinitrophenylhydrazine and state the *type of reaction* that occurs. [2]

(e) Suggest a 2-step synthesis of **D** from **C** in stage IV.

You should state the reagents and conditions needed for each step, and show clearly the structure of the intermediate compound. [3]

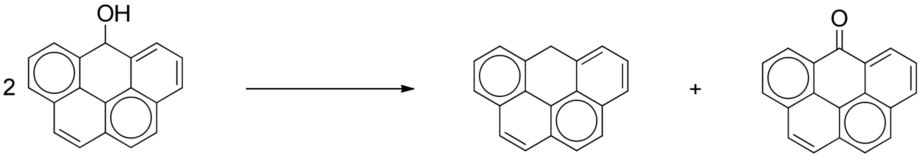
(f) State the isomeric relationship between **D** and olympicene. [1]

(g) **(i)** Deduce whether olympicene is a planar molecule. [1]

(ii) State the number of π electrons in one molecule of olympicene. [1]

(iii) Explain why olympicene has a higher boiling point than benzene. [2]

(h) Under suitable conditions, olympicene can also be formed from **E**, along with another by-product, **F**.



E olympicene **F**

State the *type of reaction* shown above. [1]

[Total: 19]

3 **(a)** Magnesium oxide, MgO, can be obtained from sea water which contains significant amounts of Mg^{2+} and Ca^{2+} ions.

The steps involved are shown in Fig. 3.1.

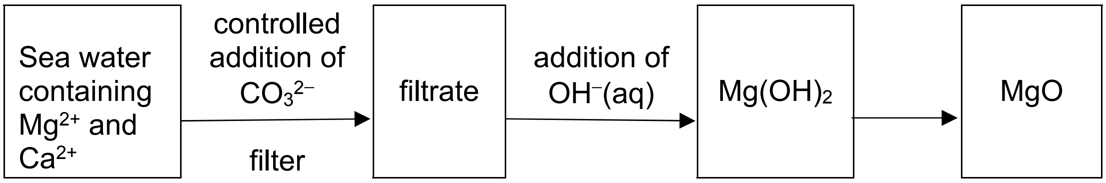


Fig. 3.1

The numerical values of the relevant solubility products are given below.

Table 3.1

compound	solubility product
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	8.7×10^{-9}
$Mg(OH)_2$	1.1×10^{-11}
$Ca(OH)_2$	5.5×10^{-6}

(i) Calculate the solubility of $MgCO_3$ and $Mg(OH)_2$ respectively in mol dm^{-3}. [2]

(ii) If the concentration of Mg^{2+} ions in the filtrate is 3.0×10^{-5} mol dm^{-3}, calculate the concentration of OH^- ions present in the filtrate when the first trace of solid $Mg(OH)_2$ appears. [1]

(iii) Explain why CO_3^{2-} ions is added to the sea water before the addition of OH^- ions, and why this must be controlled. [2]

(iv) With the aid of an equation, suggest how $Mg(OH)_2$ can be converted to MgO in the final step in Fig. 3.1. [1]

(b) Magnesium and aluminium are period 3 elements with different physical and chemical properties.

(i) With the aid of electronic configurations, explain why the first ionisation energy of aluminium is lower than that of magnesium. [2]

(ii) Both magnesium and aluminium react with chlorine to form their respective chlorides.

Describe and explain the reactions, if any, of each of these chlorides with water, suggesting the pH of the resulting solutions and writing balanced equations where appropriate. [3]

(c) Calcium metal is produced mainly by the electrolysis of molten calcium chloride at 800 °C.

(i) Determine the mass of calcium metal that can be obtained when 200 A of current is passed through an electrolytic cell for 3 hours. [1]

(ii) Using relevant data from the *Data Booklet*, explain why calcium metal cannot be obtained by the electrolysis of aqueous calcium chloride. [2]

(d) Compound **I** can be formed from compound **G** via a two-step synthesis as shown in Fig. 3.2.

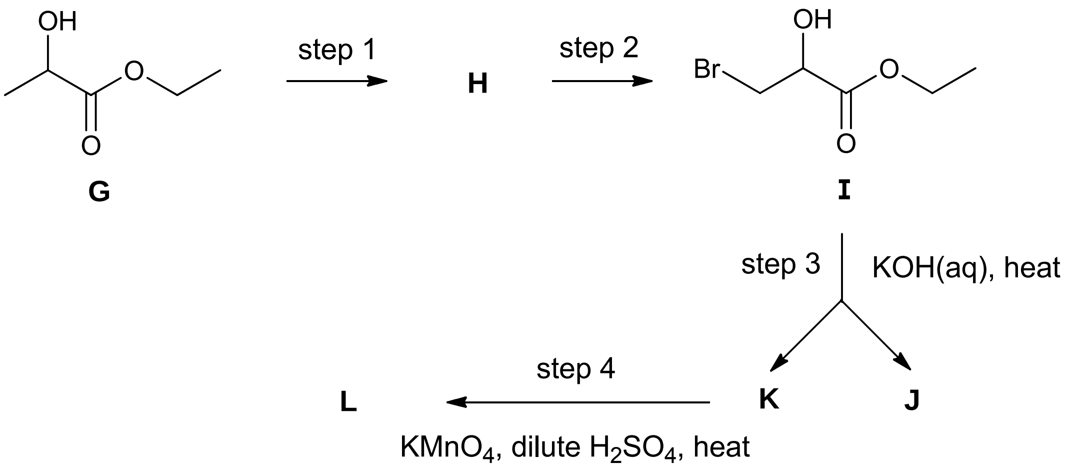


Fig. 3.2

(i) Suggest the structure of intermediate **H** in this synthesis. [1]

(ii) Name the mechanism of the reaction in step 2, and suggest the reagents and conditions used in this step. [2]

In step 3, **I** is heated with aqueous potassium hydroxide and the resulting mixture is then distilled. **J** is collected as the distillate and **K** is a salt obtained in the distillation flask.

In step 4, dilute sulfuric acid and potassium manganate(VII) solution is added to **K** and compound **L** is formed.

(iii) Suggest the structures of compounds **J**, **K** and **L**. [3]

(iv) Describe one simple chemical test to distinguish compounds **J** and **L**.

You should state the reagents and conditions required and how each compound behaves in the test. Write a balanced equation for the reaction involved. [3]

[Total: 23]

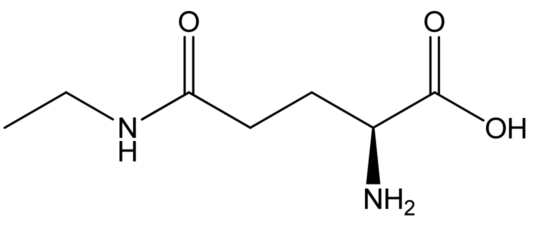
Section B

Answer **one** question from this section.

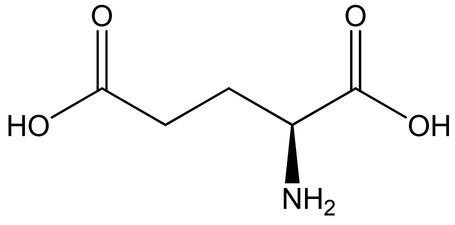
4 Amino acids are commonly found in coffee and tea.

Theanine is an amino acid found in green tea and is known to produce a calming effect. Glutamic acid can be found in coffee and it helps with neurotransmission in the brain.

The structures of theanine and glutamic acid are shown below.



theanine



glutamic acid

Fig. 4.1

(a) Compare the basicity of the nitrogen-containing groups –CONH and $–NH_2$ in theanine. Explain your answer. [2]

(b) There are three pK_a values associated with glutamic acid: 2.19, 4.25 and 9.67.

(i) Calculate the pH of 0.100 mol dm^{-3} of glutamic acid in its fully protonated form. [2]

(ii) Sketch the titration curve when 10.0 cm^3 of the *fully protonated* form of glutamic acid is being titrated with NaOH(aq) of the same concentration, until 40.00 cm^3 of NaOH(aq) has been added. [2]

(iii) Draw the structures of the major species obtained at the first and second equivalence points of the titration described in **(b)(ii)**. [2]

(iv) The isoelectric point is the pH at which there is no net charge on a particular amino acid.

Estimate a value for the isoelectric point of glutamic acid. [1]

(c) 0.0400 g of NaOH(s) was added to a 100 cm^3 portion of 0.100 mol dm^{-3} glutamic acid at pH 4.25.

(i) Write an equation to illustrate why the pH of the solution remains relatively unchanged. Show the structure of glutamic acid clearly in your equation. [1]

(ii) Calculate the final pH of the solution. [2]

(d) **M** is a neutral compound with molecular formula $C_{14}H_{18}NOCl$. When **M** is heated with aqueous sodium hydroxide, it forms the salt of compound **N**, as well as compound **P**. **N** has molecular formula $C_9H_{10}O_3$, and it contains a chiral carbon. When heated with a few drops of concentrated sulfuric acid, **N** forms **Q** which has molecular formula $C_9H_8O_2$. When **P** is heated with acidified potassium manganate(VII), $^{+}H_3NCH_2CO_2H$ and $(CH_3)_2CO$ are obtained.

Deduce the structures of compounds **M**, **N**, **P** and **Q.** Explain the chemistry of the reactions described. [8]

[Total: 20]

5 **(a)** **(i)** State the electronic configuration of the manganese atom. [1]

(ii) Explain why manganese can exhibit a number of different oxidation states in its compounds. [1]

(b) **(i)** Draw a dot-and-cross diagram to illustrate the bonding in the manganate(VII) oxyanion, MnO_4^-, showing only the electrons in the outer shells of the atoms involved. [1]

(ii) Suggest a value for the bond angle in MnO_4^-. [1]

(c) Using relevant data from the *Data Booklet*, describe and explain what you would see when acidified potassium manganate(VII), $KMnO_4$, is added slowly to aqueous potassium iodide. Write a balanced equation for any reaction that occurs. [3]

(d) The Latimer diagrams for manganese and iodine in alkaline and neutral solutions are given in Fig. 5.1.

In a Latimer diagram, the most highly oxidised form of an element is shown on the left, with successively lower oxidation states to the right. The species are connected by arrows, and the numerical value of the standard electrode potential, in volts, is written above each arrow. For example, $E^\ominus(MnO_4^- / Mn(OH)_2) = +0.34$ V.

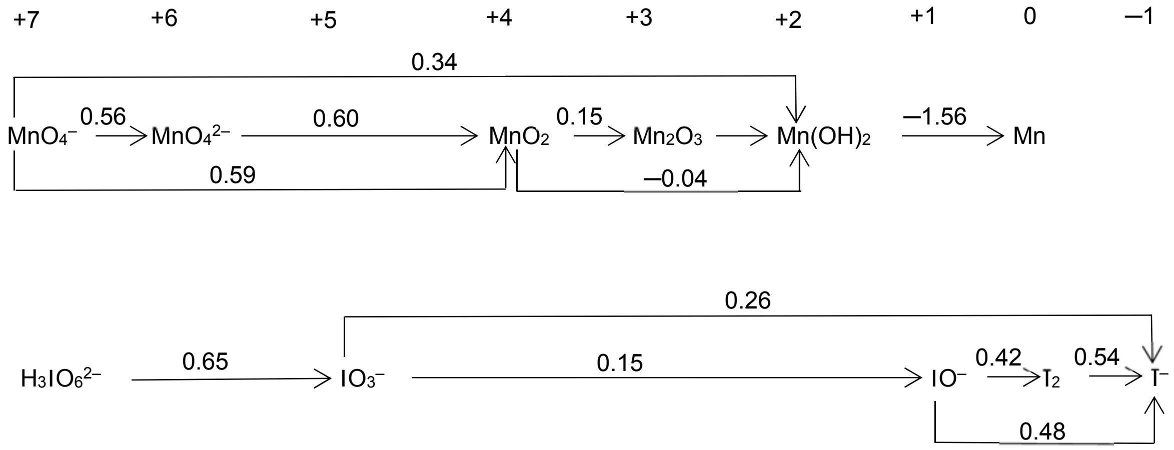


Fig. 5.1

(i) When potassium iodide reacts with $KMnO_4$ in an alkaline solution, the MnO_4^- oxyanion is reduced to manganese dioxide, MnO_2.

Use the Latimer diagrams in Fig. 5.1 to predict the final oxidation state of iodine in this reaction, explaining how you arrive at your answer. [2]

(ii) In an experiment, it is found that 100 cm³ of 0.020 mol dm⁻³ $KMnO_4$ is needed to react completely with 10.0 cm³ of 0.10 mol dm⁻³ potassium iodide under alkaline conditions.

Use this result to deduce the final oxidation state of iodine. [1]

(iii) **R** is a green compound containing potassium, manganese and oxygen. Aqueous solutions of **R** are only stable at high pH. At neutral pH, it slowly converts into a purple solution **S** and a black solid **T**. State what reaction has occurred and identify **R, S** and **T.** [2]

(e) $KMnO_4$ is commonly used as an oxidising agent in organic chemistry.

A compound **U** has the molecular formula $C_{10}H_{12}$. When treated with HBr, **U** yields the compound **V** which contains a chiral carbon.

With cold, alkaline $KMnO_4$, **U** is first oxidised to **W;** warming this mixture then gives **X,** which gives a positive tri-iodomethane test. Both **W** and **X**, on boiling with alkaline $KMnO_4$ followed by acidification, each gives benzene-1,2-dicarboxylic acid.

(i) Deduce the structures of **U** to **X**. Explain the chemistry of the reactions described. [6]

(ii) Explain why the solution containing **V** is optically inactive. [2]

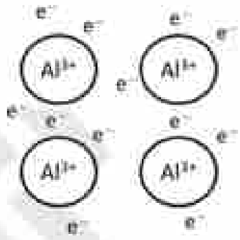
[Total:20]

END OF PAPER

HWA CHONG INSTITUTION
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 3

1 (a) Aluminium has a <u>giant metallic lattice structure</u> **[1]** and <u>metallic bonding between Al^{3+} ions and a sea of delocalised electrons</u>. **[1]**



[1] Number of electrons should be 3 times that of Al^{3+} ions

(b) (i) Oxidising agent **[1]**

(ii) $n(S_2O_3^{2-}) = 17.5 \times 0.1 / 1000 = 0.00175$ mol

$n(I_2)$ in 25.0 cm^3 = 0.00175 / 2 = 0.000875 mol **[1]**

$n(I_2)$ in 250.0 cm^3 = 0.000875 × 10 = 0.00875 mol **[1]** ecf

$n(Cu^{2+}) = 0.00875 \times 2 = 0.0175$ mol

mass of Cu in alloy = 0.0175 × 63.5 = 1.11g

percentage of mass of Cu in alloy = 1.11 / 1.20 × 100 = 92.6% **[1]** ecf

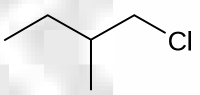
(iii) The titre value would be higher. **[1]**

Without step 3, <u>Fe^{3+} ion</u> in the solution will <u>undergo reaction with I^-</u>, causing <u>more iodine to be produced</u>. **[1]**

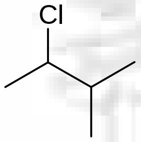
(c) (i)
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
$$\frac{101 \times 1500}{30 + 273} = \frac{81 \times V_2}{23 + 273}$$
$V_2 = 1830\ cm^3$ **[1]**

(ii) The volume will be <u>smaller</u> as CO_2 has <u>significant dispersion forces</u> between molecules. **[1]**

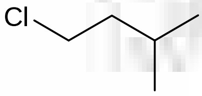
(d) **(i)**



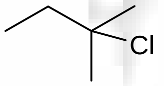
6 x 1 = 6



2 x 3.5 = 7



3 x 1 = 3



1 x 5 = 5

[0.5] x 4 = **[2]** structures, **[1]** for correct proportions.

(ii)

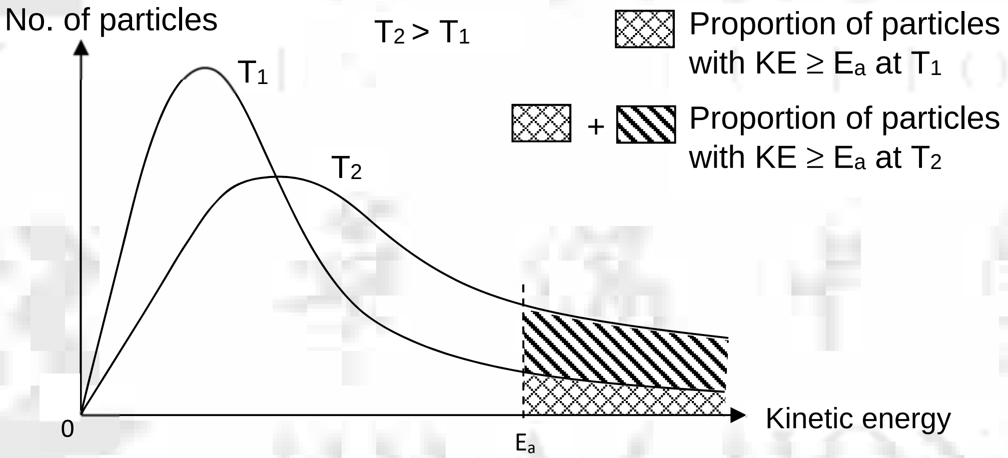


Diagram **[1]**

At higher temperatures (such as T_2), the proportion of particles with kinetic energy greater than or equal to the activation energy increases. **[1]**

Thus, the frequency of *effective* collisions increases (rate constant increases), and reaction rate increases. **[1]**

(iii) C–C*l* bond in CFCs can be broken down by UV light to form chlorine radicals, which can react with ozone. **[1]**

2 **(a)** **(i)** Accept any of the following reasons: **[1]**
Wittig reaction allows the **formation of an alkene** from a carbonyl compound
Wittig reaction allows for **number of carbon atoms to increase.**

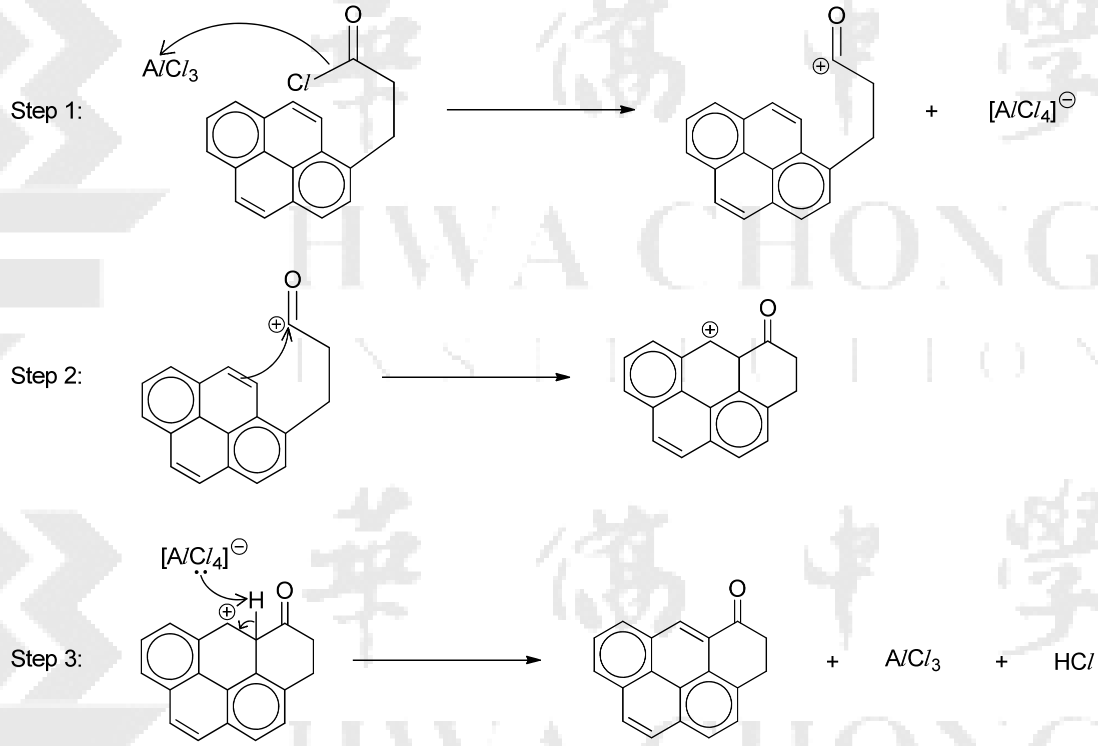
(ii)

[1]

(b) Accept any of the following: **[1] × 3**
(selective) reduction, (acid) hydrolysis, nucleophilic substitution
(acid) hydrolysis, nucleophilic substitution, (selective) reduction
(acid) hydrolysis, (selective) reduction, nucleophilic substitution
(selective) reduction, oxidation, nucleophilic substitution

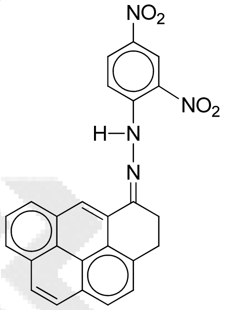
Note: **DO NOT** allow hydrogenation and **DO NOT** allow substitution

(c)



[1] x 3 steps

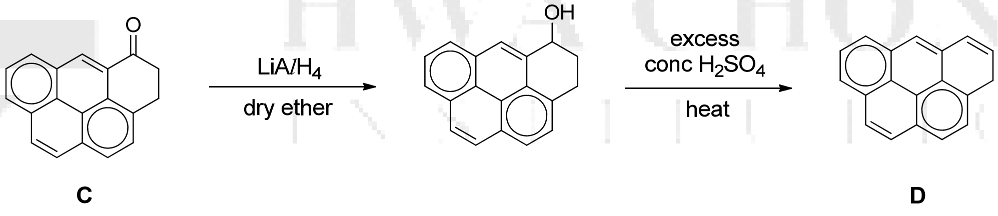
(d)



[1]

condensation **[1]**

(e)



Correct reagents and conditions 1: $LiAlH_4$ in dry ether OR $NaBH_4$ in methanol **[1]**

Correct structure of intermediate **[1]**

Correct reagents and conditions 2: excess concentrated H_2SO_4, heat OR concentrated H_3PO_4, heat OR Al_2O_3, heat **[1]**

(f) **D** is a **constitutional isomer** OR **structural isomer** OR **positional isomer** of olympicene. **[1]**

(g) **(i)** Olympicene is **not a planar molecule** since it contains a **sp^3 carbon** which has a **tetrahedral** geometry around this carbon. **[1]**

(ii) 18 π electrons **[1]**

(iii) Olympicene has a **larger electron cloud size** which causes **dispersion forces** to be much **stronger** than those in benzene, hence requiring **more energy** to overcome. **[2]**

(h) disproportionation **[1]**

3 **(a)** **(i)** Let the solubility of $MgCO_3$ and $Mg(OH)_2$ be x and y respectively in mol dm^{-3}.

For $MgCO_3$
$K_{sp} = [Mg^{2+}][CO_3^{2-}]$
$1.0 \times 10^{-5} = (x)(x)$
$x = 3.16 \times 10^{-3}$ mol dm^{-3} **[1]**

For $Mg(OH)_2$
$K_{sp} = [Mg^{2+}][OH^-]^2$
$1.1 \times 10^{-11} = (y)(2y)^2$
$y = 1.40 \times 10^{-4}$ mol dm^{-3} **[1]**

(ii) $[Mg^{2+}][OH^-]^2 = 1.1 \times 10^{-11}$
$(3.0 \times 10^{-5})[OH^-]^2 = 1.1 \times 10^{-11}$
$[OH^-] = 6.06 \times 10^{-4}$ mol dm^{-3} **[1]**

(iii) CO_3^{2-} ions are added first to precipitate Ca^{2+} as $CaCO_3$ such that the filtrate contains mainly Mg^{2+} and very little Ca^{2+}. **[1]**

The addition of CO_3^{2-} must be controlled to prevent precipitation of Mg^{2+} as $MgCO_3$ **[1]**

(iv) Heat **[½]** solid $Mg(OH)_2$ strongly.
$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$ **[½]**

(b) **(i)** Al : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ **[½]**
Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ **[½]**

The 3p subshell of Al is further away from the nucleus than the 3s subshell. There is weaker attraction between the nucleus and the outermost electron of Al. Hence less energy is needed to remove the 3p electron, resulting in lower ionisation energy. **[1]**

(ii) $MgCl_2$ dissolves and dissociates in aqueous solution. Mg^{2+} has slightly high charge density. Slight hydrolysis occurs, **[½]** forming a slightly acidic solution of pH 6.5 **[½]**

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)$ **[½]**

$AlCl_3$ dissolves in water to form aqueous ions.

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

Al^{3+} <u>having high charge density</u>, undergoes <u>hydrolysis to a greater extent</u> **[½]** to give an acidic solution with pH 3. **[½]**

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l)$ Ý $[Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$ **[½]**

(c) **(i)** $Q = I \times t = n_e \times F$

$200 \times 3 \times 3600 = n_e \times 96500$

$n_e = (200 \times 3 \times 3600)/96500 = 22.4$ mol **[½]**

$Ca^{2+} + 2e^- \rightarrow Ca$

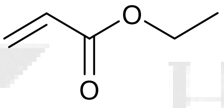
Mass of Ca formed = $\frac{22.4 \times 40.1}{2}$ = 449 g **[½]**

(ii) From Data Booklet,

$2H_2O + 2e^- = 2H_2 + 2OH^-$ $E^\ominus = -0.83$V
$Ca^{2+} + 2e^- = Ca$ $E^\ominus = -2.87$ V **[1]**

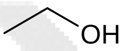
Since $E^\ominus(H_2O/H_2)$ is <u>less negative</u> than $E^\ominus(Ca^{2+}/Ca)$, H_2O will be <u>preferentially reduced</u> at the cathode instead of Ca^{2+}. No Ca metal will be obtained. **[1]**

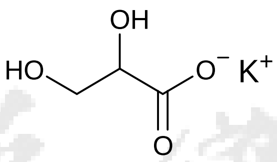
(d) **(i)**

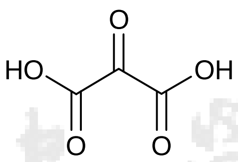
H is  **[1]**

(ii) Electrophilic addition **[1]**
$Br_2(aq)$ **[1]**

(iii)

J  **[1]**

K  **[1]**

L  **[1]**

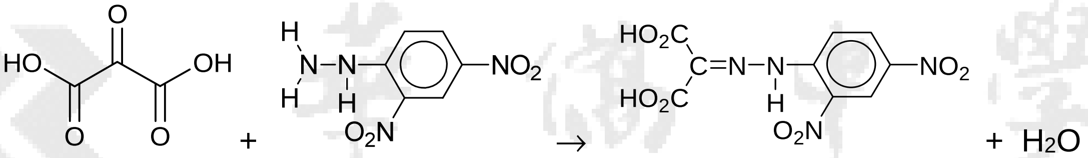
(iv) Possible simple chemical tests to distinguish compounds **J** and **L** where **J** is ethanol (C_2H_5OH) and **L** has two functional groups (carboxylic acid and ketone):

[3]
$KMnO_4(aq)$ with $H_2SO_4(aq)$, heat
Purple $KMnO_4$ decolourised for **J**. Purple colour remains for **L.**

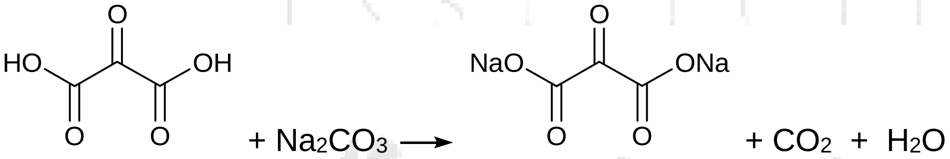
$CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$
or use $K_2Cr_2O_7$(aq) in place of $KMnO_4$(aq)

or
aqueous iodine with aqueous NaOH, warm
yellow ppt for **J** and no yellow ppt for **L**
$CH_3CH_2OH + 4I_2 + 6OH^- \rightarrow CHI_3 + HCO_2^- + 5I^- + 5H_2O$

or
2,4-dinitrophenylhydrazine
orange ppt for **L** and no orange ppt for **J**
equation (the question wants a *balanced* equation)



or
aqueous Na_2CO_3
effervescence of CO_2 for **L** and no effervescence for **J** (‘CO_2 evolved’ was rejected, please state what you expect to *see*)
equation

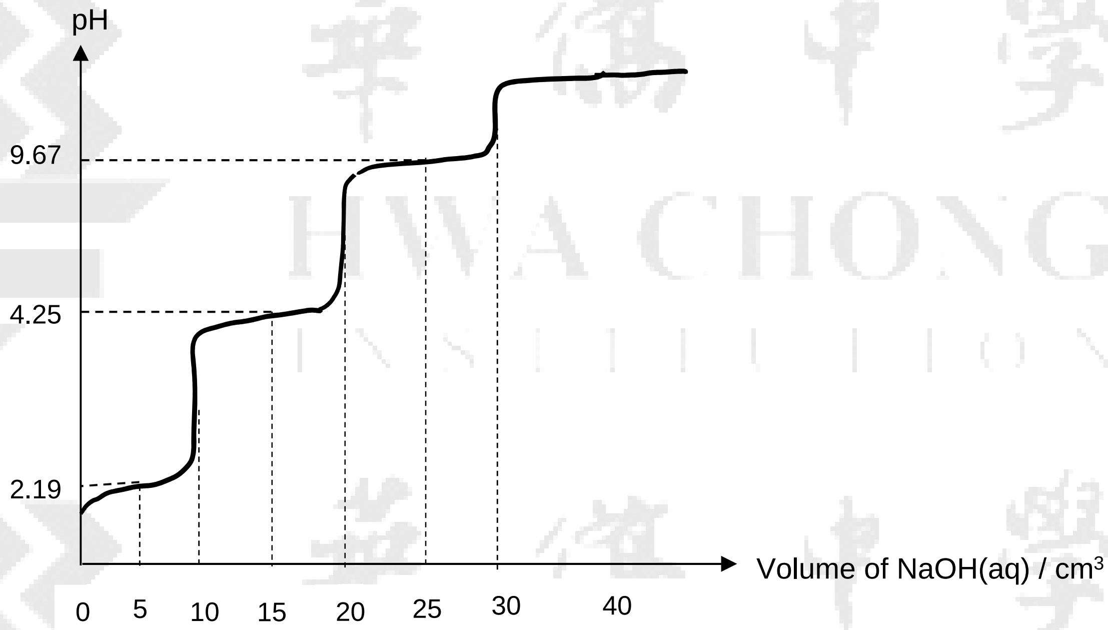


4 (a) For the amide –CONH, the lone pair of electrons on the nitrogen atom is delocalised over to the C=O bond **[1]**, reducing the availability of the lone pair of electrons on nitrogen to accept a proton. **[1]** Hence it is a weaker base than the amine $–NH_2$.

(b) (i) $K_a = 10^{-2.19} = 6.457 \times 10^{-3}$ mol dm^{-3} **[1]**

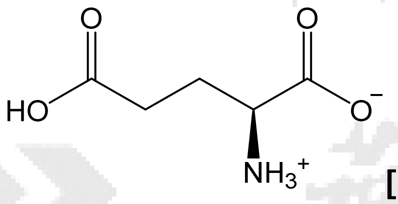
$6.457 \times 10^{-3} = \frac{x^2}{0.100}$ (assume x << 0.100)
$[H^+] = 0.02541$ mol dm^{-3}
pH = 1.60 **[1]**

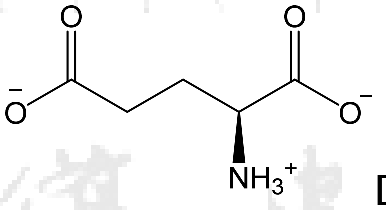
(ii)



Correct shape [0.5] **Correct axes [0.5]**
Label volumes [0.5]
Label pH of mixture at maximum buffering capacities [0.5]

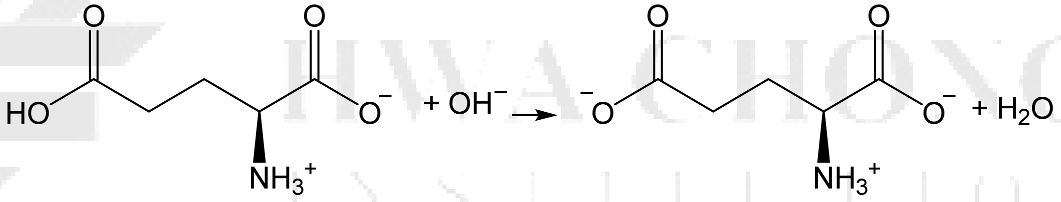
(iii) 1st equivalence point: 2nd equivalence point:


[1]


[1]

(iv) (2.19 + 4.25) ÷ 2 = 3.22 **[1]**

(c) **(i)**


[1]

(ii)

	H_2A +	OH^- →	HA^-
Initial / mol	0.1 × 0.1 ÷ 2 = 0.005	0.04 / 40 = 0.001	0.005
Final / mol	0.005 – 0.001 = 0.004	0	0.005 + 0.001 = 0.006

[1] final amounts of H_2A and HA^-

After addition of small amount of NaOH,
pH = $pK_2 + \lg [HA^-]/[H_2A]$
= 4.25 + lg [(0.006/0.100) / (0.004/0.100)]
= **4.42** **[1] ecf based on new amts of H_2A and HA^- present**

(d) **M, N or Q** has a high C:H ratio
⇒ contains a benzene ring **[0.5]**

Since **M** is neutral and contains N atom, the other functional group present in **A** is likely to be an amide **[0.5]**

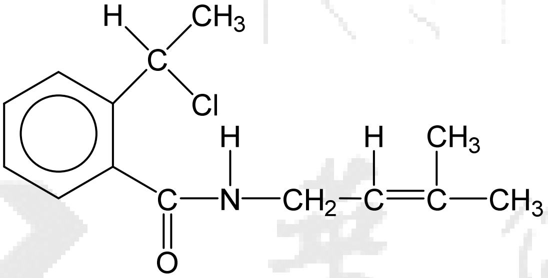
M undergoes alkaline hydrolysis **[0.5]** with NaOH(aq) to form salt of **N** and **P**
⇒ **M** contains an amide

M undergoes nucleophilic substitution **[0.5]** with NaOH(aq) to form **N**
⇒ alcohol is also present in **N** / alkyl chloride present in **M** **[0.5]**

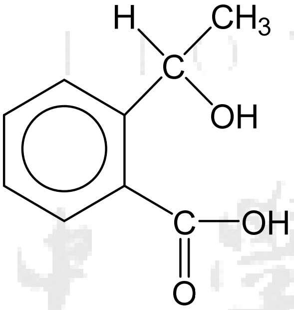
The alcohol and carboxylic acid **[0.5]** group in **N** undergoes condensation (accept esterification) **[0.5]** when heated with concentrated H_2SO_4 to give a cyclic ester **Q**. **[0.5]**

P undergoes oxidative cleavage **[0.5]** with acidified potassium manganate(VII) to form $^{+}H_3NCH_2CO_2H$ and $(CH_3)_2CO$.
⇒ **Q** contains an alkene **[0.5]**

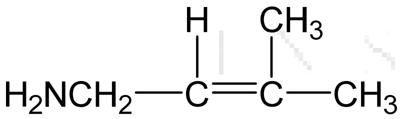
M:



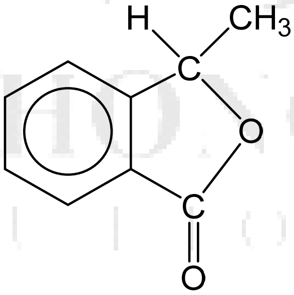
N:



P:



Q:

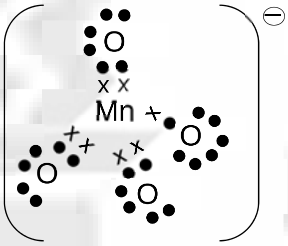


[1] x 4 for structures
Max [5] for explanation
Max [8] total

5 (a) (i) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$ **[1]**

(ii) Mn can exhibit variable oxidation states due to the close similarity in energy of the 3d and 4s electrons. Hence, once the 4s electrons are removed, some or all the 3d electrons may also be removed without requiring much more energy. **[1]**

(b) **(i)**



[1]

(ii) 109.5° **[1]**

(c) Purple MnO_4^- is <u>decolourised</u>, and a <u>brown solution</u> is obtained. **[2 x 0.5]**

[R]	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52 V
[O]	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54 V

$E^\ominus_{cell} = +1.52 - (+0.54) = +0.98$ V

[1] for quoting the two $E^\ominus$ values and stating $E^\ominus_{cell} > 0$, or calculating $E^\ominus_{cell}$ correctly.

$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5I_2(aq)$

[1] ignore state symbols

(d) **(i)** For MnO_4^- to reduce to MnO_2, I^- can be oxidised into IO_3^-, with $E^\ominus_{cell} = 0.59 - 0.26 = +0.33$ V (>0).
Final oxidation state of iodine is +5 (in IO_3^-).

[1] for explanation in terms of choosing $E^\ominus$ for iodine species to be less than +0.59 V, or calculating $E^\ominus_{cell}$ for each stepwise oxidation of I^- to IO_3^-; and **[1]** for correct oxidation state based on the explanation.

(ii) $$\frac{n(MnO_4^-)}{n(I^-)} = \frac{100 \times 0.020}{10.0 \times 0.10} = \frac{2}{1}$$

2 mol of MnO_4^- gain 2 x (7 – 4) = 6 mol of electrons to be reduced to MnO_2. Therefore, 1 mol of I^- lose 6 mol of electrons to be oxidised to IO_3^- (in the +5 oxidation state).

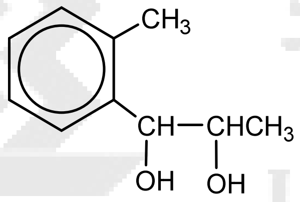
[1] for words to this effect.

(iii) In neutral solution, the green K_2MnO_4 (**R**) undergoes <u>disproportionation</u> slowly to form the purple $KMnO_4$ (**S**) solution and black solid MnO_2 (**T**).

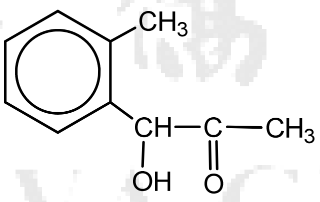
(e) **(i)** **U** **V**

(accept Br on C-2)

W



X



[1] for each correct structure, maximum **4 marks**

Accept other possible side-chains for X: –$COCOCH_3$, –$COCH(OH)CH_3$

[0.5] for any of these six underlined explanations, **maximum 3 marks for explanation**]
Maximum total: 6 marks

- **U** undergoes electrophilic addition of HBr to **V**; so **U** contains C=C double bond / is an alkene.

- **U** undergoes mild oxidation with cold alkaline $KMnO_4$ to form a diol **W**.

- **W** is further oxidised on warming to form **X**. As **X** gives a positive CHI_3 test, it must be a methyl ketone, $RCOCH_3$, or $CH_3CH(OH)R$.

- The side-chain oxidation of **W** and **X** by hot $KMnO_4$ gives benzene-1,2-dicarboxylic acid.

(ii) During the electrophilic addition of HBr to the double bond in **U**, a carbocation is formed (as a reaction intermediate). The geometry about the positively charged carbon is (trigonal) planar, hence it has equal chances of being attacked from the top or bottom by the bromide ion (the nucleophile) in the subsequent step, forming a racemic mixture/equal amounts of both enantiomers, which is optically inactive (since the optical activity of each enantiomer cancels off that of the other). **[4 x 0.5]**

2018 HCI C2 H2 Chemistry Preliminary Exam Paper 4 Preparation Instructions

Safety

Supervisors are advised to remind candidates that **all** substances in the examination should be treated with caution. Only those tests described in the Question Paper should be attempted.

Attention is drawn in particular, to certain materials used in the examination. The following codes are used where relevant.

- Explosives
- Self-Reactives
- Organic peroxides

- Flammables
- Self Reactives
- Pyrophorics
- Self-Heating
- Emit Flammable Gas
- Organic Peroxides

- Oxidisers

- Gases Under Pressure

- Corrosives

- Acute Toxicity (severe)

- Irritant
- Dermal Sensitizer
- Acute toxicity (harmful)
- Narcotic Effects
- Respiratory Tract Irritation

- Carcinogen
- Respiratory Sensitizer
- Reproductive Toxicity
- Target Organ Toxicity
- Mutagenicity
- Aspiration Toxicity

- Environmental Toxicity

'Hazard Data Sheets', relating to materials used in this examination, should be available from your chemical supplier.

Before the Examination

1 Preparation of materials

Where quantities are specified for each candidate, they are sufficient for the experiments described in the Question Paper to be completed.

In preparing materials, the bulk quantity for each substance should be increased by 25% as spare material should be available to cover accidental loss. More material may be supplied if requested by candidates, without penalty.

All solutions should be bulked and mixed thoroughly before use to ensure uniformity.

2 Labelling of materials

Materials must be labelled as specified in these instructions. Materials with an **FA** code number should be so labelled **without** the identities being included on the label. Where appropriate the identity of an **FA** coded chemical is given in the Question Paper itself.

3 Identity of materials

It should be noted that descriptions of solutions given in the Question Paper may not correspond exactly with the specifications in these Instructions. **The candidates must assume the descriptions given in the Question Paper.**

You should have the following apparatus and chemicals.

Apparatus

1 × 250 cm^3 graduated flask;
2 × 50 cm^3 burettes;
2 × stands and clamps to hold the burettes;
2 × funnels;
1 × white tile;
1 × 25 cm^3 pipette;
1 × pipette filler (or equivalent safety device);
1 × 250 cm^3 conical flask;
2 × 10 cm^3 measuring cylinders;
1 × 25 cm^3 measuring cylinder;
1 × 50 cm^3 measuring cylinder;
1 × permanent marker pen suitable for writing on glass;
1 × wash bottle containing deionised water;
1 × thermometer with range –5 °C to +100 °C, graduated to 0.5 C;
7 × test-tubes;
1 × test-tube rack;
2 × boiling tubes;
1 × Bunsen burner;
1 × 250 cm^3 beaker;
1 × test-tube holder;
1 × delivery tube;
1 × pair of disposable vinyl gloves;
1 × pair of safety goggles;
Access to deionised water;
Access to a weighing balance;
A clear plastic bag containing:
  5 × dropping pipettes;
  1 × weighing bottle;
  2 × Styrofoam cups;
  1 × plastic lid;
  1 × spatula;
  1 × wooden splint;
  3 × litmus papers;
  2 × filter papers.

Chemicals

In clear plastic bag	Collect from Teacher's bench	Beside weighing balance	Bench reagents
FA 1 **FA 2** **FA 3** **FA 4** **FA 7** **FA 8** **FA 9** **FA 10**	Starch solution	**FA 6**	aqueous ammonia aqueous sodium hydroxide limewater aqueous potassium manganate(VII) aqueous bromine

FA reagents (1 set for every candidate)

hazard	label	per candidate	identity	notes
⊙ !	**FA 1**	90 cm^3	0.0700 mol dm^{-3} potassium iodate(V)	
! 🧪	**FA 2**	120 cm^3	1.0 mol dm^{-3} sulfuric acid, H_2SO_4	
!	**FA 3**	80 cm^3	0.50 mol dm^{-3} potassium iodide	
!	**FA 4**	100 cm^3	0.1 mol dm^{-3} sodium thiosulfate	
	Starch solution	10 cm^3	20 g dm^{-3}	
!	**FA 6**	6 g	Mixture of equal mass of potassium iodide and lithium chloride	stored in a **dry**, red capped bottle labelled **FA 6 (Please cap after each shift)**, for students to weigh themselves (with big metal spatula) Fresh for each shift
!	**FA 7**	6 g	MnO_2	
!	**FA 8**	1 g	Sodium ethanedioate	
🧪 🌳 ⚕	**FA 9**	10 cm^3	0.5 mol dm^{-3} manganese(II) sulfate	
! 🌳 ⚕ 🔥	**FA 10**	0.5 cm^3	Cyclohexene	

Bench reagents (1 set per seat for 3 shifts)

hazard	label	per candidate	identity
! 🧪 🌳	aqueous ammonia	10 cm^3 per shift	2 mol dm^{-3}
🧪	aqueous sodium hydroxide	10 cm^3 per shift	2 mol dm^{-3}
!	Limewater	10 cm^3 per shift	
! 🧪 🌳 ⊙	Aqueous potassium manganate (VII)	10 cm^3 per shift	0.02 mol dm^{-3}
🧪 🌳 ☠	Bromine water	5 cm^3 per shift	

HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		**CT GROUP**	**17S**

CHEMISTRY

9729/04

Paper 4 Practical

24 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Deductions	
Total	

Answer **all** the questions in the spaces provided.

1 To determine the concentration of potassium iodate(V)

FA 1 is a solution containing potassium iodate(V), KIO_3.
FA 2 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is 0.50 mol dm^{-3} potassium iodide, KI.
FA 4 is approximately 0.1 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

You are also provided with starch solution.

You are to determine the concentration of potassium iodate(V) present in **FA 1**.

In acidic conditions, potassium iodate(V) oxidises iodide ions to iodine. Titration of this iodine with a standard solution of sodium thiosulfate allows the concentration of potassium iodate(V) to be determined.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad \textbf{reaction 1}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \qquad \textbf{reaction 2}$$

The solution of **FA 1** is too concentrated to titrate directly with the **FA 4** solution. You will prepare a diluted solution of **FA 1**.

You will then use **FA 4** to determine the concentration of potassium iodate(V) in the diluted solution by titration, and hence determine the concentration of potassium iodate(V) in **FA 1**.

(a) Dilution of FA 1

You will now follow the instructions given below to prepare a diluted solution of **FA 1.**

1. Using a burette, measure between 49.00 cm^3 and 49.50 cm^3 of **FA 1** into the 250 cm^3 graduated flask.

   In the space below, record your burette readings and the volume of **FA 1** added to the flask. Make certain that your recorded results show the precision of your working.

2. Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly. This solution is **FA 5.**

(b) **Titration of FA 5 with FA 4**

(i) **Titration**

1. Fill a burette with **FA 4**.
2. Pipette 25.0 cm^3 of **FA 5** into a conical flask.
3. Use appropriate measuring cylinders to add to this flask
    - 20 cm^3 of **FA 2**,
    - 10 cm^3 of **FA 3**.
4. Run **FA 4** from the burette into the flask until the solution becomes pale yellow.
5. Add about 10 drops of starch solution to this flask and continue adding **FA 4** until the blue-black colour **just** disappears.
6. Record your titration results in the space below. Make certain that your recorded results show the precision of your working.
7. Repeat the titration as many times as you think necessary to obtain accurate results.

Titration results

(ii) **Mean titre**

From your titrations, obtain a suitable volume of **FA 4** to be used in your calculations. Show clearly how you obtained this volume.

1	
2	
3	
4	
5	
6	
7	

Volume of **FA 4** = …………………

[7]

Standardisation of FA 4 (You are not required to carry out this experiment.)

The solution of sodium thiosulfate, **FA 4**, you are provided with is approximately 0.1 mol dm^{-3}. The exact concentration has been determined by titrating it with a standard solution of 0.750 volume hydrogen peroxide.

In acidic conditions, hydrogen peroxide oxidises iodide ions to iodine.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad \textbf{reaction 3}$$

The liberated iodine is then titrated against **FA 4**. The procedure used is given below.

- A burette was filled with **FA 4**.
- 25.0 cm^3 of hydrogen peroxide was pipetted into a conical flask.
- 50 cm^3 of **FA 2** and 20 cm^3 of **FA 3** were added to the conical flask.
- About 6 drops of ammonium molybdate was added as a catalyst as **reaction 3** is slow.
- **FA 4** was added from the burette to the flask until the solution became pale yellow.
- 10 drops of starch solution were added to the flask.
- More **FA 4** was added from the burette to the flask until the blue-black colour **just** disappeared.

The volume of **FA 4** added was 31.50 cm^3.

Calculations

(c) **(i)** Hydrogen peroxide decomposes to form water and oxygen gas only.

The concentration of hydrogen peroxide solution is often expressed as a *volume strength*.

This term refers to the volume of oxygen evolved at room temperature and pressure when the hydrogen peroxide in 1.00 cm^3 of solution is fully decomposed.

For example, *10 volume* hydrogen peroxide produces 10 cm^3 of oxygen gas at room temperature and pressure from 1.00 cm^3 of the solution.

Calculate the concentration, in mol dm^{-3}, of hydrogen peroxide used for the standardisation of **FA 4**.
(The molar volume of a gas at room temperature and pressure = 24.0 dm^3 mol^{-1}.)

Concentration of hydrogen peroxide = ……………………… mol dm^{-3} [2]

(ii) Calculate the concentration, in mol dm^{-3}, of sodium thiosulfate in **FA 4**.

[$Na_2S_2O_3$] in **FA 4** = ……………………… mol dm^{-3} [1]

(iii) Calculate the concentration, in mol dm^{-3}, of potassium iodate(V) in **FA 5**.

[KIO_3] in **FA 5** = ……………………… mol dm^{-3} [2]

(iv) Calculate the concentration, in mol dm^{-3}, of potassium iodate(V) in **FA 1**.

[KIO_3] in **FA 1** = ……………………… mol dm^{-3} [1]

(d) The standardisation of **FA 4** was repeated using hydrogen peroxide solution that was contaminated with transition metal ions, which act as catalysts for the decomposition of hydrogen peroxide. Deduce and explain what effect this would have had on the calculated value of the concentration of potassium iodate(V) in **FA 1**.

Effect ……………………………………………………………………………………………

Explanation ……………………………………………………………………………………

……………………………………………………………………………………………………...

……………………………………………………………………………………………………...

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……………………………………………………………………………………………… [2]

[Total: 15]

2 Investigation of the dissolution of potassium iodide and lithium chloride in water

FA 6 is a mixture containing equal masses of potassium iodide, KI, and lithium chloride, LiC*l*.

The change in temperature of water per gram of LiC*l* dissolved may be found by first determining the relationship between mass of KI dissolved in water and the change in temperature of the water due to the dissolution. The temperature change when **FA 6** dissolves completely in water is then determined.

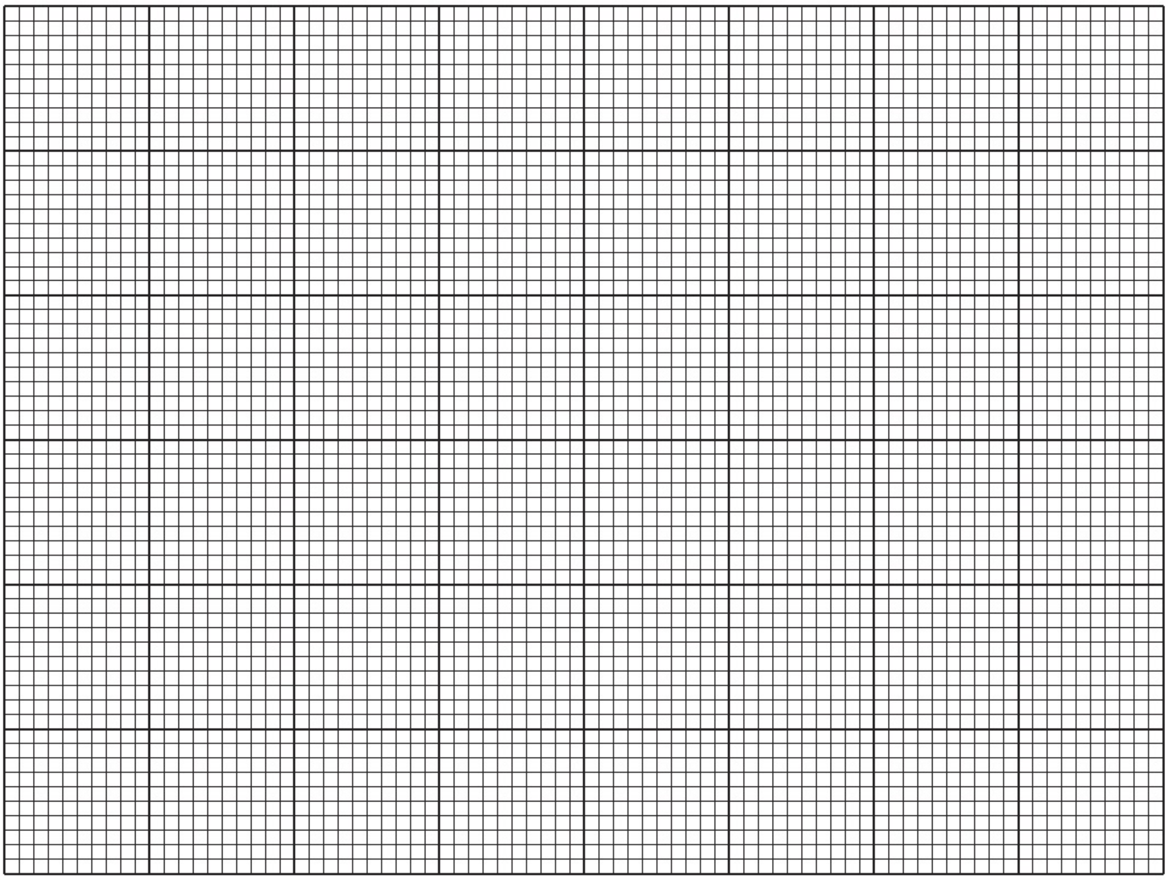
(a) Dissolution of potassium iodide

Different masses of KI were added separately to 25.0 cm^3 of water across four experiments. The initial and minimum temperatures of the water and resultant solution were recorded in Table 2.1 along with other relevant data.

Table 2.1

mass of KI /g	initial temperature of water /^{o}C	minimum temperature of solution /^{o}C	decrease in temperature, ΔT /^{o}C
2.00	29.8	27.4	2.4
4.00	29.8	25.7	4.1
6.00	29.8	23.6	6.2
8.00	29.8	22.0	7.8

Using the results above, plot a graph of ΔT, on the *y*-axis, against mass of KI, on the *x*-axis, on the grid in Fig. 2.1. Draw the most appropriate line, taking into account all of your points.



1	
2	
3	
4	

Fig. 2.1 [4]

(b) Dissolution of FA 6 in water

Follow the instructions below to determine the temperature change when **FA 6** dissolves completely in water.

In an appropriate format in the space provided below, record all relevant values for the experiment in part **(b)**.

1. Weigh accurately about 6.0 g of **FA 6** using a weighing bottle.
2. Using a measuring cylinder, transfer 25 cm^3 of deionised water into a Styrofoam cup. Place the cup inside a second Styrofoam cup which is held in a glass beaker to prevent it from tipping over. Place a lid on the cup and insert the thermometer through the lid.
3. Stir the deionised water in the Styrofoam cup with the thermometer. Read and record its temperature. This is the initial temperature of the deionised water.
4. Open the lid and empty the weighing bottle of **FA 6** into the Styrofoam cup of deionised water. Close the lid and stir the solution with the thermometer. Read and record the temperature that shows the greatest change from the initial temperature of the solution.
5. Reweigh the weighing bottle to determine the mass of **FA 6** dissolved.
6. Calculate the change in temperature, ΔT_x, for this experiment.

Results

1	
2	
3	
4	
5	

[5]

(c) Determining the change in temperature of water per gram of lithium chloride dissolved

Using the results from **(a)** and **(b)**, determine the ΔT per gram of LiC*l* dissolved in water. Indicate relevant workings on your graph as well as any calculations made.

ΔT per gram of LiC*l* = ……………………… C g^{-1} [2]

[Total: 11]

3 Planning

You are tasked to determine the enthalpy change of reaction of copper and hydrochloric acid, ΔH_r, as shown in the equation below.

$$Cu(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2(g) \qquad \Delta H_r$$

However, copper metal and hydrochloric acid do **not** react together under normal conditions. ΔH_r must therefore be determined by an **indirect** method involving two other reactions and a metal.

One of these reactions is the displacement of copper from aqueous copper(II) chloride, and the other is an acid-metal reaction.

(a) Information of some metals is shown in Table 3.1 below.

Table 3.1

element	relative atomic mass	electrode reaction	$E^\ominus$/ V
Ag	107.9	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	63.5	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
Mg	24.3	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
Na	23.0	$Na^+ + e^- \rightleftharpoons Na$	–2.71
Pb	207.2	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13

Choose a suitable metal from Table 3.1 to be used in the task.

.... [1]

(b) Using the metal you have chosen in **(a)**, construct an energy cycle to show how ΔH_r can be calculated from the enthalpy change of the displacement of copper from aqueous copper(II) chloride, ΔH_1, and the enthalpy change for the acid-metal reaction, ΔH_2.

ΔH_r = ... [2]

(c) Plan and describe a practical procedure, which would enable you to determine ΔH_2, which is exothermic. Your plan must enable you to plot a graph that includes data from the experiment.

You may assume that you are provided with:
- 1.0 mol dm^{-3} hydrochloric acid,
- the metal you have chosen in powder form,
- a stopwatch,
- chemicals and apparatus normally found in a school laboratory.

In your plan, you should include:
- apparatus and chemicals needed,
- a detailed method which provides full instruction, including any calculations you used to work out suitable quantities of the chemicals used,
- a sketch of the graph you expect to obtain,
- an outline of the calculations you would perform to calculate ΔH_2.

You may assume the density of all aqueous solutions are 1.0 g cm^{-3} and the specific heat capacity of the mixture is 4.18 J g^{-1} K^{-1}.

YOU ARE NOT REQUIRED TO CARRY OUT THIS EXPERIMENT.

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5	
6	

…………………………………………………………………………………………… [6]

(d) Identify one potential safety hazard in this experiment and state how you would minimise this risk.

……………………………………………………………………………………………

…………………………………………………………………………………………… [1]

[Total: 10]

4 Investigation of some reactions involving transition element ions

You are to explore the reactions of some compounds of an unknown transition element **Z** and determine the identities or structures of a number of different substances.

FA 7 is solid ZO_2.
FA 8 is solid potassium ethanedioate, $K_2C_2O_4$.
FA 9 is a pure solution of Z^{x+} which is also the expected product in **(a)**.
FA 10 is a pure sample of a simple hydrocarbon.

(a) Conversion of ZO_2 to Z^{x+}

Perform the tests described in Table 4.1, and record your observations in the table. Test and identify any gases produced.

Table 4.1

test	observations
Add all of the solid **FA 8** into a boiling tube. Add 15 cm^3 of **FA 2** into this boiling tube. Gently warm the boiling tube and gently stir the mixture with the thermometer, until the mixture's temperature reaches about 60 °C. Turn off the Bunsen flame. Use a spatula to add **FA 7** to the mixture, until no further change is seen. After each addition, gently stir the mixture with the thermometer and observe any changes in the mixture's temperature. When you think that the reaction is complete, stop adding **FA 7**. Filter the mixture into another boiling tube. Leave the filtrate to stand. Keep this filtrate for use in **(b)**.	

(i) Explain how you have decided to stop adding **FA 7** at the point you have chosen. Support your answer using your observations from Table 4.1.

……

……

……

…… [1]

(ii) What two conclusions can you infer about the nature of the reaction occurring between **FA 7** and **FA 8**? Support each conclusion using your observations from Table 4.1.

Conclusion 1 ……………………………………………………………………………………

Evidence …………………………………………………………………………………………

……

……

Conclusion 2 ……………………………………………………………………………………

Evidence …………………………………………………………………………………………

……

……

[2]

(b) Analysis of the filtrate from (a) and FA 9

You will analyse separate samples of the filtrate from **(a)** and **FA 9** using the reagents:

- aqueous ammonia, and
- aqueous sodium hydroxide

(i) In Table 4.2 below, describe how you would carry out the tests on separate portions of the filtrate from **(a)** and **FA 9**.

Carry out the tests and record your observations in Table 4.2.

Table 4.2

test	observations for filtrate from **(a)**	observations for **FA 9**

[1]

(ii) Based on your observations in Table 4.2, what is the identity of the transition metal ion present in **FA 9**? Suggest why there was a difference in observations when you added aqueous sodium hydroxide in **FA 9**, compared to the filtrate from **(a)**.

Ion present ………………………

Suggestion for difference ……………………………………………………………..........

…………………………………………………………………………………………..……..

……………………………………………………………………………………………….. [1]

(c) **Analysis of FA 10**

Before starting this analysis, ensure your Bunsen burner is turned off.

(i) Perform the tests described in Table 4.3, and record your observations in the table.

Table 4.3

	test	Observations
1.	Add 5 cm^3 of deionised water and 1 drop of **FA 10** into a test-tube. Add aqueous bromine dropwise with shaking, until no further change is seen.	
2.	Add 5 cm^3 of **FA 2** and 1 drop of **FA 10** into a test-tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen.	
3.	Add 5 cm^3 of aqueous sodium hydroxide and 1 drop of **FA 10** into a test-tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen.	

[8]

(ii) The main organic product formed in test 3 in Table 4.3 has the molecular formula $C_5H_{10}O_2$.

What is the molecular formula of **FA 10**? Explain your reasoning based on your observations in tests 1 and 3 in Table 4.3.

Molecular formula …………………………..

Explanation ……………………………………………………………………….…..…………..

………………………………………………………..………………………………….…………

………………………………………………………..………………………………….…………

………………………………………………………..……………………………………………

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……………………………………………………………………………………..………… [1]

(iii) Draw the structure of **FA 10**.

[1]

(d) Planning

Consider the following organic compounds.

3-hydroxybenzaldehyde phenol 2-phenylethanal

Plan an investigation, using test-tube reactions involving reagents containing **transition elements other** than those in **(c)**, which would allow you to identify each of these three organic compounds.

You are provided with either pure liquid samples of these compounds or samples containing the compounds dissolved in an inert organic solvent.

Each compound should be identified by at least one positive test result. It is **not** sufficient to identify a compound simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

YOU ARE NOT REQUIRED TO CARRY OUT THIS EXPERIMENT.

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……………………………………………………………………………………………

1	
2	
3	
4	

[4]

[Total: 19]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	-
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of aqueous anions

ion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated on warming with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

HWA CHONG INSTITUTION
2018 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 4

1 (a) Tabulates initial and final burette readings and volume added in each of the tables.
(b) (i) Tables have correct headers and units. **[1]**
Mark is lost if any final and initial burette readings are inverted.

All the burette readings are recorded to the nearest 0.05 cm^3. **[1]**

Has at least two uncorrected titres (refers to student's computed titres) for end-point within 0.10 cm^3. **[1]**

(b) (ii) Student correctly obtains appropriate 'average' from any experiments with uncorrected end-point titre values within 0.10 cm^3. **[1]**
Mark is lost if the titres used are not identified either in the table (by, for example, a tick) or in a calculation or identified wrongly or no titre within 0.10 cm^3. Mark is lost if there are arithmetic errors in the titration results table. Mark is lost if the candidate made an arithmetic error in the calculation of the mean titre.

Calculate the Supervisor's and the student's scaled mean titre values using the following expression:

$$\text{Scaled mean titre} = \frac{49.25 \times \text{mean titre}}{\text{volume of FA 1 diluted}}$$

Calculate the difference between the student's scaled mean titre value and the Supervisor's scaled mean titre value.

Give 3 marks if this difference is ≤ 0.2
Give 2 marks if this difference is > 0.2 but ≤ 0.3
Give 1 mark if this difference is > 0.3 but ≤ 0.5
Give 0 marks if this difference is > 0.5 **[3]**

(c) (i) nO_2 produced by 1cm^3 of H_2O_2 = 0.75 ÷ 24000
nH_2O_2 in 1 cm^3 = 0.75 ÷ 24000 × 2 = 6.25×10^{-5} mol **[1]**

$[H_2O_2]$ = ans ÷ 1/1000 = 0.0625 mol dm^{-3} **[1]**

(ii) nH_2O_2 in 25.0 cm^3 = 0.0625 x 25/1000 = 1.56×10^{-3} mol = nI_2

$nS_2O_3^{2-}$ = $1.56 \times 10^{-3} \times 2 = 3.125 \times 10^{-3}$ mol
$[S_2O_3^{2-}]$ = 3.125×10^{-3} ÷ 31.50/1000 = 0.0992 mol dm^{-3} **[1]**

(iii)
1. $nS_2O_3^{2-}$ = 0.0992(or ecf) × (titre in (b) ÷ 1000)
2. $nKIO_3$ = ANS ÷ 6
3. $[KIO_3]$ in **FA 5** = ANS ÷ 25/1000

Award 1 mark for the correct use of the mole ratio in step 2 and 1 mark for steps 1 and 3 if both correct (allow ecf for step 3 if step 2 is wrong). **[2]**

(iv) [KIO_3] in **FA 1** = ANS(c(iii)) x (250 ÷ volume of **FA1** used) **[1]**

(d) The transition metal would cause the hydrogen peroxide to decompose leading to less hydrogen peroxide reacting with the iodide. **[1]**
Less iodine would be produced, so volume of sodium thiosulfate used will be lower than expected.

Hence, it would give the false impression that the concentration of thiosulfate is higher than what it actually is. So the concentration of potassium iodate calculated will be higher than expected. **[1]**

2 (a) Axes correct way round **+** correct labels **+** units **+** scale (must be chosen so that plotted points occupy at least half the graph grid in both *x* and *y* directions).
Sensible scales must be chosen. Awkward scales (e.g. 3:10) are not allowed. **[1]**

Plotting – <u>all points</u> within ± ½ small square. Check all points and put ticks if correct. **[1]**

Draws <u>best fit straight line</u> through plotted points. **[1]**

(c) **From 2(c)**
Correctly extrapolates ΔT for M g of potassium iodide, ΔT_M, from plotted graph at the point

$$M = \frac{\text{mass } \textbf{FA 6} \text{ dissolved}}{2}$$

Or correctly calculates using ΔT per gram of potassium iodide by finding gradient

Working on the graph, e.g. dotted lines or otherwise, must be shown. **[1]**

(b) Record mass of empty weighing bottle, mass of weighing bottle + **FA 6**, mass of weighing bottle + residual solid, mass of **FA 6** used.
and
Table has correct headers and units. **[1]**

Follows instructions – weighs 5.95 g to 6.04 g of **FA 6**
*Final mass of **FA 6** dissolved may be out of range, but initially weighed mass must be within range.* **[1]**

Records initial water temperature and final temperature of solution, **and**
Table has correct headers and units. **[1]**

All temperature recorded and calculated ΔT_x value are to 0.5 ^{o}C, **and** all mass recorded calculated mass of FA 6 used are to 2 d.p. **[1]**

Correctly calculates ΔT_x. **[1]**

(c) **Method 1:**

Correctly calculates change in temperature due to lithium chloride,
$\Delta T_x + \Delta T_M = \Delta T_{LiCl}$ **[1]**

Correctly calculates the value of change in temperature of water per gram of lithium chloride =

$\dfrac{\Delta T_{LiCl}}{M}$ where M = mass of **FA 6** dissolved ÷ 2

[1]

Method 2:

Calculates the value of change in temperature of water per gram of FA 6,

$$\frac{\Delta T_x}{\text{mass of } \textbf{FA 6} \text{ dissolved, m}}$$

Since **FA 6** contains equal masses of lithium chloride and potassium iodide, ΔT_x/m gives the total temperature change for 0.5 g of lithium chloride and 0.5 g of potassium iodide. Therefore, to obtain the total temperature change for 1 g of each compound, ΔT_x/m needs to be multiplied by two.

The temperature change per gram of lithium chloride
= $2(\Delta T_x/m) - (-\Delta T$ per gram of potassium iodide)
[1 mark for addition; 1 mark for correct computation]

3 (a) Magnesium **[1]**

(b)

$$\begin{tikzcd}
Mg(s) + Cu(s) + 2HCl\,(aq) \arrow[rr, "\Delta H_r"] \arrow[dr, "\Delta H_2"'] & & CuCl_2(aq) + H_2(g) + Mg(s) \arrow[dl, "\Delta H_1"] \\
& MgCl_2(aq) + Cu(s) + H_2(g) &
\end{tikzcd}$$

OR

$$\begin{tikzcd}
MgCl_2(aq) + Cu(s) + 2HCl\,(aq) \arrow[rr, "\Delta H_r"'] & & CuCl_2(aq) + H_2(g) + MgCl_2(aq) \\
& 2HCl(aq) + CuCl_2(aq) + Mg(s) \arrow[ul, "\Delta H_1"] \arrow[ur, "\Delta H_2"'] &
\end{tikzcd}$$

Correct energy cycle **[1]**

From correct energy cycle, $\Delta H_r = \Delta H_2 - \Delta H_1$ **[1]**

(c) **M1**: [Justification of quantities]
Either choose a suitable mass of metal powder or suitable volume of HCl, and show calculations to obtain the minimum quantity of the other reagent needed, and state chosen quantities of reagents.

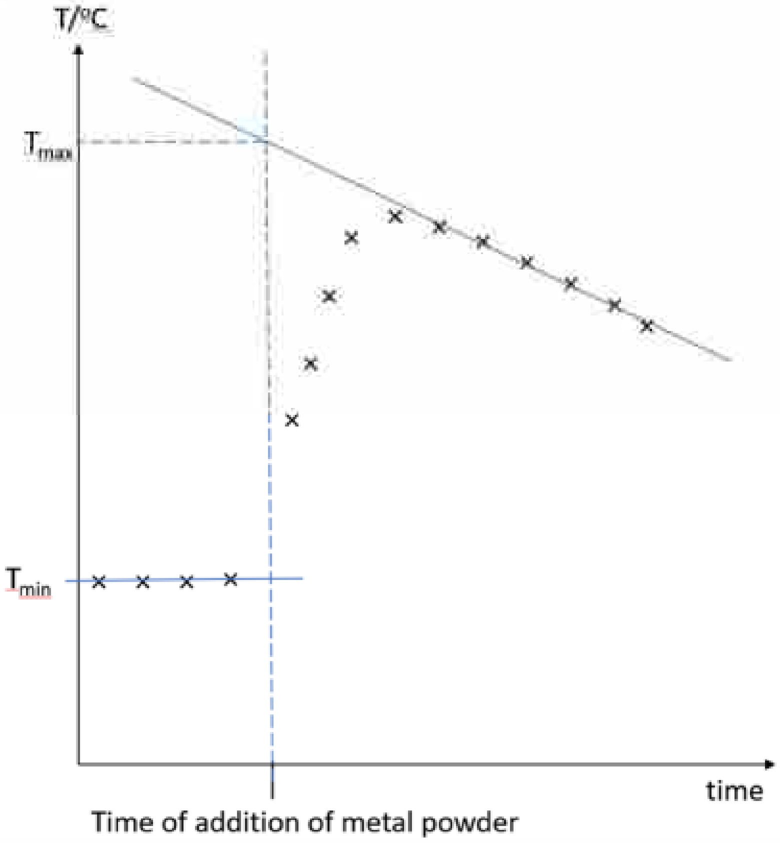
[1]

M2: [Data to be collected]
CORRECT temperature taking procedure. Describes taking temperature readings over time from before addition of metal until at least 6 extra readings after maximum temperature is reached.

[1]

M3: [Sketch of graph]
Sketch of cooling curve and show correctly how to extrapolate min/max or ΔT temperatures from sketch. Axes must be temperature against time.

[1]



M4 & M5: [Details in procedure] – dot-tick marking, up to 2m, no half marks

- <u>weighing balance</u> for weighing metal powder
- <u>suitable apparatus (burette/pipette/measuring cylinder)</u> for measuring volume of HC*l*(aq)
- <u>thermometer</u> for measuring temperature
- measures taken to ensure accuracy of expt / minimise hazards, e.g. stirring/ use lid/ double styrofoam cup / beaker for support

[2]

M6: [Processing of results]
Correct sample calculation for obtaining ΔH_2. Answer may differ depending on whether metal or acid chosen as limiting reactant, and students' chosen metal.

$Q = 1.0 \times V_{HCl} \times 4.18 \times (T_{max} - T_{min}) = a\ \text{J}$

[if metal is limiting]

$$\Delta H_2 = -\frac{a}{m_M \div A_r} \div 1000\ \text{kJ mol}^{-1}$$

[if acid is limiting]

$$\Delta H_2 = -\frac{a}{V_{HCl} \div 1000 \times 1.0} \times 2 \div 1000\ \text{kJ mol}^{-1}$$

[1]

Sample procedure:

Amount of Mg in 1 g of magnesium = 1 ÷ 24.3 = 0.0412 mol
Volume of HCl required for complete reaction = (0.0412 × 2) × 1.0 × 1000 = 82.3 cm^3
Volume of HCl to be used = 100 cm^3 (excess)

Using a weighing balance and weighing bottle, weigh accurately about 1.0 g of Mg metal.
Using a measuring cylinder, transfer 100 cm^3 of HC*l*(aq) into a Styrofoam cup.
Place the Styrofoam cup into another Styrofoam cup and place both into a 250 cm^3 beaker for stability.
Cover with a lid and insert a thermometer through the lid.
Record the temperature of the solution, and start the stopwatch.
Take the temperature every 30 seconds until 2.5 min.
At 3 min, add the magnesium from the weighing bottle to the HC*l*(aq) in the Styrofoam cup.
From 3.5 min, take temperature readings every 30 seconds until there are at least 6 readings after the temperature starts decreasing linearly.
Reweigh the weighing bottle to obtain the mass of magnesium used, $\mathbf{m_M}$.
Plot a graph of temperature /°C against time /min.

(graph sketch)

$Q = 1.0 \times 100 \times 4.18 \times (T_{max} - T_{min}) = \mathbf{a}$ J

$$\Delta H_2 = -\frac{\mathbf{a}}{\mathbf{m_M}/24.3} \div 1000 \text{ kJ mol}^{-1}$$

(d) $H_2(g)$ / metal powder is flammable. Avoid naked flames. **[1]**

4 (a)

1. White solid ($K_2C_2O_4$) dissolves
2. Effervescence/bubbles after each addition (REJECT: gas evolved)
3. Gas gives white ppt with limewater. Gas is CO_2.
4. Temperature of mixture increases
5. Black/grey residue obtained.
6. Colorless / pale yellow filtrate.

(b) (i)

7. Filtrate from **(a)** forms light brown ppts with both NaOH(aq) and NH_3(aq).
8. **FA 9** forms off-white/ very light brown ppts with both NaOH(aq) and NH_3(aq) (Note: the colour of these ppts must be lighter than those in point 7.)
9. **All** 4 ppts insoluble in excess.
10. Ppts darken on standing (mentioned at least twice)

(c) (i)

11. Yellow bromine water decolourised (test 1).
12. Purple $KMnO_4$ decolourises (test 2).
13. Colourless solution turns progressively darker brown (test 2).
14. Solution turns green (test 3).
15. Colour deepens/turns darker green as more drops added (test 2).

Observation points
14 – 15 = 7 marks
12 – 13 = 6 marks
10 – 11 = 5 marks
8 – 9 = 4 marks
6 – 7 = 3 marks
4 – 5 = 2 marks
2 – 3 = 1 mark
0 – 1 = 0 mark **[7]**

(a) **(i)** Either a convincing explanation based on the cessation of effervescence/bubbles (on addition of more **FA 7**)
Or
a convincing explanation based on the temperature starting to fall on addition of more **FA 7**) **[1]**

(ii) Conclusion: the reaction is exothermic
Evidence: the temperature increased as more **FA 7** was added (even without further heating) **[1]**

Conclusion: redox reaction
Evidence: effervescence of CO_2 shows that ethanedioate ions are oxidised (while **FA 7** is reduced). **[1]**

(b) **(i)** Procedure should describe the addition of a small volume/ dropwise addition, and the addition of an excess, of NaOH(aq) and NH_3(aq), both with shaking, to separate samples. **[1]**

(ii) Ion present is Mn^{2+}.

The darker colour of the precipitates is due to incomplete reduction of **FA 7**/ some Mn^{3+} present. **[1]**

(c) **(ii)** Molecular formula is C_5H_8. **[1]**

- Br_2(aq) decolourised so C=C present
- Cold alkaline $KMnO_4$ oxidised alkene to a diol OR $C_5H_{10}O_2 - 2 \times OH = C_5H_8$

[1]

(iii) Clear structure of cyclopentene **[1]**

(d) Tests include warming with Fehling's solution; warming with potassium dichromate(VI) $K_2Cr_2O_7$ in the presence of dilute H_2SO_4; adding neutral iron(III) chloride $FeCl_3$; warming with Tollens' reagent.

Selects reagents and conditions that would unambiguously identify all 3 compounds with positive tests for each [2] **or**
Selects reagents and conditions that would unambiguously identify 2 compounds with positive tests for each [1]

[2]

Outlines a logical sequence/order of testing; doesn't test compounds already identified.

[1]

Clearly and unambiguously links the testing sequence with the compounds to be identified.

[1]

An example of the plan is as follow:

All tests should be carried out in a separate test-tubes, and fresh samples of the organic compound should be used each time.

1. To 1 cm^3 of each organic compound, add 1 cm^3 of Tollens' reagent and warm in a water bath. The test-tubes showing the formation of silver mirror would be either 3-hydroxybenzaldehyde or 2-phenylethanal. The test-tube that does not give the silver mirror would contain phenol.

2. To 1 cm^3 of the compound that does not give a positive test in step 1, add a few drops of neutral $FeCl_3$. The formation of violet colouration would confirm the identity of phenol.

3. To 1 cm^3 of separate samples of the organic compounds that give silver mirror in step 1, add 1 cm^3 of Fehling's solution and heat in a water bath. The test-tube that shows the formation of brick-red ppt would contain 2-phenylethanal while the one with no brick-red ppt would contain 3-hydroxybenzaldehyde.

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY 9729/01

Paper 1 Multiple Choice

14 Sep 2018
1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

This document consists of **16** printed pages and **1** blank page.

For each question there are four possible answers, **A, B, C,** and **D**. Choose the **one** you consider to be correct.

1 In an experiment, 0.002 mol acidified iron (II) sulfate is quantitatively oxidised by 0.001 mol of an oxidising agent, $\mathbf{Z}O_3^-$. Given that Fe^{2+} is oxidised to Fe^{3+}, what is the final oxidation state of **Z**?

A +1 **B** +2 **C** +3 **D** +4

2 Gaseous particle **X** has a proton number n and a charge of +1.

Gaseous particle **Y** has a proton number of (n + 1) and is isoelectronic with **X**.

Which of the following statements correctly describe **X** and **Y**?

1 **Y** has a smaller radius than **X**.

2 **Y** requires less energy than **X** when a further electron is removed from each particle.

3 **Y** releases less energy than **X** when an electron is added to each particle.

A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

3 What is the electronic configuration of an element with a **second** ionisation energy higher than that of each of the elements either side of it in the Periodic Table?

A $1s^22s^22p^63s^2$

B $1s^22s^22p^63s^23p^1$

C $1s^22s^22p^63s^23p^2$

D $1s^22s^22p^63s^23p^3$

4 The table shows the charge and radius of each of six ions.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. What is the correct order of their lattice energies, placing the most exothermic first?

A JX, MZ, LY

B LY, MZ, JX

C MZ, JX, LY

D MZ, LY, JX

5 In certain microwave ovens, the wave energy produced is absorbed by certain polar molecules.

Which of the following would absorb microwave energy?

1 CH_3CH_2OH

2 $AlCl_3$

3 CO_2

4 CH_3F

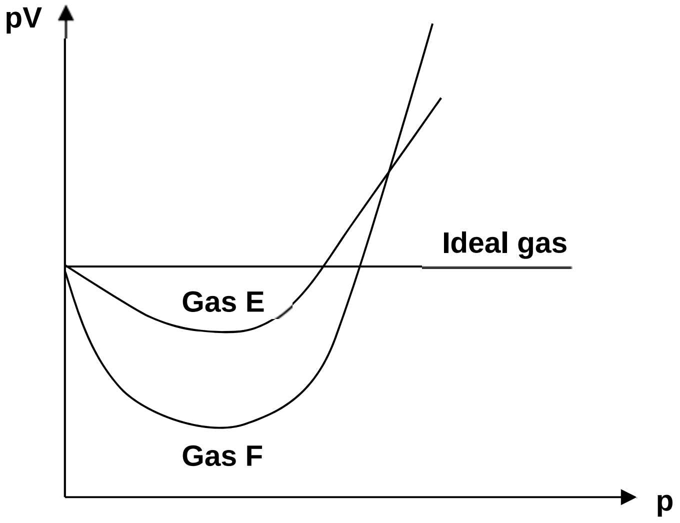
A 1 and 2 only

B 1 and 4 only

C 2 and 3 only

D 3 and 4 only

6



Which one of the following statements is true for the observation?

A Gas **E** could be He while gas **F** could be CO_2.

B Gas **E** could be NH_3 while gas **F** could be H_2.

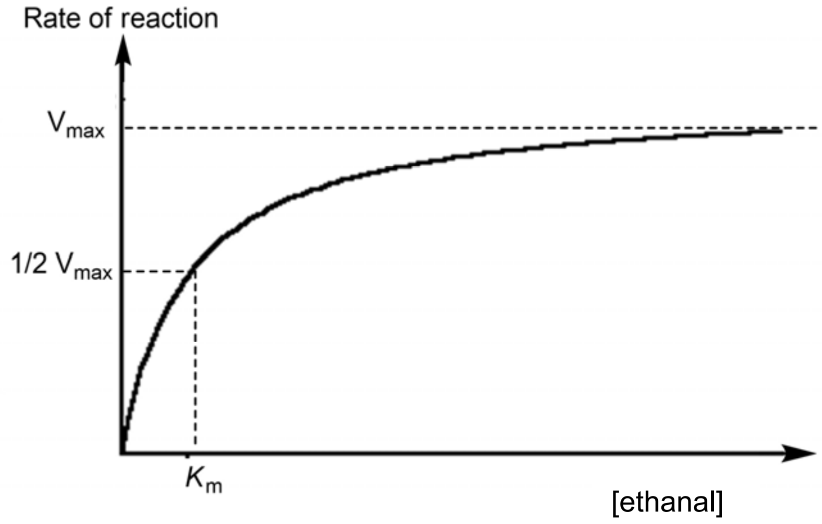
C Gas **E** could form intermolecular hydrogen bonds while gas **F** could form intermolecular permanent dipole-permanent dipole.

D Gas **E** could form stronger intermolecular instantaneous dipole-induced dipole than gas **F**.

7 The enzyme alcohol dehydrogenase catalyses an important step in the production of ethanol by fermentation.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The graph shows how the rate of this enzyme-catalysed reaction varies with the concentration of ethanal.



Which statement best explains the reason for the flattening off of the curve?

A All the ethanal has been used up and the reaction has finished.

B As the ethanol product builds up the reaction slows down.

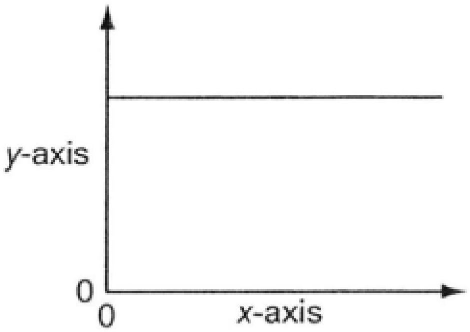
C At high ethanal concentrations all the active sites in the enzyme molecules are occupied by ethanal molecules.

D At high ethanal concentrations the ethanal inhibits the action of enzyme.

8 The kinetics of the zero order reaction P → Q were investigated under different conditions.

The table shows pairs of quantities that were plotted as graphs.

Which pairs gave the following graph?



	y-axis	x-axis
1	rate	time
2	rate constant	time
3	rate constant	temperature
4	rate	concentration

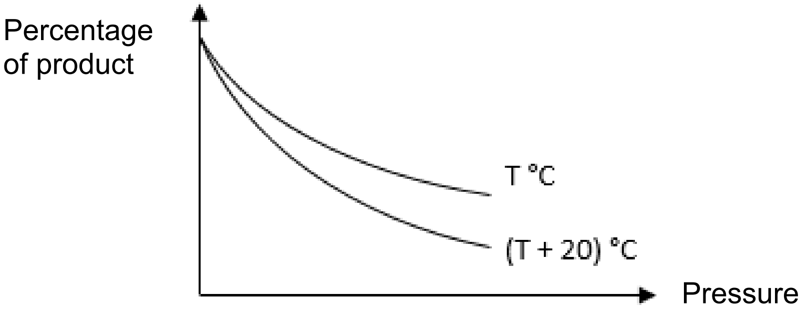
A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

9 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$ $\Delta H = -1644$ kJ mol^{-1}

B $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57.2$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

10 The standard enthalpy change of the following reaction is −896.4 kJ mol^{-1}.

$$2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$$

	NO(g)	$H_2O_2(l)$
ΔH^{θ}_f/kJ mol^{-1}	+ 90.3	− 187.8

Using the standard enthalpy change of formation in the above table, what is the standard enthalpy change of formation, in kJ mol^{-1}, of $HN_3(l)$?

A +264

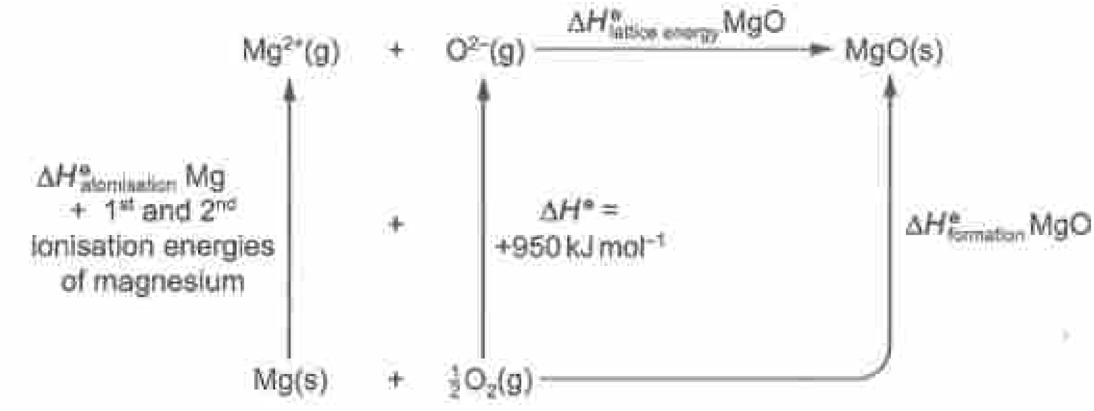
B +528

C +618

D +632

11 A student calculated the lattice energy for magnesium oxide using the cycle shown.

The enthalpy change of atomisation of magnesium, $\Delta H^{\theta}_{atomisation}$ Mg, is the energy needed when 1 mol of gaseous magnesium atoms is formed from 1 mol of solid magnesium under standard conditions.



However, the value calculated by the student for the lattice energy was **less** exothermic than the correct value.

Which errors could have been made in the calculation?

1 omitting the enthalpy change of atomisation of magnesium

2 omitting the first ionisation energy of magnesium

3 using the standard enthalpy change of combustion of magnesium rather than the standard enthalpy change of formation of magnesium oxide

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

12 Which changes are accompanied by an increase in entropy of the system?

1 freezing of water
2 sublimation of iodine
3 vaporisation of ethanol
4 conversion of $O_2(g)$ to $O_3(g)$

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 1 and 4 only

13 The value of the ionic product of water, K_w, varies with temperature.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

What can be deduced from this information?

A The ionic dissociation of water is an exothermic process.

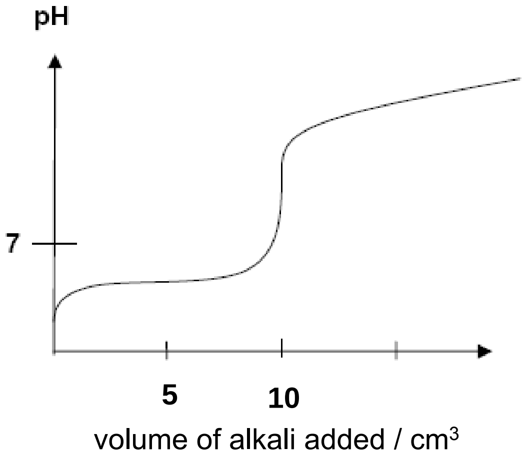
B The association of water molecules by hydrogen bonding increases as temperature increases.

C The pH of pure water increases with temperature.

D At 62 °C, water with a pH of 6.5 is neutral.

14 The following graph shows the changes in pH of 20.0 cm^3 of 1.0 mol dm^{-3} acid solution when excess 1.0 mol dm^{-3} alkali solution is added gradually.

Which one of the following pairs of solution with a suitable indicator could have resulted in the graph below?



	alkali	acid	indicator
A	NaOH	H_2SO_4	Methyl orange
B	NH_3	HNO_3	Phenolphthalein
C	KOH	CH_3CO_2H	Methyl orange
D	$Ba(OH)_2$	$CH_3CH_2CO_2H$	Phenolphthalein

15 *Use of the Data Booklet is relevant to this question.*

The AgC*l* / Ag reference electrode is based on the following reaction:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

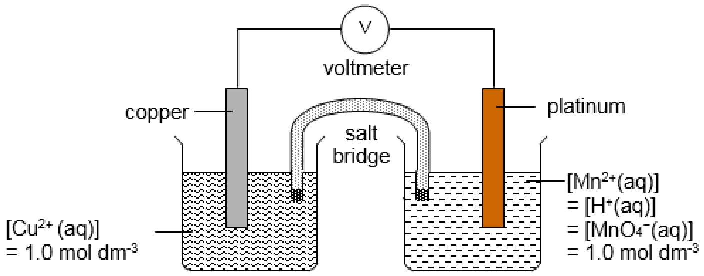
The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgC*l* / Ag reference electrode.

What is the reduction potential of the AgC*l* / Ag electrode with respect to the standard hydrogen electrode?

A −1.10 V **B** −0.20 V **C** +0.20 V **D** +1.10 V

16 *Use of the Data Booklet is relevant to this question.*

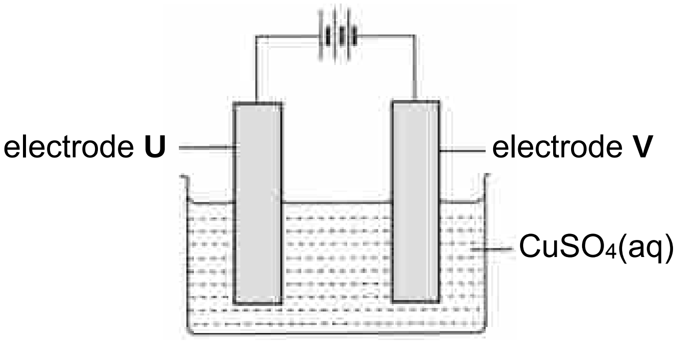
A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	change	effect on e.m.f of cell
A	addition of excess NH_3 (aq) into oxidation half-cell	increases
B	addition of concentrated H_2SO_4 into reduction half-cell	decreases
C	increase the size of the copper electrode	increases
D	replace copper with an alloy of copper and zinc	remains the same

17 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below. Electrode **V** is pure copper and electrode **U** is the copper-silver alloy.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

What is the percentage of silver by mass in the electrode **U**?

A 20%

B 40%

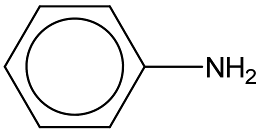
C 60%

D 80%

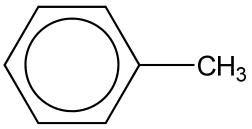
18 Which of the following is a planar molecule?

A $H-C\equiv C-CH_2CH_3$

B



C

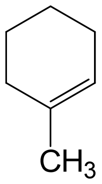


D $H_2C=CH-CHO$

19 A hydrocarbon, on heating with an excess of hot concentrated acidic $KMnO_4$ produces $HO_2CCH_2CH_2CH_2COCH_3$.

What could the hydrocarbon be?

1



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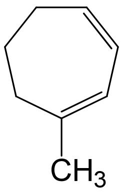

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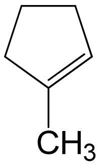


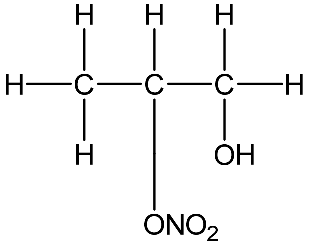
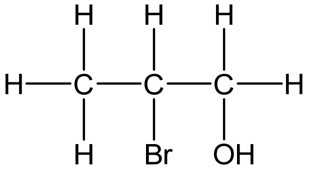
A 1 and 2 only

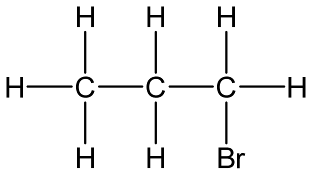
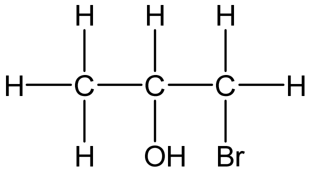
B 1 and 3 only

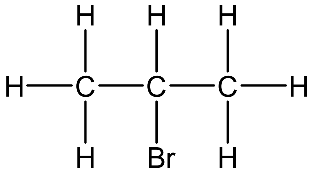
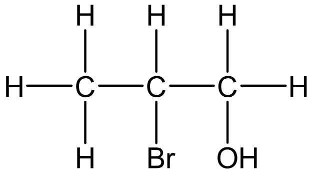
C 2 and 3 only

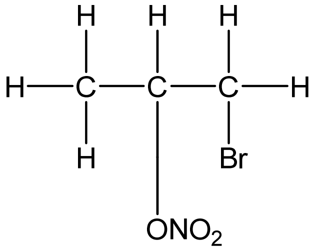
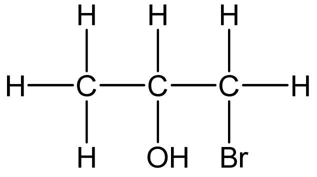
D 1, 2 and 3

20 When propene reacts with Br_2 in the presence of excess aqueous KNO_3, what are the two major products formed?

A  and 

B  and 

C  and 

D  and 

21 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements are true for benzene?

1 It prevents benzene from undergoing addition reactions.

2 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

3 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

4 The presence of π electrons enables benzene to be a good electrical conductor.

A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

22 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

C $CH_3CH_2CCl_2CH_3$ and $ClCH_2CH_2CH_2CHCl_2$

D $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

23 Deuterium, D, is the ${}^{2}_{1}H$ isotope of hydrogen.

Which of the following reactions yield a carbon compound containing deuterium?

1 $CH_3CH_2CN \xrightarrow[\text{heat}]{D_2\text{, Ni catalyst}}$

2 $CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4\text{, }D_2O}$

3 $CH_3COCI_3 \xrightarrow[D_2O]{NaOD}$

4 $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc }D_2SO_4}$

A 1 and 2 only

B 1 and 4 only

C 1, 2 and 3 only

D 2, 3 and 4 only

24 Which of the following synthetic routes **does not** produce ethanoic acid?

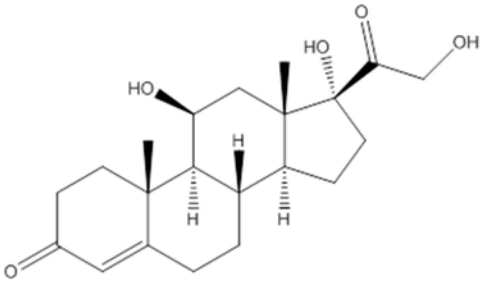
A $CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} \xrightarrow[\text{heat}]{\text{dil HC}l}$

B $CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} \xrightarrow[\text{r.t.p.}]{H^+}$

C $CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} \xrightarrow[\text{r.t.p.}]{H^+}$

D $CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^\circ C]{\text{excess conc }H_2SO_4} \xrightarrow[\text{heat}]{\text{acidic }K_2Cr_2O_7}$

25 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



Hydrocortisone

Which of the following statements about Hydrocortisone is true?

A When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing 5 hydroxy groups.

B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C When treated with cold dilute $KMnO_4$, it forms a compound containing 2 hydroxy groups.

D When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 7 chiral centres.

26 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water. The pH of each resultant solution is then measured.

$CH_3CH_2CO_2H$	CH_3CH_2COCl	$ClCH_2CH_2CO_2H$	$BrCH_2CH_2CO_2H$
P	**Q**	**R**	**S**

Which of the following shows the correct order of increasing order of acidity of the solutions formed?

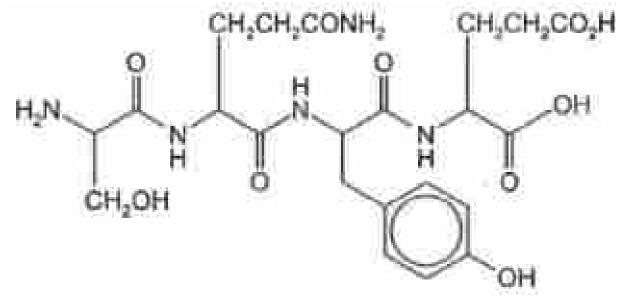
A P, R, S, Q

B P, S, R, Q

C Q, P, S, R

D Q, S, R, P

27 The diagram shows the structure of the tetrapeptide **T**.

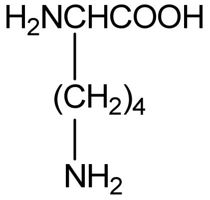


T

When 0.1 mole of **T** is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?

A	0.4	**B**	0.5
C	0.6	**D**	0.7

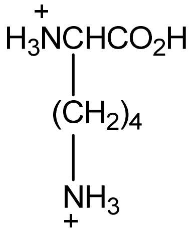
28 Lysine is an α-amino acid.



$$\begin{array}{c}\mathrm{H_2NCHCOOH}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

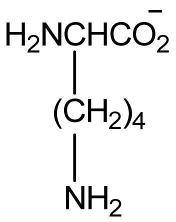
Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?

A



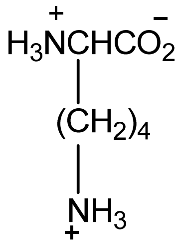
$$\begin{array}{c}\overset{+}{\mathrm{H_3N}}\mathrm{CHCO_2H}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \underset{+}{\mathrm{NH_3}}\end{array}$$

B



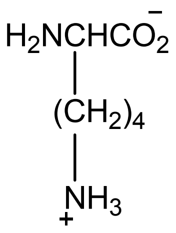
$$\begin{array}{c}\mathrm{H_2NCHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{NH_2}\end{array}$$

C



$$\begin{array}{c}\overset{+}{\mathrm{H_3N}}\mathrm{CHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \underset{+}{\mathrm{NH_3}}\end{array}$$

D



$$\begin{array}{c}\mathrm{H_2NCHC\overset{-}{O_2}}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \underset{+}{\mathrm{NH_3}}\end{array}$$

29 Element **J** is in Period 3 of the Periodic Table. The following three statements are the properties of element **J** or its compounds.

- Adding NaOH(aq) to the solution resulting from the reaction of a chloride of **J** with water produces a white precipitate which is soluble in an excess of NaOH(aq).
- Element **J** is a solid at room temperature.
- The oxide of element **J** is soluble in hydrochloric acid.

What is the identity of element **J**?

A	magnesium	**C**	silicon
B	aluminium	**D**	phosphorus

30 *The use of the Data Booklet is relevant to this question.*

The colours of various vanadium ions in aqueous solution are given in the table below.

Oxidation state	V	IV	III	II
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	yellow	blue	green	violet

What is the final colour of the solution when excess zinc powder is added to an acidified solution containing VO_2^+ ions?

A	yellow	**C**	green
B	blue	**D**	violet

End of Paper

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INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	MARK SCHEME
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

XX XXX 2018

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

1	**C**	6	**A**	11	**A**	16	**A**	21	**C**	26	**B**
2	**A**	7	**C**	12	**B**	17	**A**	22	**D**	27	**D**
3	**B**	8	**D**	13	**D**	18	**D**	23	**C**	28	**D**
4	**C**	9	**B**	14	**D**	19	**C**	24	**D**	29	**B**
5	**B**	10	**A**	15	**C**	20	**D**	25	**A**	30	**D**

A: 7 B: 6 C:7 D: 10

This document consists of **X** printed pages.

For each question there are four possible answers, **A, B, C,** and **D**. Choose the **one** you consider to be correct.

1 In an experiment, 0.002 mol acidified iron (II) sulfate is quantitatively oxidised by 0.001 mol of an oxidising agent, ZO_3^-. Given that Fe^{2+} is oxidised to Fe^{3+}, what is the final oxidation state of **Z**?

A +1 **B** +2 **C** +3 **D** +4

Answer: C

Amount of electrons released by Fe^{2+} = 0.002 mol

= amount of electrons accepted by YO_3^-

Amount of YO_3^- ; amount of e = 1 : 2

Oxidation number of Y in YO_3^- = +5

New oxidation number of Y = +5 – 2 = +3

2 Gaseous particle **X** has a proton number n and a charge of +1.

Gaseous particle **Y** has a proton number of (n + 1) and is isoelectronic with **X**.

Which of the following statements correctly describe **X** and **Y**?

1 **Y** has a smaller radius than **X**.

2 **Y** requires less energy than **X** when a further electron is removed from each particle.

3 **Y** releases less energy than **X** when an electron is added to each particle.

A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

Answer: A

particle	proton number	electron number	charge
X	n	n-1	+1
Y	n+1	n-1	+2

Since **Y** has higher nuclear charge than **X**, and both **X** and **Y** have same shielding effect (same electron number), **Y** has higher effective nuclear charge and valence electrons are more strongly attracted to the nucleus.

Thus, **Y** has smaller radius than **X**. (Option 1 is correct)

Y requires more energy than **X** when a further electron is removed from each particle. (Option 2 is wrong)

Y releases more energy than **X** when an electron is added to each particle. (Option 3 is wrong)

3 What is the electronic configuration of an element with a **second** ionisation energy higher than that of each of the elements either side of it in the Periodic Table?

A $1s^22s^22p^63s^2$

B $1s^22s^22p^63s^23p^1$

C $1s^22s^22p^63s^23p^2$

D $1s^22s^22p^63s^23p^3$

Answer: B

The electronic configuration for second ionisation energy of the above species:

A: $1s^22s^22p^63s^1$

B: $1s^22s^22p^63s^2$

C: $1s^22s^22p^63s^23p^1$

D: $1s^22s^22p^63s^23p^2$

As there is a decrease in ionisation energy between the species between ns^2 and ns^2np^1, species that have electronic configuration of ns^2 will have second ionisation energy higher than that of each of the elements either side of it (ns^1 and ns^2np^1) in the Periodic Table.

4 The table shows the charge and radius of each of six ions.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. What is the correct order of their lattice energies, placing the most exothermic first?

A JX, MZ, LY

B LY, MZ, JX

C MZ, JX, LY

D MZ, LY, JX

Answer: C

Since $\left|\text{Lattice energy, } \Delta H_{\text{latt}}^{\theta}\right| \propto \left|\dfrac{q_+q_-}{r_+ + r_-}\right|$, compound MZ has the most exothermic lattice energy as M^{2+} and Z^{2-} has higher charge than that of J^+, L^+, X^- and Y^-. Compound LY has the least exothermic lattice energy as L^+ and Y^- has larger ionic radius than that of J^+ and Y^-.

5 In certain microwave ovens, the wave energy produced is absorbed by certain polar molecules.

Which of the following would absorb microwave energy?

1 CH_3CH_2OH
2 $AlCl_3$
3 CO_2
4 CH_3F

A 1 and 2 only

B 1 and 4 only

C 2 and 3 only

D 3 and 4 only

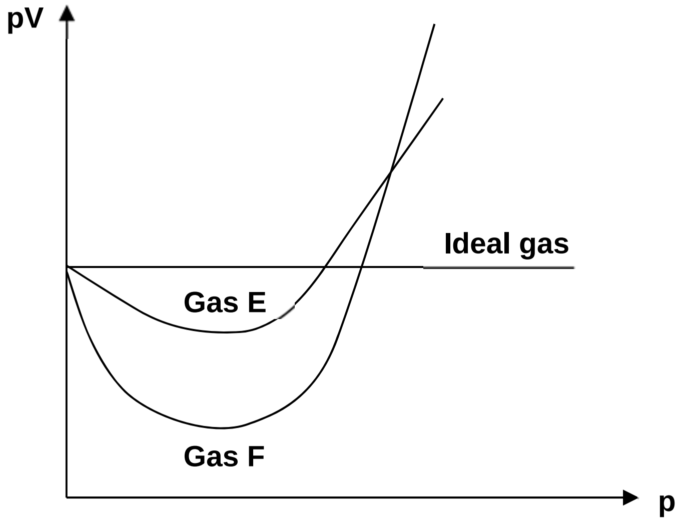
Answer: B

Option 2 is non polar molecule. $AlCl_3$ is trigonal planar in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 3 is non polar molecule. CO_2 is linear in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 1 and 4 are polar as there is net dipole moment in the molecule.

6



Which one of the following statements is true for the observation?

A Gas **E** could be He while gas **F** could be CO_2.

B Gas **E** could be NH_3 while gas **F** could be H_2.

C Gas **E** could form intermolecular hydrogen bonds while gas **F** could form intermolecular permanent dipole-permanent dipole.

D Gas **E** could form stronger intermolecular instantaneous dipole-induced dipole than gas **F**.

Answer: A

$pV = nRT$
$1.5 \times 101325 \times V = 1 \times 8.31 \times (273+27)$
$V = 0.0164\ m^3$
$V = 16.4\ dm^3$
From the above calculation, it can be deduced that gas **E** behave more ideally than gas **F**.

Option A is correct. He behaves more like an ideal gas as it has smaller electron cloud size and weaker i.d.-i.d. than that of CO_2. Intermolecular forces of attraction between He is negligible.

Option B is wrong. NH_3 can form hydrogen bonds between molecules and there is significant intermolecular forces of attraction. NH_3 deviates more from ideal gas.

Option C is wrong. Gas **E** should form weaker i.d.-i.d. between molecules than that of **F** as gas **E** behave more ideally than gas **F**.

Option D is wrong. Gas **E** should form weaker i.d.-i.d. than gas **F** as gas **E** behave more ideally than gas **F**.

7 The enzyme alcohol dehydrogenase catalyses an important step in the production of ethanol by fermentation.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The graph shows how the rate of this enzyme-catalysed reaction varies with the concentration of ethanal.

[ethanal]

Which statement best explains the reason for the flattening off of the curve?

A All the ethanal has been used up and the reaction has finished.

B As the ethanol product builds up the reaction slows down.

C At high ethanal concentrations all the active sites in the enzyme molecules are occupied by ethanal molecules.

D At high ethanal concentrations the ethanal inhibits the action of enzyme.

Answer: C

Option A is wrong as there is an increase in the concentration of ethanal. The ethanal has not been used up and the reaction has not finished.

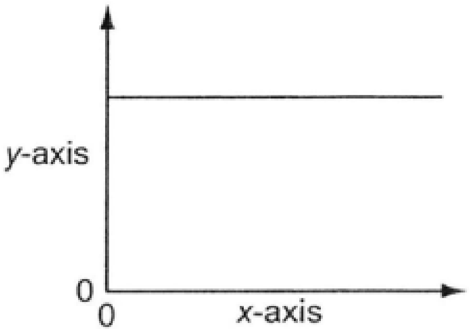
Option B is wrong as the concentration of the ethanol product builds up the reaction will not slow down the rate of reaction.

Option D is wrong as ethanal is not an inhibitor but substrate (reactant) of this reaction.

8 The kinetics of the zero order reaction P → Q were investigated under different conditions.

The table shows pairs of quantities that were plotted as graphs.

Which pairs gave the following graph?



	y-axis	*x*-axis
1	rate	time
2	rate constant	time
3	rate constant	temperature
4	rate	concentration

A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

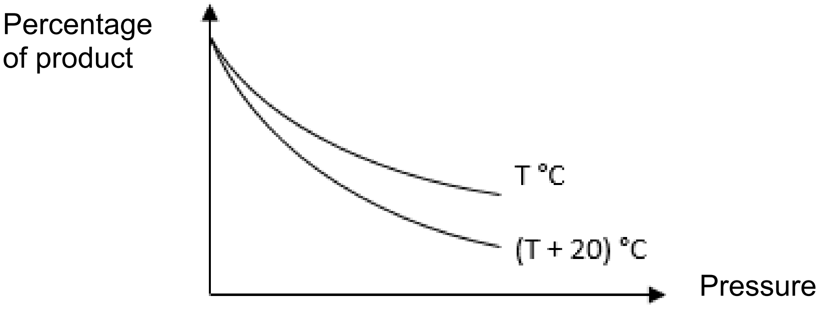
D 1, 2 and 4 only

Answer: D

For a zero order reaction, rate of the reaction is independent of time and concentration.

Also, rate constant is dependent on temperature and activation energy (from Arrhenius equation.)

9 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe (s) + 3O_2 (g) \rightleftharpoons 2Fe_2O_3 (s)$ $\Delta H = -1644$ kJ mol^{-1}

B $2C (s) + O_2 (g) \rightleftharpoons 2CO (g)$ $\Delta H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57.2$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

Answer: B

From the graph, when the pressure increases, the proportion of product molecules decrease. This indicates that when pressure increases, the equilibrium position shifts to left (which have fewer gaseous molecules to decrease the pressure). Option A and option D is wrong.

From the graph, when the temperature increases, the proportion of product molecules decrease too. This indicates that when temperature increases, the equilibrium position shifts to left (which is endothermic to reduce the temperature. Since option B is exothermic in the forward reaction, it would be endothermic in the backward reaction.

Only Option B shows the correct trend when temperature and pressure increase.

10 The standard enthalpy change of the following reaction is −896.4 kJ mol⁻¹.

$$2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$$

	NO(g)	$H_2O_2(l)$
ΔH^θ_f/kJ mol^{-1}	+ 90.3	− 187.8

Using the standard enthalpy change of formation in the above table, what is the standard enthalpy change of formation, in kJ mol^{-1}, of $HN_3(l)$?

A +264

B +528

C +618

D +632

Answer: A

Using $\Delta H_r^\theta = \sum n\Delta H_f^\theta$ (products) $-$ $\sum m\Delta H_f^\theta$ (reactants)

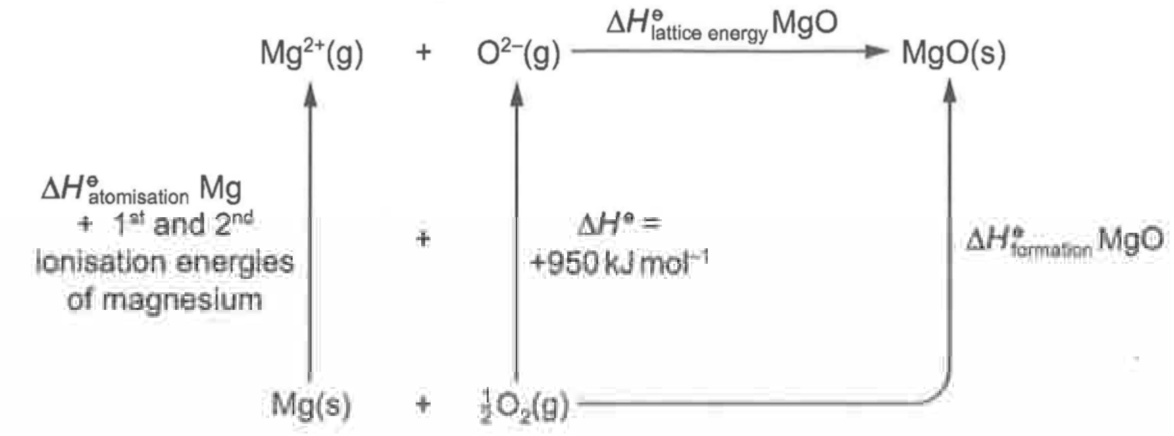
$\Delta H_r^\theta = \Delta H_f (H_2O_2) - [\,2\,\Delta H_f (HN_3) + 2\,\Delta H_f (NO)]$

$-896.4 = -187.8 - (2\,\Delta H_f (HN_3) + 2 \times 90.3)$

$\Delta H_f (HN_3) = +264$ kJ mol^{-1}

11 A student calculated the lattice energy for magnesium oxide using the cycle shown.

The enthalpy change of atomisation of magnesium, $\Delta H^{\theta}_{\text{atomisation}}$ Mg, is the energy needed when 1 mol of gaseous magnesium atoms is formed from 1 mol of solid magnesium under standard conditions.



However, the value calculated by the student for the lattice energy was **less** exothermic than the correct value.

Which errors could have been made in the calculation?

1 omitting the enthalpy change of atomisation of magnesium

2 omitting the first ionisation energy of magnesium

3 using the standard enthalpy change of combustion of magnesium rather than the standard enthalpy change of formation of magnesium oxide

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

Ans: A

By Hess's law,

Lattice energy = – [$\Delta H^{\theta}_{\text{atomisation}}$Mg] –[1st and 2nd I.E. of Mg] – 950
+ $\Delta H^{\theta}_{\text{formation}}$MgO

1 is correct as the lattice energy will be less exothermic if the enthalpy change of atomisation of Mg is omitted. This is because, the enthalpy change of atomisation of Mg is a positive term.

2 is correct as the lattice energy will be less exothermic if the first ionisation energy of Mg is omitted. This because, the first ionisation energy of Mg is a positive term

3 is incorrect as the replacing the standard enthalpy change of formation of MgO with the standard enthalpy change of combustion of Mg will have no effect on the value of the lattice energy. This is because both values are the same.

12 Which changes are accompanied by an increase in entropy of the system?

1 freezing of water
2 sublimation of iodine
3 vaporisation of ethanol
4 conversion of O_2(g) to O_3(g)

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 1 and 4 only

Answer: B

For option 2 and 3, there is an increase in the number of gaseous molecules (from solid to gas and from liquid to gas), there is an increase in the disorderness of the system, entropy increases.

For option 1, there is a decrease in the disorderness of the system (from liquid to solid) and similarly for that of option 4. $3O_2(g) \rightarrow 2O_3(g)$

13 The value of the ionic product of water, K_w, varies with temperature.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

What can be deduced from this information?

A The ionic dissociation of water is an exothermic process.

B The association of water molecules by hydrogen bonding increases as temperature increases.

C The pH of pure water increases with temperature.

D At 62 °C, water with a pH of 6.5 is neutral.

Answer: D

Option A is wrong as ionic dissociation of water involves bond breaking of water molecules, this is an endothermic reaction.

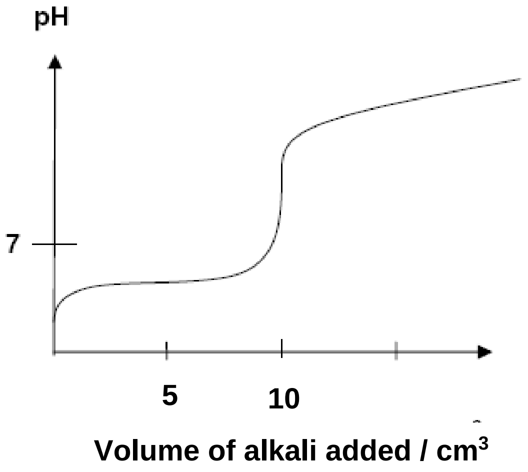
Option B is wrong. As temperature increases, more hydrogen bonds between molecules are broken.

Option C is wrong. The pH of pure water decreases with temperature. (pH = 7 at 25 °C and pH = 6.5 at 62 °C)

Option D is correct as water is neutral at all temperature as $[H^+] = [OH^-]$.

14 The following graph shows the changes in pH of 20.0 cm^3 of 1.0 mol dm^{-3} acid solution when excess 1.0 mol dm^{-3} alkali solution is added gradually.

Which one of the following pairs of solution with a suitable indicator could have resulted in the graph below?



	alkali	acid	indicator
A	NaOH	H_2SO_4	Methyl orange
B	NH_3	HNO_3	Phenolphthalein
C	KOH	CH_3CO_2H	Methyl orange
D	$Ba(OH)_2$	$CH_3CH_2CO_2H$	Phenolphthalein

Answer: D

Since the volume of alkali needed for neutralisation is half of that of acid, this indicates that there should be 2 OH^- per base molecules. Since this is a weak acid-strong base titration, pH at equivalence point should be greater than 7 as a basic salt is formed. Phenolphthalein is a suitable indicator as its working range is greater than 7.

15 *Use of the Data Booklet is relevant to this question.*

The AgC*l* / Ag reference electrode is based on the following reaction:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgC*l* / Ag reference electrode.

What is the reduction potential of the AgC*l* / Ag electrode with respect to the standard hydrogen electrode?

A −1.10 V **B** −0.20 V **C** +0.20 V **D** +1.10 V

Answer: C

The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.44 V when measured using the standard hydrogen electrode.

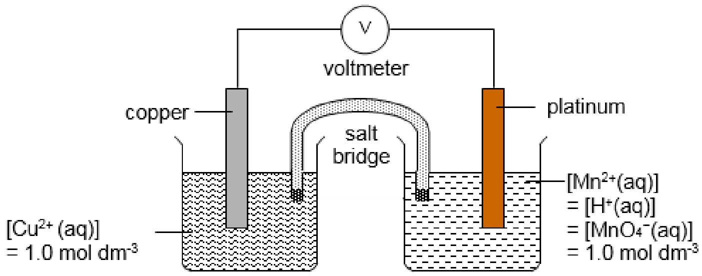
$E^o_{cell} = E^o_{red} - E^o_{ox}$

$-0.44\ V = E^o_{red} - 0.64$

$E^o_{red} = +0.20\ V$

16 *Use of the Data Booklet is relevant to this question.*

A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	change	effect on e.m.f of cell
A	addition of excess NH_3 (aq) into oxidation half-cell	increases
B	addition of concentrated H_2SO_4 into reduction half-cell	decreases
C	increase the size of the copper electrode	increases
D	replace copper with an alloy of copper and zinc	remains the same

Answer: A

$Cu^{2+} + 2e \rightleftharpoons Cu$ $\quad$ +0.34 V
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad$ +1.52 V

$E^o_{cell} = E^o_{red} - E^o_{ox} = +1.52 - (+0.34) = +1.18$ V

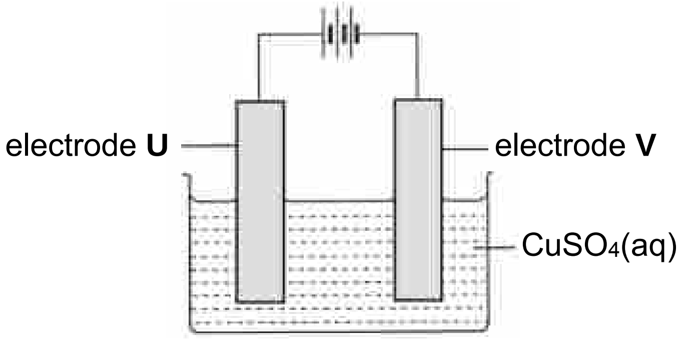
Option A is correct: when excess NH_3 (aq) into oxidation half-cell, [Cu^{2+}] decreases as Cu^{2+} reacts with NH_3 to form $[Cu(NH_3)_4]^{2+}$. Since [Cu^{2+}] decreases, equilibrium position shifts to the left, E^o_{ox} is less positive, E^o_{cell} becomes more positive.

Option B is wrong. When concentrated H_2SO_4 is added into reduction half-cell, [H^+] increases. Since [H^+] increases, equilibrium position shifts to the right, E^o_{red} is more positive, E^o_{cell} becomes more positive.

Option C is wrong. Increase the size of the copper electrode will not have effect on e.m.f. of the cell.

Option D is wrong. Replace copper with an alloy of copper and zinc will result in more positive E^o_{cell}. (+1.52 – (–0.76) = +2.28 V)

17 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below. Electrode **V** is pure copper and electrode **U** is the copper-silver alloy.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

What is the percentage of silver by mass in the electrode **U**?

A 20%

B 40%

C 60%

D 80%

Answer: A

$I \times t = n_e \times F$
$40 \times 26.8 \times 60 = n_e \times 96500$
$n_e = 0.6665$ mol

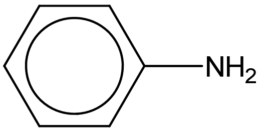
Since Cu : e = 1 : 2,
Amount of Cu formed = ½ x 0.6665 = 0.3332 mol
Mass of Cu formed = 0.3332 x 63.5 = 21.16 g

% silver by mass = (26.47-21.16)/26.47 x 100% = 20%

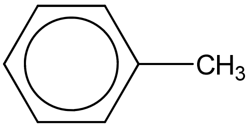
18 Which of the following is a planar molecule?

A $H-C \equiv C-CH_2CH_3$

B



C



D $H_2C=CH-CHO$

Answer: D

Option A is wrong. There are 2 sp^3 carbon atoms (tetrahedral around the C) in the molecule.

Option B is wrong. The molecule is trigonal pyramidal around the N atom.

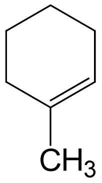
Option C is wrong. There are 1 sp^3 carbon atom (tetrahedral around the C) in the molecule.

Option D is correct. All the carbons are sp^2 carbon in the molecule.

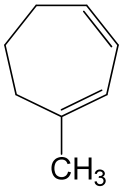
19 A hydrocarbon, on heating with an excess of hot concentrated acidic $KMnO_4$ produces $HO_2CCH_2CH_2CH_2COCH_3$.

What could the hydrocarbon be?

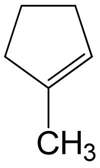
1



2



3



A 1 and 2 only

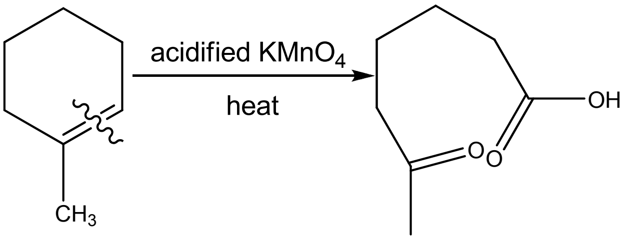
B 1 and 3 only

C 2 and 3 only

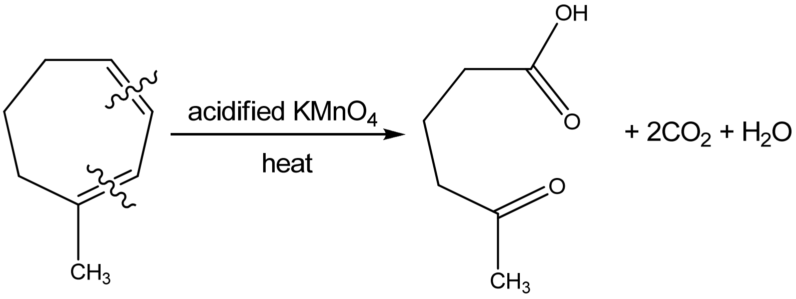
D 1, 2 and 3

Answer: C

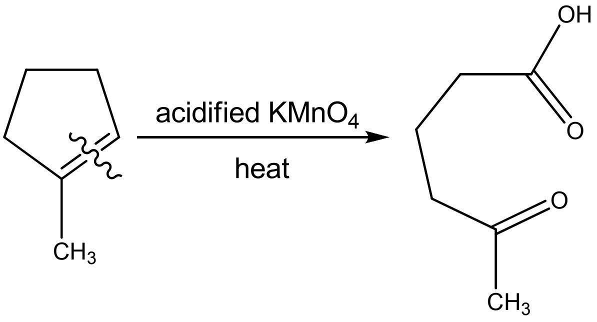
Option A is wrong.



Option B is correct.

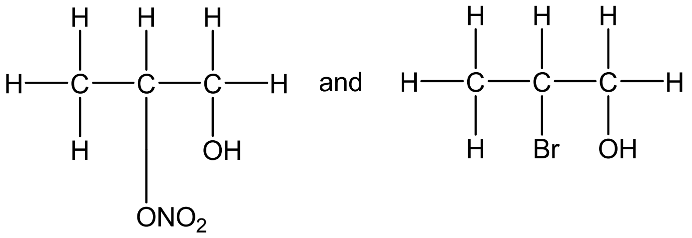


Option C is correct.

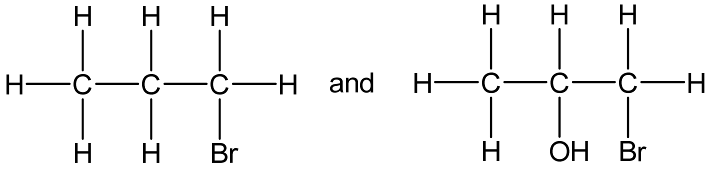


20 When propene reacts with Br_2 in the presence of excess aqueous KNO_3, what are the two major products formed?

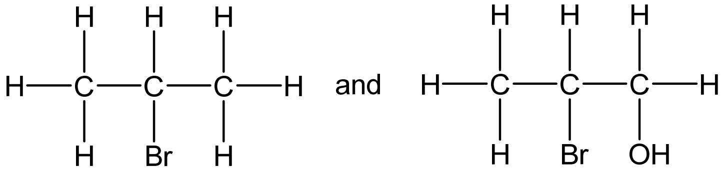
A



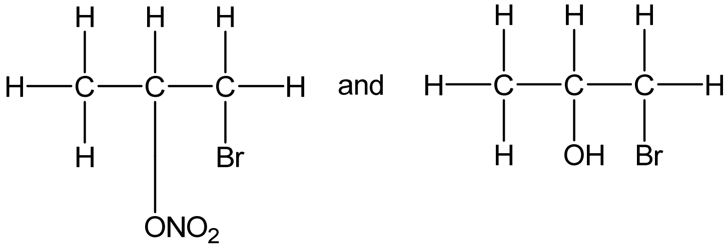
B



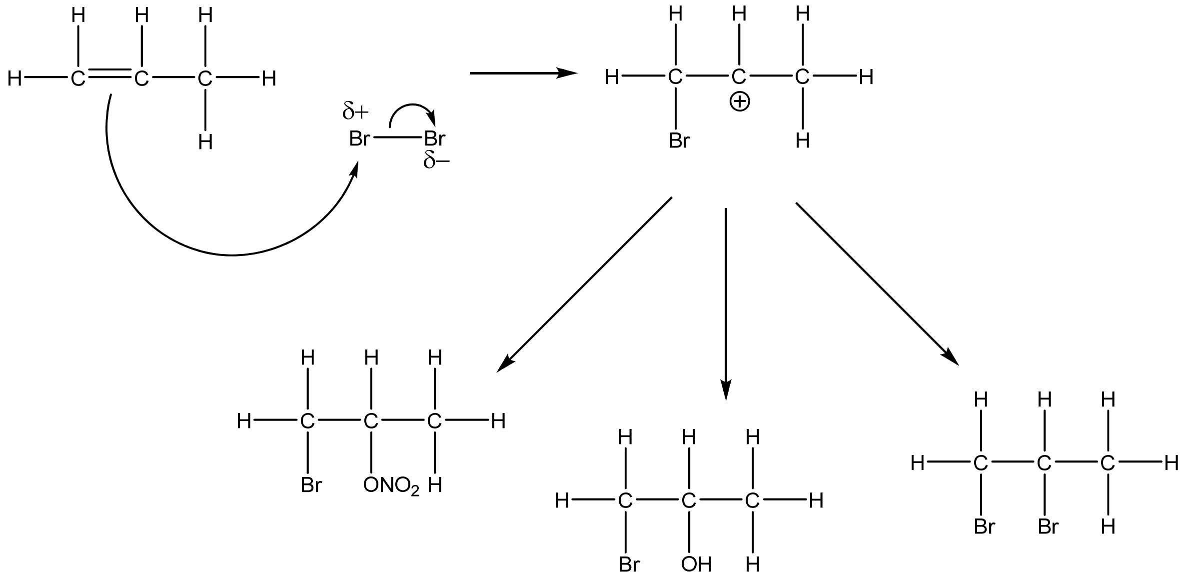
C



D



Answer: D



21 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements are true for benzene?

1 It prevents benzene from undergoing addition reactions.

2 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

3 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

4 The presence of π electrons enables benzene to be a good electrical conductor.

A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

Answer: C

Option 1 is correct. Benzene undergoes substitution reaction to remain its aromaticity.

Option 2 is correct. As the π electrons are delocalised in the benzene ring, all the C-C bonds have partial double bond character.

Option 3 is correct. As the π electrons are delocalised in the benzene ring, benzene is more stable and it occupies lower energy level as it is more stable due to its aromaticity. As a result, less energy is released from hydrogenation of benzene.

Option 4 is wrong. Although the π electrons are delocalised in the benzene ring, there is no free mobile electrons and ions in liquid benzene, thus benzene is not a good conductor of electricity.

22 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

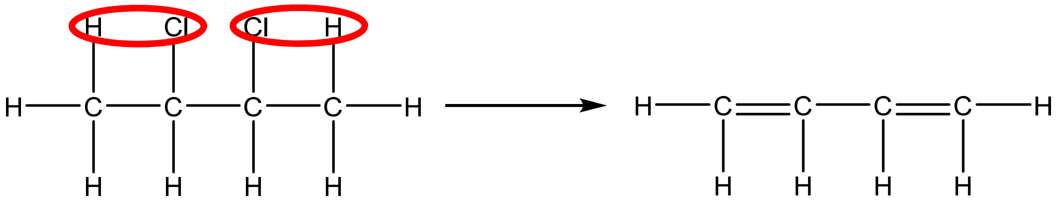
C $CH_3CH_2CCl_2CH_3$ and $ClCH_2CH_2CH_2CHCl_2$

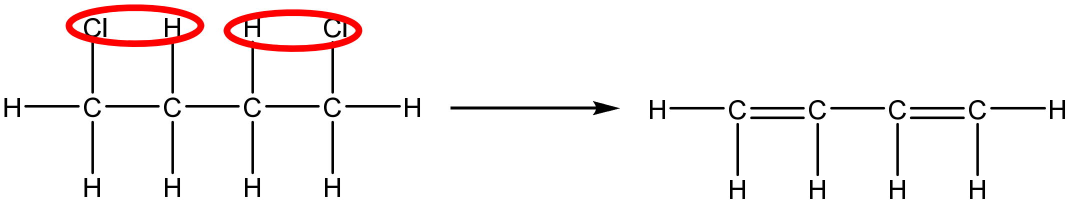
D $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

Answer: D

For option A, B and C, there is at least one molecule in the option contain 1 or 3 Cl atoms which after elimination can only form 1 or 3 C=C bond.

For option D, the two compounds can produce the same compound, as shown below:





23 Deuterium, D, is the ${}^{2}_{1}H$ isotope of hydrogen.

Which of the following reactions yield a carbon compound containing deuterium?

1 $CH_3CH_2CN \xrightarrow[\text{heat}]{D_2\text{, Ni catalyst}}$

2 $CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4\text{, }D_2O}$

3 $CH_3COCI_3 \xrightarrow[D_2O]{\text{NaOD}}$

4 $(CH_3)_3COH \xrightarrow[\text{heat}]{\text{conc }D_2SO_4}$

- **A** 1 and 2 only
- **B** 1 and 4 only
- **C** 1, 2 and 3 only
- **D** 2, 3 and 4 only

Answer: C

Option 1 is correct.

$CH_3CH_2CN \xrightarrow[\text{heat}]{D_2\text{, Ni catalyst}} CH_3CH_2CD_2ND_2$

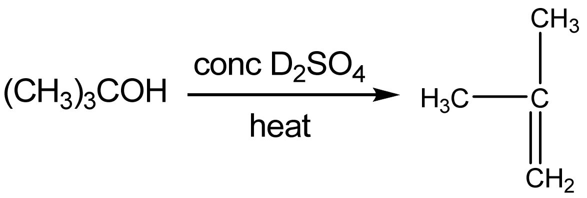
Option 2 is correct.

$CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4\text{, }D_2O} CH_3COOD + CH_3CH_2OD$

Option 3 is correct.

$CH_3COCI_3 \xrightarrow[D_2O]{\text{NaOD}} CH_3COO^- + CDI_3$

Option 4 is wrong.



24 Which of the following synthetic routes **does not** produce ethanoic acid?

A $CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} \xrightarrow[\text{heat}]{\text{dil HC}l}$

B $CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} \xrightarrow[\text{r.t.p.}]{H^+}$

C $CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} \xrightarrow[\text{r.t.p.}]{H^+}$

D $CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^oC]{\text{excess conc } H_2SO_4} \xrightarrow[\text{heat}]{\text{acidic } K_2Cr_2O_7}$

Answer: D

Option A is correct.

$$CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} CH_3CN \xrightarrow[\text{heat}]{\text{dil HC}l} CH_3COOH$$

Option B is correct.

$$CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} CH_3COO^- \xrightarrow[\text{r.t.p.}]{H^+} CH_3COOH$$

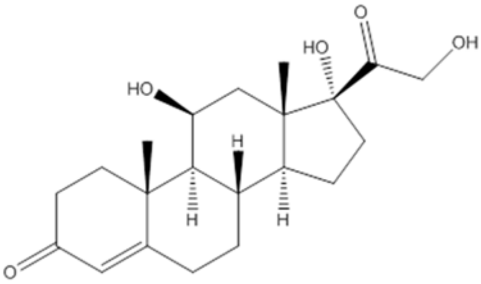
Option C is correct.

$$CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} CH_3COO^- \xrightarrow[\text{r.t.p.}]{H^+} CH_3COOH$$

Option D is wrong.

$$CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^oC]{\text{excess conc } H_2SO_4} \begin{matrix} CH_3CH{=}CH_2CH_3 \\ CH_2{=}CHCH_2CH_3 \end{matrix} \xrightarrow[\text{heat}]{\text{acidic } K_2Cr_2O_7} \text{no reaction}$$

25 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



Hydrocortisone

Which of the following statements about hydrocortisone is true?

A When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing 5 hydroxy groups.

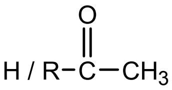
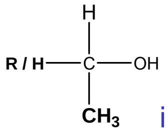
B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C When treated with cold dilute $KMnO_4$, it forms a compound containing 2 hydroxy groups.

D When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 7 chiral centres.

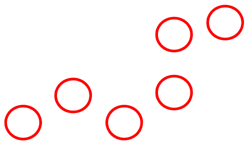
Answer: A

Option A is correct. The two ketone is reduced to secondary alcohol. Together with the other three alcohol in the molecule, the molecule has 5 hydroxy group.

Option B is wrong. There is no  $H / R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ or  $R / H-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C}}-OH$ in the molecule.

Option C is wrong. When treated with cold dilute $KMnO_4$, the alkene in the molecule will be converted to diol. Together with the other three alcohol in the molecule, the molecule has 5 hydroxy group.

Option D is wrong. When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 6 chiral centres.



26 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water. The pH of each resultant solution is then measured.

$CH_3CH_2CO_2H$	CH_3CH_2COCl	$ClCH_2CH_2CO_2H$	$BrCH_2CH_2CO_2H$
P	**Q**	**R**	**S**

Which of the following shows the correct order of increasing order of acidity of the solutions formed?

A P, R, S, Q

B P, S, R, Q

C Q, P, S, R

D Q, S, R, P

Answer: B

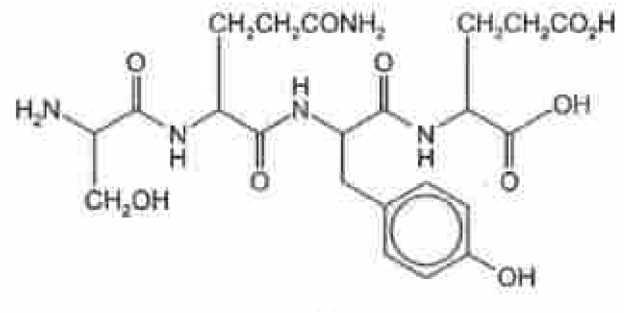
$CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2CO_2H + HCl$

Solution is most acidic.

Cl group is more electronegative than Br and the negative charge of $ClCH_2CH_2CO_2^-$ is dispersed to a greater extent than $BrCH_2CH_2CO_2^-$. Thus, $ClCH_2CH_2CO_2^-$ is more stable than $BrCH_2CH_2CO_2^-$. $ClCH_2CH_2CO_2H$ is more acidic than $BrCH_2CH_2CO_2H$.

$CH_3CH_2CO_2H$ is the least acidic among the four compounds.

27 The diagram shows the structure of the tetrapeptide **T**.

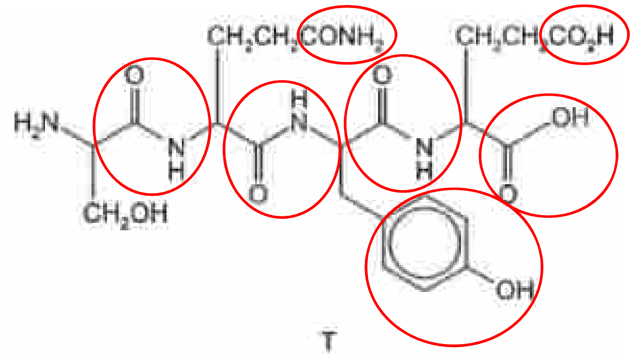


T

When 0.1 mole of **T** is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?

A	0.4	**B**	0.5
C	0.6	**D**	0.7

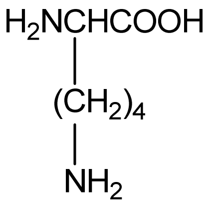
Answer: D



T

The circled functional group can react with NaOH(aq), heat with reflux.

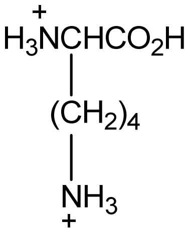
28 Lysine is an α-amino acid.



$H_2NCH((CH_2)_4NH_2)COOH$

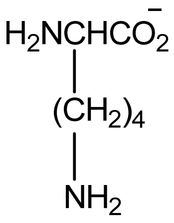
Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?

A



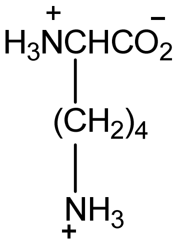
$H_3\overset{+}{N}CH((CH_2)_4\overset{+}{N}H_3)CO_2H$

B



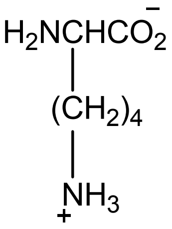
$H_2NCH((CH_2)_4NH_2)CO_2^-$

C



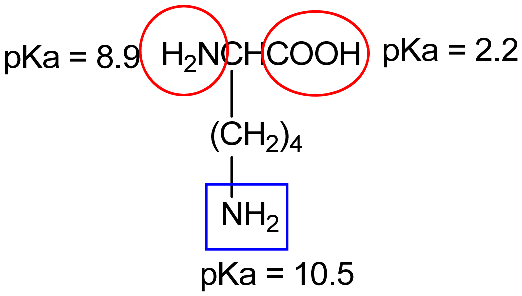
$H_3\overset{+}{N}CH((CH_2)_4\overset{+}{N}H_3)CO_2^-$

D

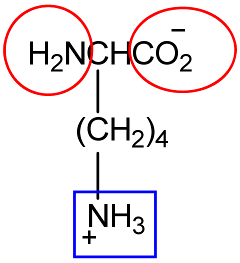


$H_2NCH((CH_2)_4\overset{+}{N}H_3)CO_2^-$

Answer: D



When pH > pKa, the functional group circled will be deprotonated.
When pH < pKa, the functional group squared will be protonated.



$H_2NCH((CH_2)_4\overset{+}{N}H_3)CO_2^-$

29 Element **J** is in Period 3 of the Periodic Table. The following three statements are the properties of element **J** or its compounds.

- Adding NaOH(aq) to the solution resulting from the reaction of a chloride of **J** with water produces a white precipitate which is soluble in an excess of NaOH(aq).
- Element **J** is a solid at room temperature.
- The oxide of element **J** is soluble in hydrochloric acid.

What is the identity of element **J**?

A	magnesium	**C**	silicon
B	aluminium	**D**	phosphorus

Answer: B

Based on the information provided, the only possible Period 3 element for **J** is Al.

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$
$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$

Al is a solid at room temperature.

The oxide of Al is soluble in hydrochloric acid.
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

30 *The use of the Data Booklet is relevant to this question.*

The colours of various vanadium ions in aqueous solution are given in the table below.

Oxidation state	V	IV	III	II
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	yellow	blue	green	violet

What is the final colour of the solution when excess zinc powder is added to an acidified solution containing VO_2^+ ions?

A	yellow	**C**	green
B	blue	**D**	violet

Answer: D

$V^{3+} + e^- \rightleftharpoons V^{2+}$ -0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$ $+0.34$
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$ $+1.00$
$Zn^{2+} + 2e^- \rightleftharpoons Zn$ -0.76

$E^o_{cell} = E^o_{red} - E^o_{ox} = E^o_{red} - (-0.76)$

For reaction to be spontaneous, $E^o_{cell} > 0$ V. In order for E^o_{cell} to be > 0, E^o_{red} must be > -0.76
Thus, VO_2^+ will be eventually reduced to V^{2+}

End of Paper

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	
CLASS	
INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions **27 August 2018**

Candidates answer on the question paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

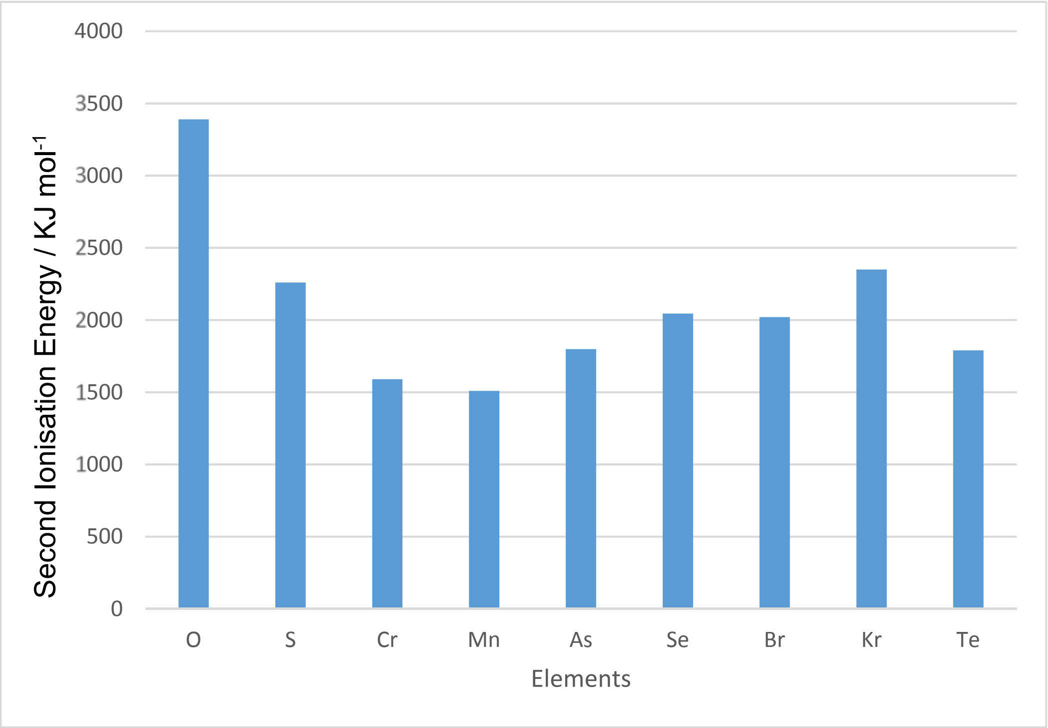
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

For Examiner's Use	
1	**9**
2	**8**
3	**6**
4	**15**
5	**13**
6	**12**
7	**12**
Significant Figures and Units	
Handwriting and Presentation	
Total	**75**

This document consists of **19** printed pages **1** blank page.

1 **(a)** The following diagram shows the second ionisation energy of some elements.



(i) Explain why the second ionisation energies of elements O, S, Se and Te show a decreasing trend.

....

....

....[1]

(ii) Explain why the second ionisation energy of Br is lower than that of Se.

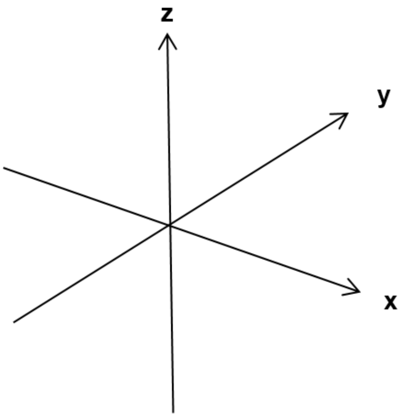
....

....[1]

(iii) Write the full ground state electronic configuration for Cr.

....[1]

(iv) Draw the d_{xy} orbital in the axes provided below. [1]



(b) Oxygen–oxygen bond lengths in some molecules are given below:

Molecule	Bond Length
Oxygen, O_2	0.121 nm
Hydrogen peroxide, H_2O_2	0.149 nm
Ozone, O_3	0.128 nm

(i) Draw the structure of the molecule ozone, O_3. [1]

(ii) With reference to the data given above, comment and explain the oxygen–oxygen bond length in ozone as compared to oxygen and hydrogen peroxide.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

(iii) Explain clearly why hydrogen peroxide is a liquid while oxygen is a gas at room conditions in terms of structure and bonding.

…………………………………………………………………………………………

…………………………………………………………………………………………

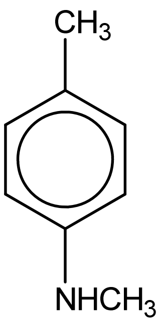
…………………………………………………………………………………………

…………………………………………………………………………………[2]

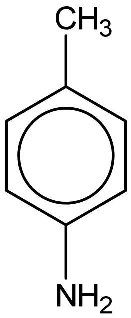
[Total: 9]

2 Compounds containing nitrogen are important to life and have applications in science and medicine.

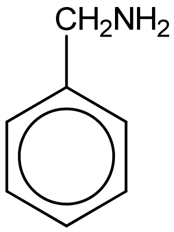
Three nitrogeneous bases have the following structures.



N,4-dimethylbenzenamine



4-methylphenylamine



benzylamine

(a) **(i)** Arrange the three bases above in increasing order of pK_b.

…………………………………………………………………………………[1]

(ii) Explain in terms of their molecular structures why benzylamine and 4-methylphenylamine have different pK_b values.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………[2]

(iii) Outline how *N*,4-dimethylbenzenamine may be produced from 4-methylphenylamine.

……………………………………………………………………………………………..

……………………………………………………………………………………………..[1]

(b) The pK_b of benzylamine is 4.66.

25.0 cm^3 of 0.025 mol dm^{-3} benzylamine was completely neutralised by dilute hydrochloric acid of the same concentration. The salt formed reacts with water and the pH of the resultant solution is less than 7.

(i) Write the equation to show the reaction between the salt formed and water.

……………………………………………………………………………………………..[1]

(ii) With reference to your equation in **(b)(i)**, write an expression for the acid dissociation constant of the salt.

[1]

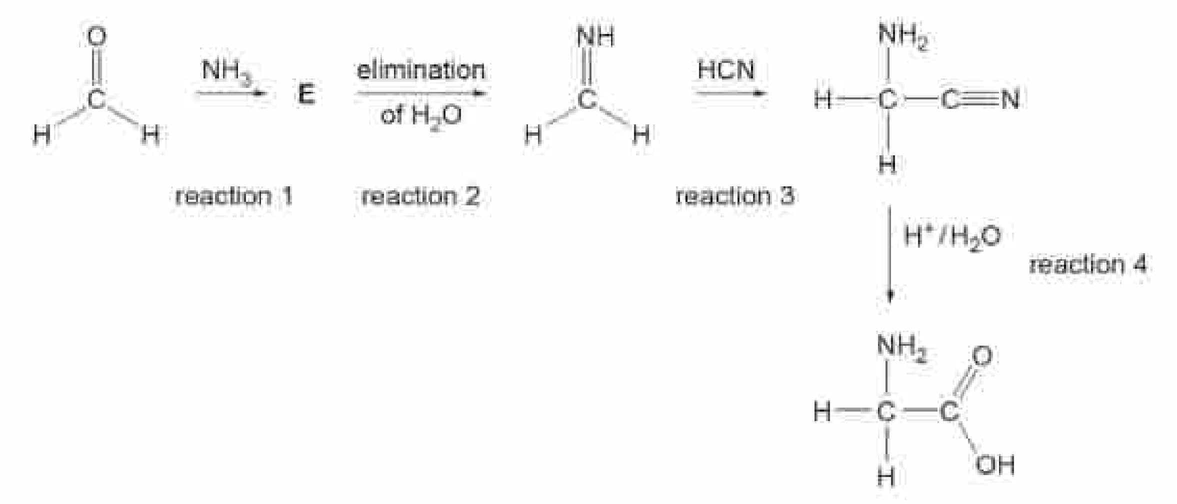
(iii) Hence, determine the pH of the resultant solution.

[2]

[Total: 8]

3 Methanal is a colorless, strong-smelling gas used in making building materials and many household products.

The Strecker synthesis is a route to preparing amino acids. Glycine, 2-aminoethanoic acid, can be prepared from methanal in this way. This is shown in the four steps reaction scheme below.



2-aminoethanoic acid

(a) **(i)** Suggest the role of ammonia in this synthesis.

……………………………………………………………………………………..[1]

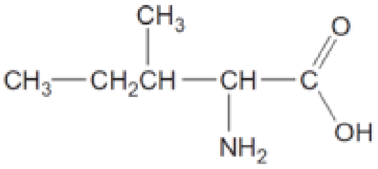
(ii) Compound **E** has the molecular formula CH_5NO.
Suggest a structure for compound **E**.

[1]

(iii) State the type of reaction for reaction 4.

……………………………………………………………………………………..[1]

(b) The amino acid shown below is isoleucine, 2-amino-3-methylpentanoic acid.



2-amino-3-methylpentanoic acid

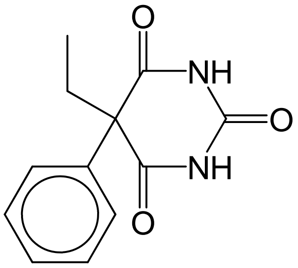
Molecule **F** can be used as the starting material to prepare this amino acid using a Strecker synthesis.

Draw the skeletal structure of **F**.

[1]

(c) An amide bond is formed when two amino acids react together.

Phenobarbital, which is a medication used to treat epilepsy, also has an amide bond in it.



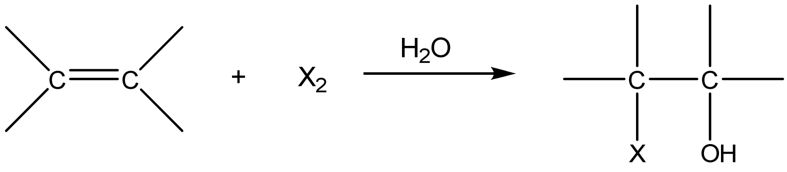
phenobarbital

Predict all the products formed when phenorbarbital undergoes acidic hydrolysis.

[2]

[Total: 6]

4 **(a)** Formation of 1,2-halo alcohols, also known as halohydrins, occurs via the addition reaction between an alkene and a halogen in the presence of water.



halohydrin

where X = C*l* or Br

In a series of experiments, the reaction between propene and aqueous bromine was carried out with different concentrations of the two reagents, and the following relative initial rates were obtained.

Experiment	[$CH_3CH=CH_2$] / mol dm^{-3}	[Br_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.020	0.020	1.00×10^{-3}
2	0.030	0.020	1.50×10^{-3}
3	0.040	0.030	3.00×10^{-3}

(i) Use these data to deduce the order of reaction with respect to each of the two reagents, showing how you arrive at your answers.

[2]

(ii) Hence write a rate equation for the reaction.

……………………………………………………………………………………..……………[1]

(iii) Calculate the rate constant for the reaction, giving its units.

[2]

(iv) State and explain how the rate of reaction may change if chlorine is used instead of bromine in the reaction with propene.

…………………………………………………………………………………..………..[1]

(b) **(i)** The mechanism of the addition reaction between propene and aqueous Br_2 involves three steps.

- There is an initial attack by the π electron pair of the alkene on Br_2 to yield a carbocation intermediate.
- This is followed by the nucleophilic attack of the lone pair of electrons on oxygen in water on the carbocation intermediate.
- The third step involves the loss of H^+ ion which then yields the neutral bromohydrin.

Using the information given above, describe a mechanism for this reaction.

[3]

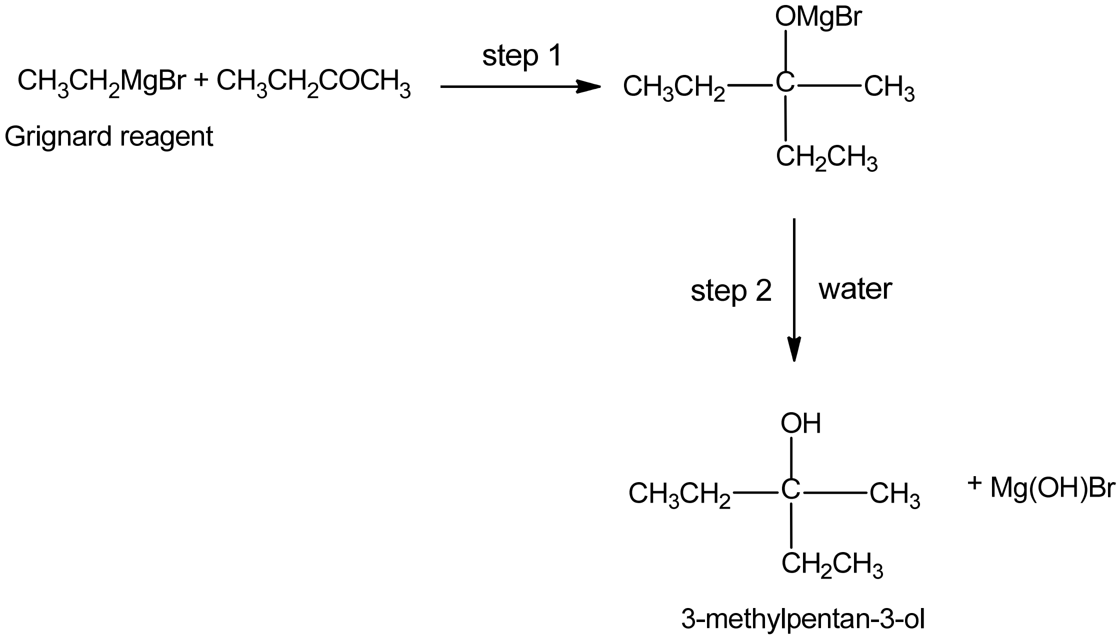
(ii) Based on your mechanism drawn, explain whether it is consistent with the rate equation proposed.

…………………………………………………………………………………………………

…………………………………………………………………………………..………..[1]

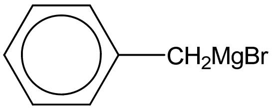
(c) Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of CH_3CH_2MgBr with butanone, $CH_3CH_2COCH_3$, to form 3-methylpentan-3-ol.



(i) Suggest the type of reaction that has taken place in step 1.

....[1]

(ii) Suggest the structural formula of the final organic product formed when 

is reacted with propanone, CH_3COCH_3, in a similar two-step process.

[1]

(iii) Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process.

[2]

(iv) The Grignard reagent $CH_3CH_2CH_2MgBr$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula for the organic product formed.

[1]

[Total: 15]

5 **(a)** Cobalt forms many coloured complexes. Cobalt(III) chloride combines with ammonia to form a pink coloured compound **A**, $CoCl_3.H_2O.5NH_3$ (M_r = 268.4) in which the coordination number of cobalt is 6.

1.00 g of **A** is dissolved in 25 cm^3 of water and the solution is titrated with 0.500 mol dm^{-3} silver nitrate solution. It is found that 22.40 cm^3 of silver nitrate is required for complete reaction.

(i) Calculate the number of moles of free chloride ions per mole of **A**.

[2]

(ii) Draw the structure of the complex ion in **A.**

[1]

(iii) When the pink compound **A** is heated, water vapour and ammonia were evolved to give a purple solid **B**.
A and **B** have the same coordination number.

Suggest the formula of the complex in the purple solid **B**.

....[1]

(iv) Account for the difference in the colour of **A** and **B**.

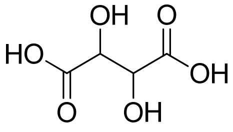
....

....

....

....[2]

(b) Aqueous hydrogen peroxide is fairly stable, but when a mixture of a cobalt(II) salt and tartaric acid is added to aqueous hydrogen peroxide, the initially pink solution slowly turns into a green cobalt(III) species.



tartaric acid

After a while, oxygen gas is vigorously evolved and the solution turns back to pink again.

(i) State the role of the cobalt(II) salt in this reaction and support your answer by referring to the observations.

Role of the cobalt(II) salt: ……………………………..………………………………[1]

Observation with explanation:

………………..………………………………………………………………………………

………………..………………………………………………………………………………

……………………………..……………………………………………………………………

……………………………………..…………………………………………………...[1]

(ii) Tartaric acid acts as a complexing agent in this reaction to stabilise the Co^{3+} cation.

With the aid of relevant data from the *Data Booklet*, show that Co^{3+} is not stable in aqueous solution.

………………..………………………………………………………………………………

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……………………………………..…………………………………………………...[2]

(c) A student wanted to measure the standard cell potential, $E^{\varnothing}_{cell}$, between the Co^{2+}/Co half-cell and the Fe^{3+}/Fe^{2+} half-cell. She set up and connected the two half cells and obtained a reading.

(i) Calculate the value $E^{\varnothing}_{cell}$ that will be obtained by the student.

[1]

(ii) State and explain what happens to the standard cell potential, $E^{\varnothing}_{cell}$ when ammonia is added to the Co^{2+}/Co half-cell.

………………..……………………………………………………………………

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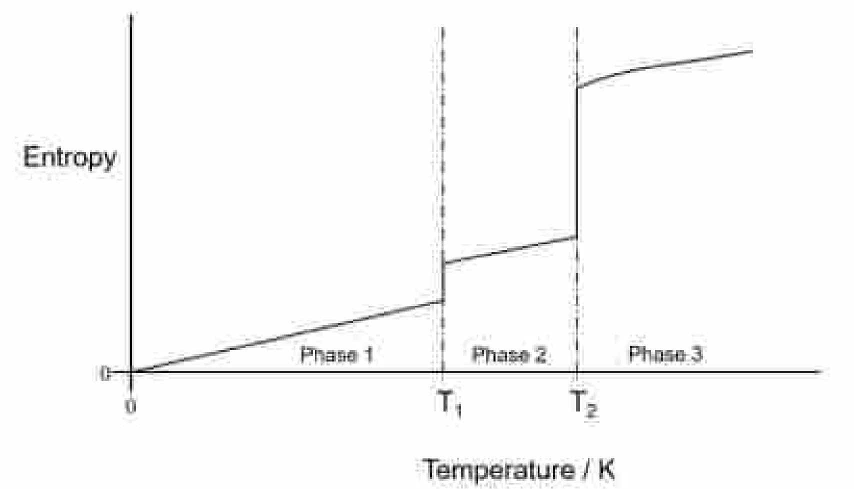
……………………………………..…………………………………………...[2]

[Total: 13]

6 A student plotted the sketch graph below to show how the entropy of a sample of H_2O varies with temperature.



(a) Identify the state of H_2O in Phase 2 and 3 respectively. Suggest a value of T_2.

In phase 2:……………… In phase 3: ……………… value of T_2: ……………… [1]

(b) Suggest why entropy of H_2O is zero at 0 K.

…………………………………………………………………………………………[1]

(c) Explain why the entropy change, ΔS, at temperature T_2 is much larger than that at temperature T_1.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of H_2O from the state in phase 2 to phase 3 at temperature T_2 and 100kPa.

Use these data and your value of T_2 in part **(a)** to calculate the value of ΔS, including units, for the conversion of one mole of H_2O from the state in phase 2 to phase 3 at temperature T_2.

[3]

(e) The student wants to find out if dissolving a salt, silver fluoride in water is always a spontaneous process. He must first find the enthalpy change of solution of silver fluoride in water.

Some enthalpy changes for silver fluoride are shown in the table.

	ΔH / kJ mol^{-1}
Lattice energy of silver fluoride	–950
Enthalpy change of hydration for silver ions	–464
Enthalpy change of hydration for fluoride ions	–506

(i) Use the data provided to calculate a value for the enthalpy change of solution of silver fluoride in water.

[2]

(ii) If entropy change for dissolving silver fluoride in water has a positive value, explain why dissolving of silver fluoride in water is always a spontaneous process.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(iii) Explain why the enthalpy change of hydration of the fluoride ions is more negative than the enthalpy change of hydration of the chloride ions.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

[Total: 12]

7 The uses of carboxylic acids are so extensive that they can be divided into several industries, such as pharmaceuticals or food among others.

(a) Ethanol and ethanoic acid react reversibly to form ethyl ethanoate and water according to the equation:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

A student mixed 0.0800 mol of ethanoic acid and 0.120 mol of ethanol in a conical flask and the flask was sealed with a bung and allowed to reach equilibrium at 20 °C.

The equilibrium mixture is placed in a graduated flask and the volume made up to 250 cm^3 with distilled water. A 10.0 cm^3 sample of this equilibrium mixture was placed in a conical flask with a few drops of phenolphthalein and titrated with 0.100 mol dm^{-3} of sodium hydroxide from a burette. The indicator turned pink when 6.40 cm^3 of NaOH had been added.

(i) Calculate the amount of CH_3COOH in the 250 cm^3 equilibrium mixture.

[1]

(ii) Hence, calculate the value for K_c for the reaction of ethanoic acid and ethanol at 20 °C.

[2]

(b) The following table compares the pK_a values of two dicarboxylic acids with that of ethanoic acid.

Acid	Formula	pK_1	pK_2
ethanoic	CH_3COOH	4.8	–
malonic	$HOOCCH_2COOH$	2.8	5.7
succinic	$HOOC(CH_2)_2COOH$	4.2	5.6

(i) Suggest a reason why the pK_1 value of malonic acid is so much less than the pK_1 of ethanoic and succinic acid.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(ii) Suggest a reason why the pK_2 value of malonic and succinic acid is higher than its respective pK_1 value.

……………………………………………………………………………………………

……………………………………………………………………………………………[1]

(c) Malonic acid can undergo dehydration with P_4O_{10} to give a foul-smelling gas, **A**. At 30.5 kPa, 0.1057 g of A occupies 200 cm^3 at a temperature of 200°C. Determine the relative molecular mass of **A**.

[2]

(d) At high temperature, succinic acid can also undergo dehydration to produce a neutral compound **B**, $C_4H_4O_3$ which does not react with sodium metal or Brady's reagent.

Compound **B** reacts with ammonia to give a compound **C**, $C_4H_7NO_3$, which reacts with cold NaOH(aq), but not with cold HC*l*(aq).

Suggest structures for **B** and **C** and explain the observations.

[4]

[Total: 12]

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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

27 August 2018

Candidates answer on the question paper.

2 hours

Additional Materials: *Data Booklet*

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You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

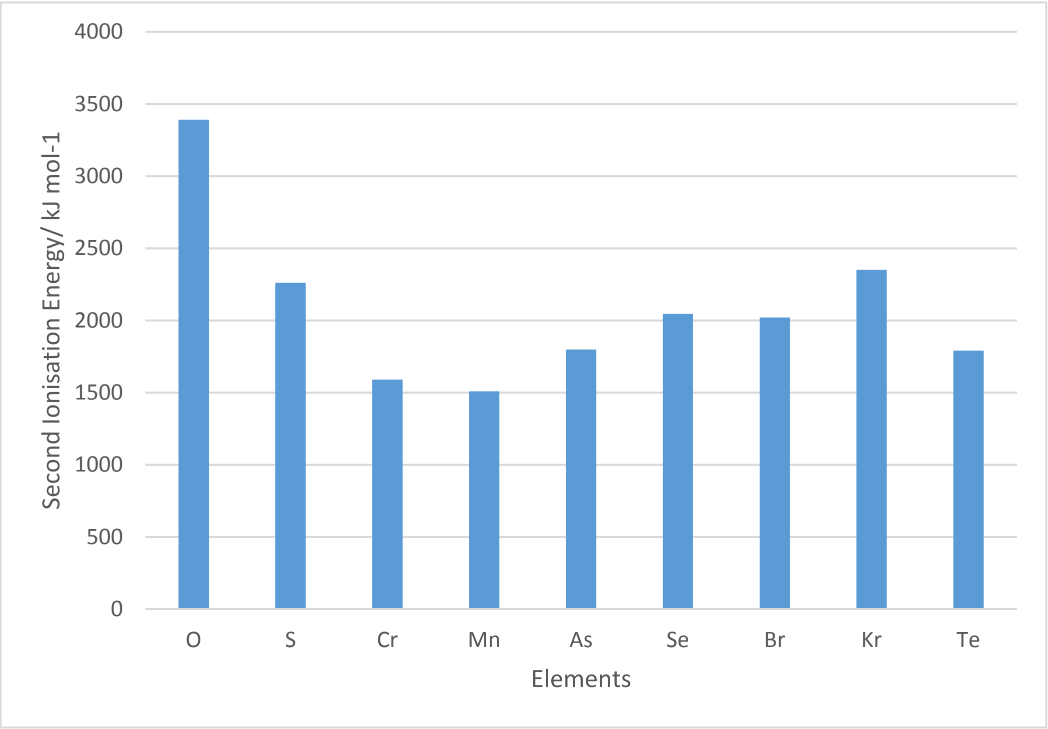
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

For Examiner's Use	
1	9
2	8
3	6
4	15
5	13
6	12
7	12
Significant Figures and Units	
Handwriting and Presentation	
Total	75

This document consists of **19** printed pages and **1** blank page.

1 **(a)** The following diagram shows the second ionisation energy of some elements.



(i) Explain why the second ionisation energies of elements O, S, Se and Te show a decreasing trend. [1]

The number of principal quantum shells increases/ The valence electrons are further away [√]
It is less strongly attracted to the nucleus OR Less energy is required to remove the valence electrons [√], hence second ionisation energy decreases.

(ii) Explain why the second ionisation energy is Br is lower than that of Se. [1]

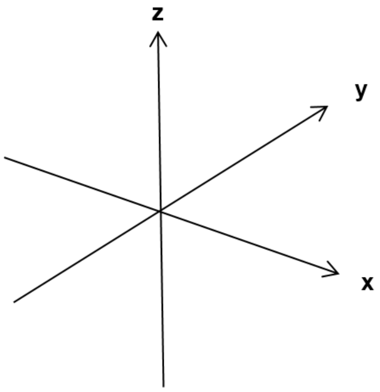
Se^+: [Ar]$4s^2 4p^3$ Br^+:[Ar]$4s^2 4p^4$

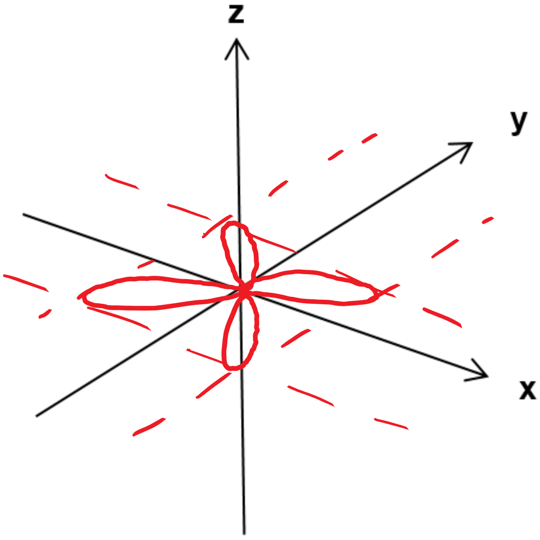
The paired 4p/np electrons[√] / 2 electrons in the same 4p orbital in Br^+ experience interelectronic repulsion [√], less energy is required to remove an electron from this orbital.

(iii) Write the full ground state electronic configuration for Cr. [1]

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$[1]

(iv) Draw the d_{xy} orbital in the axes provided below. [1]



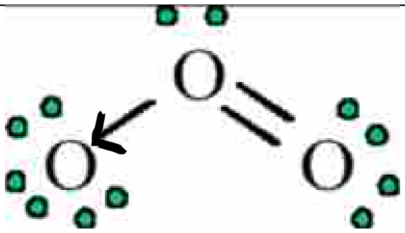


[1]

(b) Oxygen–oxygen bond lengths in some molecules are given below:

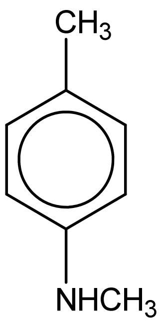
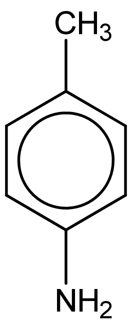
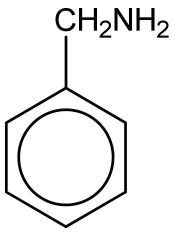
Molecule	Bond Length
Oxygen, O_2	0.121 nm
Hydrogen peroxide, H_2O_2	0.149 nm
Ozone, O_3	0.128 nm

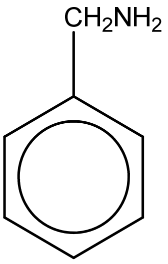
(i) Draw the structure of the molecule ozone, O_3. [1]



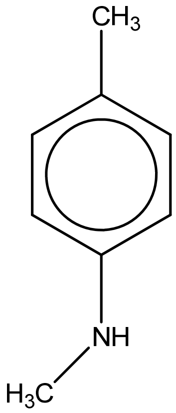
[1]

		(ii)	With reference to the data given above, comment and explain the oxygen–oxygen bond length in ozone as compared to oxygen and hydrogen peroxide. [2]
			Oxygen–oxygen bond length in ozone is longer than O=O in oxygen but shorter than O-O in hydrogen peroxide. [1] P orbital of oxygen overlap with π orbital of adjacent oxygen-oxygen double bond. OR Lone pair on oxygen atom can delocalised into the π electron cloud of adjacent oxygen- oxygen double bond [1]
		(iii)	Explain clearly why hydrogen peroxide is a liquid while oxygen is a gas at room conditions in terms of structure and bonding. [2]
			Both hydrogen peroxide and oxygen have simple molecular structure. [√] Oxygen have instantaneous dipole induced dipole forces of attraction between molecules [√] while hydrogen peroxide have hydrogen bonding between the molecules. [√] More energy is needed to overcome the stronger hydrogen bond [√], hence it has stronger intermolecular forces of attraction and exist as a liquid.
			[Total: 9]

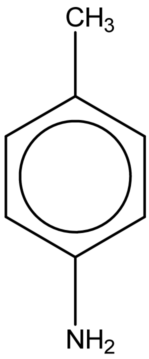
2	Compounds containing nitrogen are important to life and have applications in science and medicine. Three nitrogeneous bases have the following structures.  *N*,4-dimethylbenzenamine  4-methylphenylamine  benzylamine		
	(a)	**(i)**	Arrange the three bases above in increasing order of pK_b. [1]
			Lowest p*K*b ⟶ Highest p*K*b



benzylamine

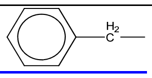


N,4-dimethyl benzenamine



4-methylphenylamine [1]

(ii) Explain in terms of their molecular structures why benzylamine and 4-methylphenylamine have different pK_b values. [2]

In benzylamine, the presence of electron donating  increases the electron density on N [✓], making the lone pair of electron on N more available [✓] to accept a proton. Hence, benzylamine is the most basic.

In 4-methylphenylamine, the lone pair of electron on N delocalised into the π orbital of the benzene ring, decreasing the electron density on N [✓], making the lone pair of electron on N less available [✓] to accept a proton. Hence, 4-methylphenylamine is the least basic.

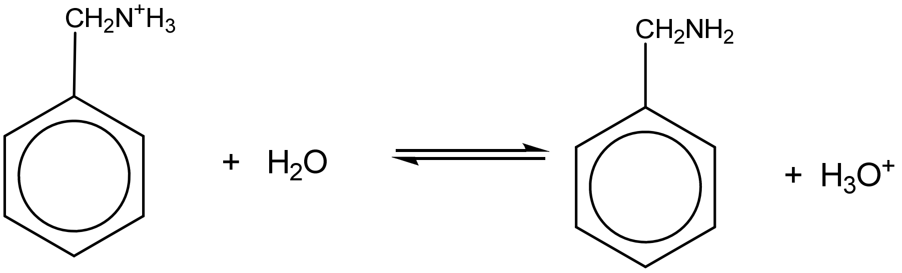
(iii) Outline how N,4-dimethylbenzenamine may be produced from 4-methylphenylamine. [1]

Heat 4-methylphenylamine with (ethanolic) CH_3Cl (in a sealed tube). [1]

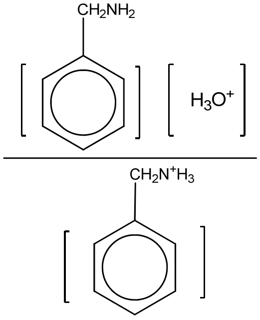
(b) The pK_b of benzylamine is 4.66.

25.0 cm^3 of 0.025 mol dm^{-3} benzylamine was completely neutralised by dilute hydrochloric acid of the same concentration. The salt formed reacts with water and the pH of the resultant solution is less than 7.

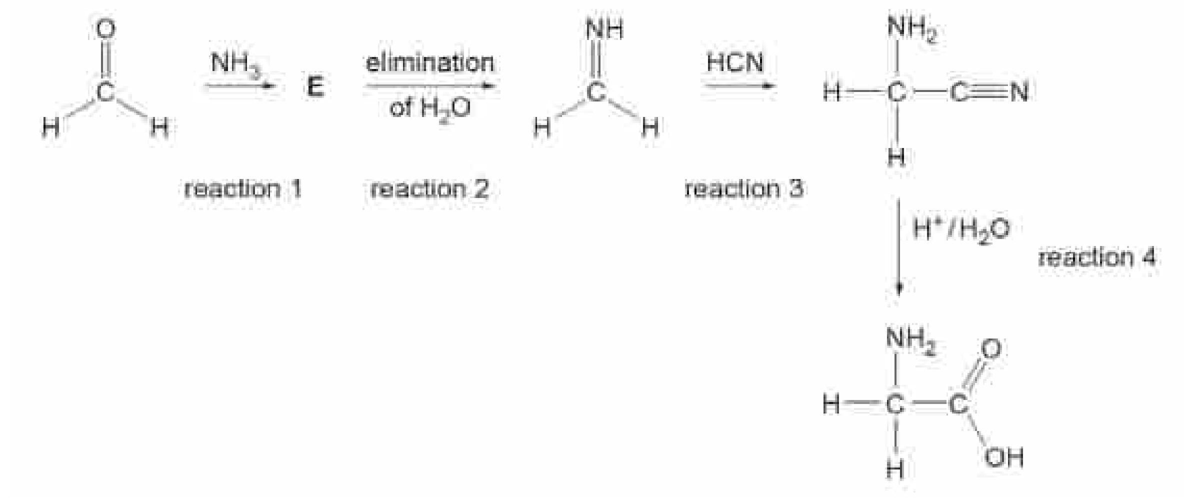
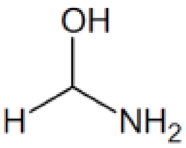
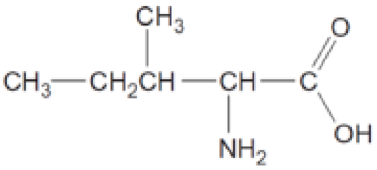
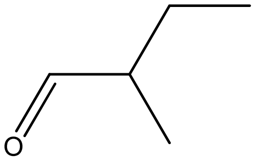
(i) Write the equation to show the reaction between the salt formed and water. [1]



[1]

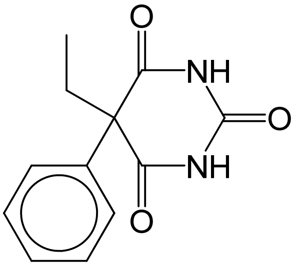
		(ii)	With reference to your equation in (b)(i), write an expression for the acid dissociation constant of the salt. [1]
			Ka =  [1]
		(iii)	Hence, determine the pH of the resultant solution. [2]
			$[salt] = (6.25 \times 10^{-4}) \div (50/1000)$ $= 0.0125$ mol dm^{-3} [✓] $K_a = K_w / K_b$ $= \frac{10^{-14}}{10^{-4.66}}$ $= 4.571 \times 10^{-10}$ [✓] $[H^+] = \sqrt{Ka \times [salt]}$ $= \sqrt{4.571 \times 10^{-10} \times 0.0125}$ $= 2.390 \times 10^{-6}$ [✓] pH = 5.62 [✓]
		[Total: 8]	

3	Methanal is a colorless, strong-smelling gas used in making building materials and many household products. The Strecker synthesis is a route to preparing amino acids. Glycine, 2-aminoethanoic acid, can be prepared from methanal in this way. This is shown in the four steps reaction scheme below.

	 2-aminoethanoic acid		
	(a)	**(i)**	What is the role of ammonia, in the context of this synthesis? [1]
			Nucleophile [1] Allow Nucleophilic or Lewis base or Lone-pair donor
		(ii)	Compound **E** has the molecular formula CH_5NO. Suggest a structure for compound **E**. [1]
			 [1]
		(iii)	State the type of reaction for reaction 4. [1]
			Acidic hydrolysis [1]
	(b)	The amino acid shown below is isoleucine, 2-amino-3-methylpentanoic acid.  Molecule **F** can be used as the starting material to prepare this amino acid using a Strecker synthesis. Draw the skeletal structure of **F**. [1]	
			 [1]

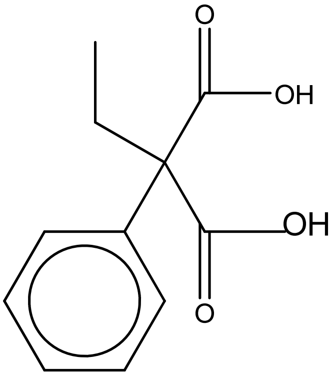
(c) An amide bond is formed when two amino acids react together.

Phenobarbital, which is a medication used to treat epilepsy, also has an amide bond in it.



phenobarbital

Predict all the products formed when phenorbarbital undergoes acidic hydrolysis.

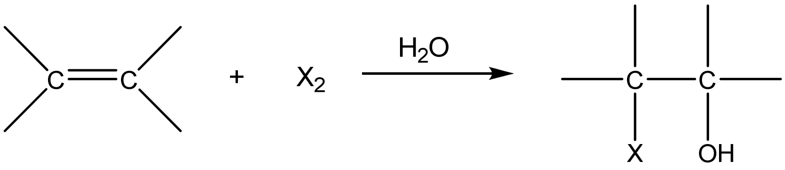


[1] , CO_2 [✓], NH_4^+ [✓]

[2]

[Total: 6]

4 **(a)** Formation of 1,2-halo alcohols, also known as halohydrins, occurs via the addition reaction between an alkene and a halogen in the presence of water.



where X = C*l* or Br

halohydrin

In a series of experiments, the reaction between propene and aqueous bromine was carried out with different concentrations of the two reagents, and the following relative initial rates were obtained.

Experiment	$[CH_3CH=CH_2]$ / mol dm^{-3}	$[Br_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.020	0.020	1.00×10^{-3}
2	0.030	0.020	1.50×10^{-3}
3	0.040	0.030	3.00×10^{-3}

(i) Use these data to deduce the order of reaction with respect to each of the two reagents, showing how you arrive at your answers. [2]

Let the rate equation be: Rate = $k[CH_3CH=CH_2]^x[Br_2]^y$

Comparing experiments 1 & 2,	Comparing experiments 1 & 3,
$\frac{Rate_1}{Rate_2} = \frac{k[CH_3CH=CH_2]^x[Br_2]^y}{k[CH_3CH=CH_2]^x[Br_2]^y}$ $\frac{1.00\times10^{-3}}{1.50\times10^{-3}} = \frac{k[0.020]^x[0.020]^y}{k[0.030]^x[0.020]^y}$ x = 1 [1m]	$\frac{Rate_1}{Rate_3} = \frac{k[CH_3CH=CH_2]^x[Br_2]^y}{k[CH_3CH=CH_2]^x[Br_2]^y}$ $\frac{1.00\times10^{-3}}{3.00\times10^{-3}} = \frac{k[0.020]^x[0.020]^y}{k[0.040]^x[0.030]^y}$ y = 1 [1m]

(ii) Hence write a rate equation for the reaction. [1]

Rate = $k[CH_3CH=CH_2][Br_2]$

(iii) Calculate the rate constant for the reaction, giving its units. [2]

Using experiment 1,

$$k = \frac{Rate}{[CH_3CH=CH_2][Br_2]}$$

$$k = \frac{1.00\times10^{-3}}{[0.020][0.020]} = 2.50$$ [1m] mol^{-1}dm^{3}s^{-1} [1m]

(iv) State and explain how the rate of reaction may change if chlorine is used instead of bromine in the reaction with propene. [1]

Rate will decrease [√] because C*l*-C*l* bond is stronger than Br-Br [√].

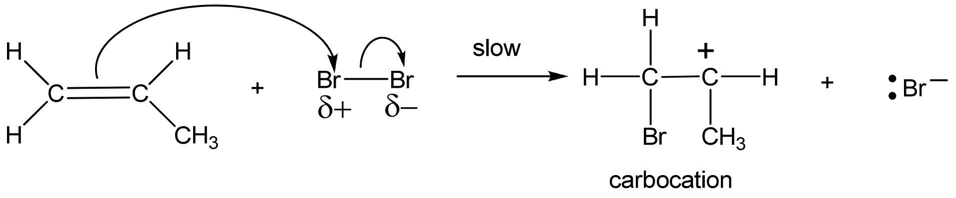
(b) **(i)** The mechanism of the addition reaction between propene and aqueous Br_2 involves three steps.

- There is an initial attack by the π electron pair of the alkene on Br_2 to yield a carbocation intermediate.

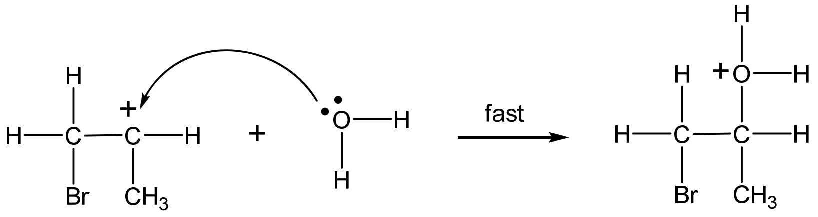
- This is followed by the nucleophilic attack of the lone pair of electrons on oxygen in water on the carbocation intermediate.
- The third step involves the loss of H^+ ion which then yields the neutral bromohydrin.

Using the information given above, describe a mechanism for this reaction.

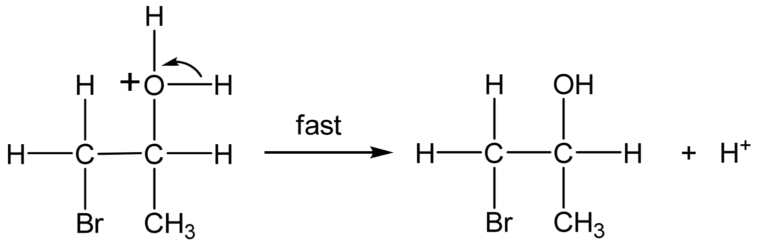
[3]



Dipoles [√], two curvy arrows [√], correct carbocation [√], label slow step [√], Br^- [√]



Lone pair + curvy arrow [√], intermediate [√], label fast step [√]



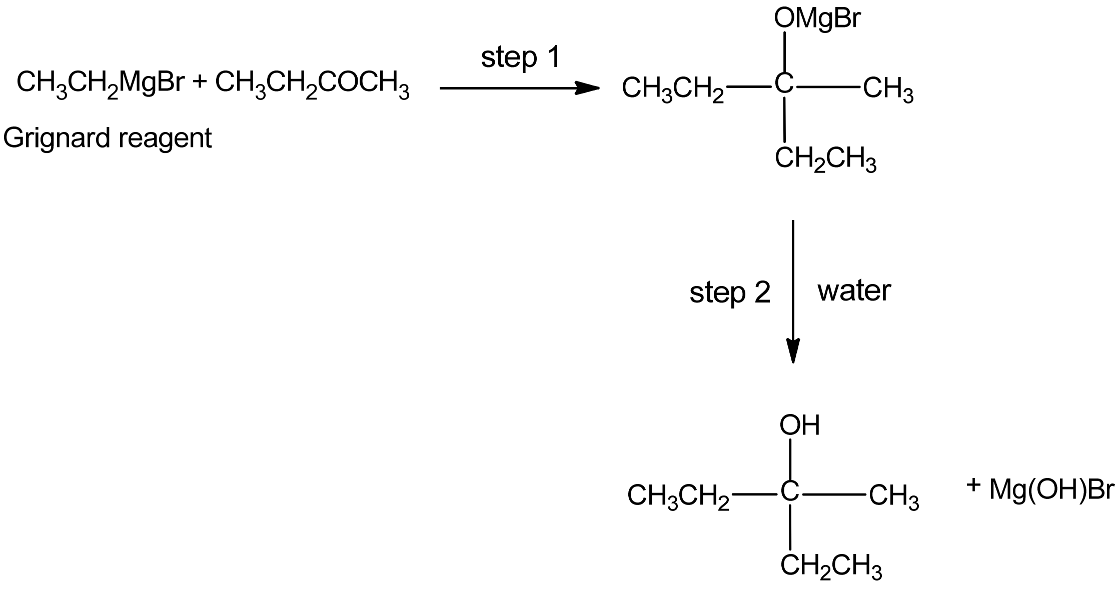
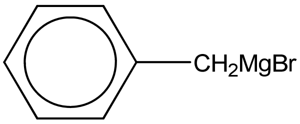
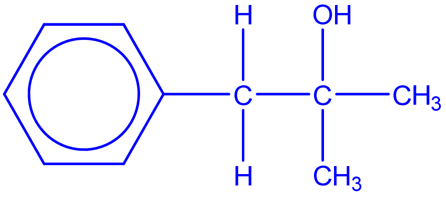
Curvy arrow [√], final organic product [√], H^+ [√]
11 [√] – 3m
6 to 10 [√] – 2m
3 to 5 [√] – 1m

-

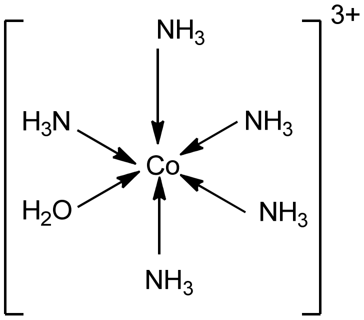
(ii) Based on your mechanism drawn, explain whether it is consistent with the rate equation proposed. [1]

It is **consistent** as there is **1 propene molecule and 1 Br_2 molecule in the rate determining step**, which is consistent with the rate equation.

Or

			To allow ecf if rate equation is wrong
	(c)	Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds. The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of CH_3CH_2MgBr with butanone, $CH_3CH_2COCH_3$, to form 3-methylpentan-3-ol.  3-methylpentan-3-ol	
		(i)	Suggest the type of reaction that has taken place in step 1. [1]
			Nucleophilic addition [1]
		(ii)	Suggest the structural formula of the final organic product formed when  is reacted with propanone, CH_3COCH_3, in a similar two-step process. [1]
			 [1]

		(iii)	Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process. [2]
			CH_3MgBr [1] CH_3CHO [1]
		(iv)	The Grignard reagent $CH_3CH_2CH_2MgBr$ can be readily converted into a carboxylic acid by using carbon dioxide. Suggest the structural formula for the organic product formed. [1]
			$CH_3CH_2CH_2COOH$
			[Total: 15]

5	**(a)**	Cobalt forms many coloured complexes. Cobalt(III) chloride combines with ammonia to form a pink coloured compound **A**, $CoCl_3.H_2O.5NH_3$ (M_r = 268.4) in which the coordination number of cobalt is 6. 1.00 g of **A** is dissolved in 25 cm^3 of water and the solution is titrated with 0.500 mol dm^{-3} silver nitrate solution. It is found that 22.40 cm^3 of silver nitrate is required for complete reaction.	
		(i)	Calculate the number of moles of free chloride ions per mole of **A**.
			no. of moles of $AgNO_3$ = 0.500 x (22.40/1000) = 1.12 x 10^{-2} mol [1] no. of moles of Cl^- = 1.12 x 10^{-2} mol no. of moles of **A** = 1.00/268.4 = 3.73 x 10^{-3} mol no. of moles of free Cl^- ions per mole of **A** = (1.12 x 10^{-2})/(3.73 x 10^{-3}) = 3 [1] [2]
		(ii)	Draw the structure of the complex ion in **A.**  [1] [1]
		(iii)	When the pink compound **A** is heated, water vapour and ammonia were evolved to give a purple solid **B**. **A** and **B** have the same coordination number. Suggest the formula of the complex in the purple solid **B**.
			$[Co(NH_3)_4Cl_2]^+$ or $[Co(NH_3)_3Cl_3]$ [1]

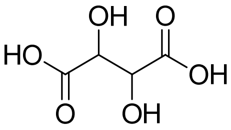
[1]

(iv) Account for the difference in the colour of **A** and **B**.

The **different ligands** in **A** and **B** cause the **energy gap between the split d–orbitals to be different**. **[1]** The **wavelength of light absorbed is different [1]** for **A** and **B** and thus the colour observed are different.

[2]

(b) Aqueous hydrogen peroxide is fairly stable, but when a mixture of a cobalt(II) salt and tartaric acid is added to aqueous hydrogen peroxide, the initially pink solution slowly turns into a green cobalt(III) species.



tartaric acid

After a while, oxygen gas is vigorously evolved and the solution turns back to pink again.

(i) State the role of the cobalt(II) salt in this reaction and support your answer by referring to the observations.

Role of the cobalt(II) salt: catalyst [1]

Observation with explanation:

- The **oxygen gas is vigorously evolved** showing that the **reaction speeds up** [1] OR
- The solution turns from **pink to green to pink (WTTE)** showing that **Co^{2+} is regenerated** [1]

[2]

(ii) Tartaric acid acts as a complexing agent in this reaction to stabilise the Co^{3+} cation.

With the aid of relevant data from the *Data Booklet*, show that Co^{3+} is not stable in aqueous solution.

$Co^{3+} + e \rightleftharpoons Co^{2+}$ E_{red} = +1.89V

$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ E_{red} = +1.23V

E^o cell = +1.89 – (+1.23) = + 0.66 V [1]

Co^{3+} oxidises water readily to form Co^{2+} / Co^{3+} is readily reduced by water to form Co^{2+}. [1]

[2]

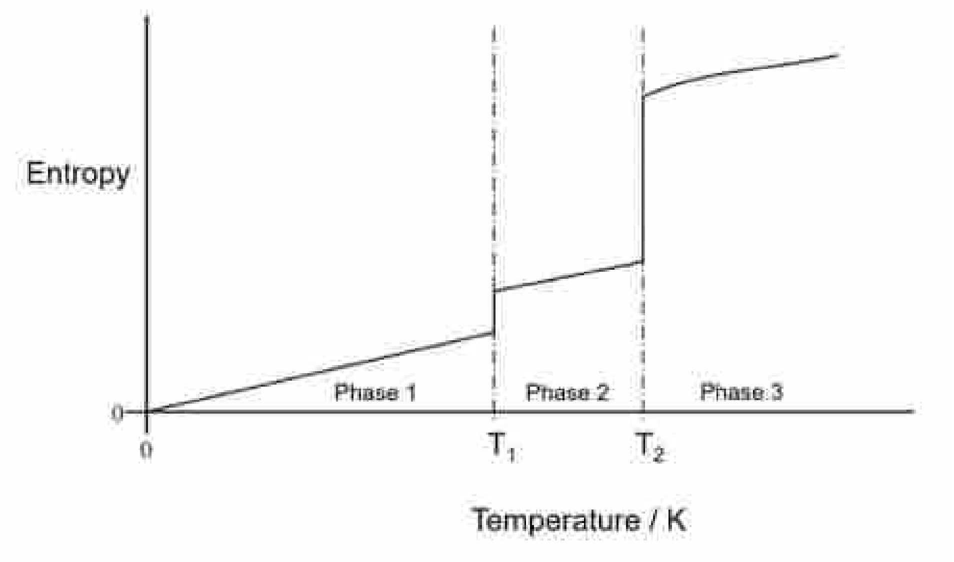
(c) A student wanted to measure the standard cell potential, $E^{Ø}_{cell}$, between the Co^{2+}/Co half-cell and the Fe^{3+}/Fe^{2+} half-cell. She set up and connected the two half cells and obtained a reading.

(i) Calculate the value $E^{Ø}_{cell}$ that will be obtained by the student.

[R] $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ E_{red} = +0.77V

[O] $Co^{2+} + 2e \rightleftharpoons Co$ E_{red} = -0.28V

			$E^{\varnothing}_{cell}$ = +0.77 – (–0.28) = +1.05 V [1] [1]
		(ii)	State and explain what happens to the standard cell potential, $E^{\varnothing}_{cell}$ when ammonia is added to the Co^{2+}/Co half-cell.
			When NH_3 is added, the following equilibrium is set up in the Co^{2+}/Co half-cell: Either: $[Co(NH_3)_6]^{2+}$ + 2e $\rightleftharpoons$ Co + $6NH_3$ E_{red} = –0.43V **[1]** (Give B.O.D. if the value -0.43V is not quoted in the answer) **OR $[Co^{2+}]$ decreases** as $Co(OH)_2(s)$ is formed. **[1]** the E_{ox} of Co^{2+}/Co **will become more negative/ position of the equilibrium** Co^{2+} + 2e $\rightleftharpoons$ Co **will shift left** Hence, the $E^{\varnothing}_{cell}$ becomes **more positive**. **[1]** [2]
			[Total: 13]

6	A student plotted the sketch graph below to show how the entropy of a sample of H_2O varies with temperature.	
		
	(a)	Identify the state of H_2O in Phase 2 and 3 respectively. Suggest a value of T_2.
		In phase 2:……………… In phase 3: ……………… value of T_2: ……………… [1]
		In phase 2: liquid In phase 3: gas T_2 : 373K
	(b)	Suggest why entropy of H_2O is zero at 0 K.
		……………………………………………………………………………………………[1]
		It is at maximum state of order or no disorder or perfectly ordered or pure crystalline structure.

(c) Explain why the entropy change, ΔS, at temperature T_2 is much larger than that at temperature T_1.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

At T_2, the increase form phase 2 to 3 is much larger as the gas molecules in phase 3 have more ways in which the particles can be arranged than particles in liquid. [1]

At T_1, the particles in phase 2 (liquid) are still orderly arranged compared to the ordered arrangement of particles in phase 1. [1] Thus, the increase in disorder is smaller from phase 1 to 2.
(2nd marking point: mention of smaller increase from phase 1 to 2 as it is from an ordered arrangement to slightly disordered arrangement in liq.)

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of H_2O from the state in phase 2 to phase 3 at temperature T_2 and 100kPa.

Use these data and your value of T_2 in part **(a)** to calculate the value of ΔS, including units, for the conversion of one mole of H_2O from the state in phase 2 to phase 3 at temperature T_2.

[3]

Amt of water = $\frac{1.53}{18} = 0.0850$

enthalpy change reaction per mole of water = $\frac{3.49}{0.0850} = +41.1$ kJ mol^{-1} **[1]**

award if + sign is omitted, but penalise negative sign is included

$\Delta G = \Delta H - T\Delta S = 0$

$+41.1 - (373)\Delta S = 0$ equate ΔG =0, substitute ΔH, T_2 into equation **[1]** ecf

$\Delta S = 0.110$ kJ K^{-1} mol^{-1} correct computation (allow ecf) and units **[1]** ecf

(e) The student wants to find out if dissolving a salt, silver fluoride in water is always a spontaneous process. He must first find the enthalpy change of solution of silver fluoride in water.

Some enthalpy changes for silver fluoride are shown in the table.

	ΔH / kJ mol^{-1}
Lattice energy of silver fluoride	–950
enthalpy change of hydration for silver ions	–464
enthalpy change of hydration for fluoride ions	–506

(i) Use the data provided to calculate a value for the enthalpy change of solution of silver fluoride in water.

			[2]
			$\Delta H_{\text{solution}} = \Delta H_{\text{hyd}}$ Ag+ + ΔH_{hyd} F^{-} –LE = (–464) + (–506) – (–950) [1] working = –20 kJ mol^{-1} [1] answer
		(ii)	If entropy change for dissolving silver fluoride in water has a positive value, explain why dissolving of silver fluoride in water is always a spontaneous process.
			[2]
			$\Delta G = \Delta H - T\Delta S$ Relate to signs of ΔS and ΔH [1]: Since ΔS is positive, the term (– TΔS) is always negative. Thus, since ΔH is negative, ΔG is always negative at all temperature. [1]
		(iii)	Explain why the enthalpy change of hydration of the fluoride ions is more negative than the enthalpy change of hydration of the chloride ions.
			[1]
			$\Delta H_{\text{hydration}}$ α charge density [√] Fluoride (ions) are smaller (than chloride), with **higher charge density [√]**
			[Total: 12]

7			The uses of carboxylic acids are so extensive that they can be divided into several industries, such as pharmaceuticals or food among others.
	(a)		Ethanol and ethanoic acid react reversibly to form ethyl ethanoate and water according to the equation: $CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ A student mixed 8.00 x 10^{-2} mol of ethanoic acid and 1.20 x 10^{-1} mol of ethanol in a conical flask and the flask was sealed with a bung and allowed to reach equilibrium at 20 °C. The equilibrium mixture is placed in a graduated flask and the volume made up to 250 cm^3 with distilled water. A 10.0 cm^3 sample of this equilibrium mixture was placed in a conical flask with a few drops of phenolphthalein and titrated with 0.100 mol dm^{-3} of sodium hydroxide from a burette. The indicator turned pink when 6.40 cm^3 of NaOH had been added.
		(i)	Calculate the amount of CH_3COOH in the equilibrium mixture. Amount of NaOH = 0.100 x $\frac{6.40}{1000}$ = 0.00064 mol Amount of CH_3COOH in 10.0 cm^3 = 0.00064 mol Amount of CH_3COOH in 250 cm^3 = $\frac{250}{10}$ x 0.00064 = 0.016 mol **[1]**

[1]

(ii) Hence, calculate the value for K_c for the reaction of ethanoic acid and ethanol at 20 °C.

	CH_3CO_2H (l)	**C_2H_5OH (l)**	**$CH_3CO_2C_2H_5$ (l)**	**H_2O (l)**
Initial amt / mol	0.08	0.12	0	0
Equilibrium amt / mol	**0.016**	**0.056**	**0.064**	**0.064**

Equilibrium amount **[1]**

$$K_c = \frac{[H_2O][CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{(\frac{0.064}{V})(\frac{0.064}{V})}{(\frac{0.016}{V})(\frac{0.056}{V})}$$

= 4.57 [1]

[2]

(b) The following table compares the pK_a values of two dicarboxylic acids with that of ethanoic acid.

acid	Formula	pK_1	pK_2
ethanoic	CH_3COOH	4.8	–
malonic	$HOOCCH_2COOH$	2.8	5.7
succinic	$HOOC(CH_2)_2COOH$	4.2	5.6

(i) Suggest a reason why the pK_1 value of malonic acid is so much less than the pK_1 of ethanoic and succinic acid.

Malonic acid is **more acidic** than ethanoic or succinic acid **[1]** as **its monoanion is stabilised by intra hydrogen bonds between the COO^- group and unionised COOH group [1]**.

[2]

(ii) Suggest a reason why the pK_2 value of malonic and succinic acid is higher than its respective pK_1 value.

The removal of an H^+ from the monoanion that already carries a negative charge would be electrostatically unfavourable. **[1]**

[1]

(c) Malonic acid can undergo dehydration with P_4O_{10} to give a foul-smelling gas, **A**. At 30.5 kPa, 0.1057 g of A occupies 200 cm^3 at a temperature of 200°C. Determine the relative molecular mass of **A**.

pV = nRT

$$30.5 \times 10^3 \times \frac{200}{10^6} = \frac{0.1057}{M_r} \times 8.31 \times (200 + 273)$$ **[1]**

M_r = 68.1 (1 d.p) **[1]**

[2]

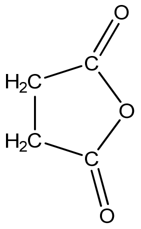
(d) At high temperature, succinic acid can also undergo dehydration to produce a neutral compound **B**, $C_4H_4O_3$ which does not react with sodium metal or Brady's reagent.

Compound **B** reacts with ammonia to give a compound **C**, $C_4H_7NO_3$, which reacts with cold NaOH(aq), but not with cold HCl(aq).

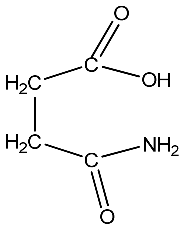
Suggest structures for **B** and **C** and explain the observations.

- **B** does not react with Na; **absence of –OH group**. **[√]**
- **B** does not react with Brady's reagent; **absence of carbonyl group**. **[√]**
- **C** does not react with cold HCl(aq); **absence of basic group [√]**, **amide** likely to be present **[√]**.
- **C** undergoes **acid base** with cold NaOH(aq) **[√]**; it contains an **acidic group** (carboxylic acid). **[√]**

Max [2] for explanations



compound B



compound C

[1] each

[4]

[Total: 12]

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **10 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

This document consists of **13** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 This question is about the chemistry of ethene and its derivatives.

(a) Ethene is the starting material to form ethanedioic acid.

(i) Suggest the synthetic route for the formation of ethanedioic acid from ethene. [2]

(ii) 0.200 mol of ethene is stored in a 20.0 dm^3 flask with 0.800 mol of ethane at 127 °C.

Calculate the total pressure in the flask. Hence or otherwise, calculate the partial pressure of ethene in the flask. [2]

(iii) The total pressure that you calculated in **(a)(ii)** is different from the actual pressure exerted. Suggest an explanation for the difference. [1]

(iv) Ethene reacts with hydrogen in the presence of nickel catalyst to form ethane.

Explain why nickel can be used as a catalyst in this reaction. [2]

(v) Outline the mode of action of the catalyst in this reaction. [2]

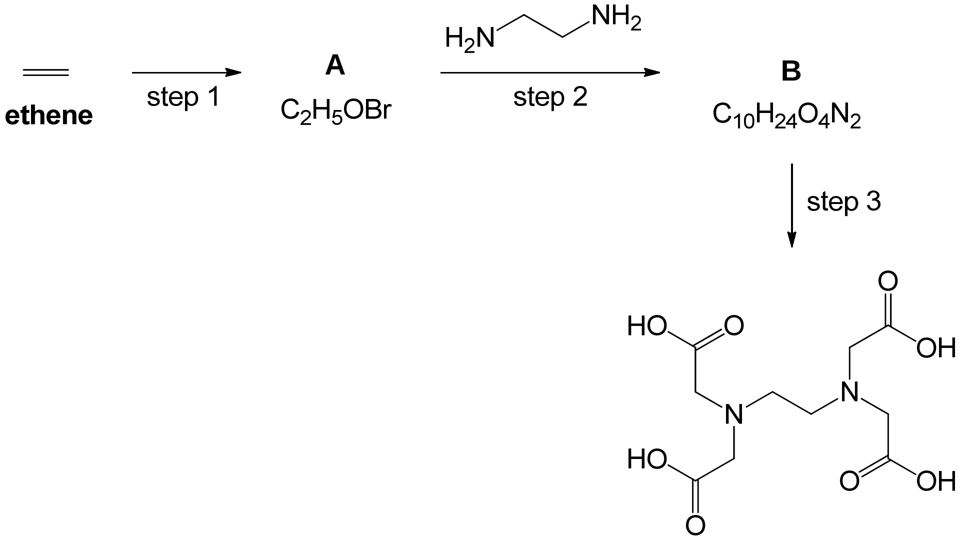
(b) Dissolving 4.82×10^{-5} mol calcium ethanedioate, CaC_2O_4, in 1 dm^3 of water forms a saturated solution.

(i) Write an expression for the solubility product of calcium ethanedioate and state its units. [1]

(ii) Calculate the solubility product of calcium ethanedioate. [1]

(iii) 50.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ and 50.0 cm^3 of 0.300 mol dm^{-3} $Na_2C_2O_4$ are mixed together. Determine if CaC_2O_4 will be precipitated out. [2]

(c) Synthesis of the unionised form of EDTA (H_4Y) can be carried out in the laboratory using ethene as the starting material.



unionised form of EDTA (H_4Y)

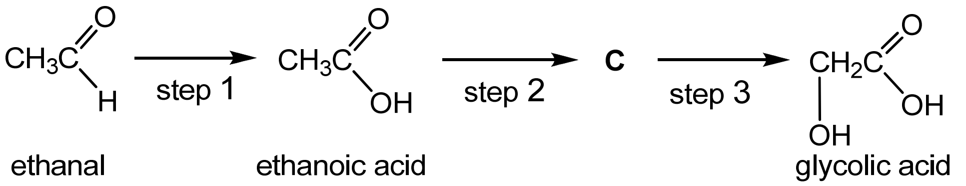
(i) Draw the structures of **A** and **B**.

[2]

(ii) Suggest appropriate reagents and conditions for step 3.

[1]

(d) Ethene can be used to form ethanal. Ethanal in turn is used to synthesize glycolic acid via the reaction shown below.



(i) Identify the intermediate **C** and state the reagent and condition for step 3.

[2]

(ii) Explain the difference in acidity between glycolic acid and ethanoic acid.

[2]

(iii) Two molecules of glycolic acid can react with one another under suitable conditions to form a neutral compound with the loss of two water molecules.

Suggest a possible structure for the compound formed.

[1]

(iv) Suggest a simple chemical test to distinguish between ethanoic acid and glycolic acid.

[2]

[Total: 23]

2 Iron is the fourth most common element in the Earth's crust. It is a d-block element which is known to exhibit different characteristics from the s-block elements. Since ancient times, iron has been widely employed in a variety of applications.

(a) **(i)** One well-known property of iron and its compounds is the ability to catalyse reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I^- and $S_2O_8^{2-}$, to form I_2 and SO_4^{2-} ions.

Using relevant $E^\ominus$ values from the *Data Booklet*, explain why iron(II) chloride can be used as a catalyst for this reaction.

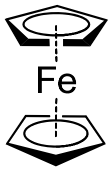
[2]

(ii) A sample of iron was vapourised, ionised and passed through an electric field. Analysis of deflection occurring at the electric field region revealed that a sample of $^{32}S^{2-}$ ions would be deflected by +20° towards the positive potential.

What is the angle, and direction of deflection for a sample of $^{56}Fe^{3+}$ ions passing through the same electric field?

[2]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange solid which is known to exhibit anti-cancer activity. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



ferrocene

(i) State the oxidation number of Fe in ferrocene.

[1]

(ii) Suggest why ferrocene is a coloured complex.

[2]

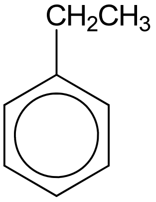
(iii) Light of a longer wavelength is lower in energy than light of a shorter wavelength. The following table shows the spectral colours and the corresponding wavelengths.

Colour	**Wavelength / nm**
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

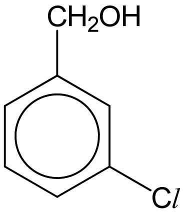
Given that aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$.

[2]

(c) Ethylbenzene is used to synthesize (3-chlorophenyl)methanol which is used as a general solvent for inks, paints, lacquers, epoxy resin coatings and as a degreasing agent.



ethylbenzene



(3-chlorophenyl)methanol

Starting with ethylbenzene, outline a three-step reaction scheme to obtain (3-chlorophenyl)methanol. Your answer should include clearly the reagents and conditions in each step, and the structures of all intermediates formed.

[3]

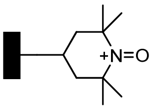
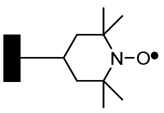
(d) **D** is an achiral organic compound with the molecular formula C_2H_7NO. It can be formed from the reaction between a primary amide and lithium aluminium hydride. In the presence of a suitable catalyst, 1 mole of **D** reacts with 1 mole of benzoic acid to form **E**, $C_9H_{11}NO_2$. However, 1 mole of **D** requires 2 moles of benzoyl chloride to react completely to form **F**, $C_{16}H_{15}NO_3$ and copious white fumes. 2 moles of **D** can also react with gaseous PCl_5 to form a cyclic **G**, $C_4H_{10}N_2$, which contains a 6-membered ring.

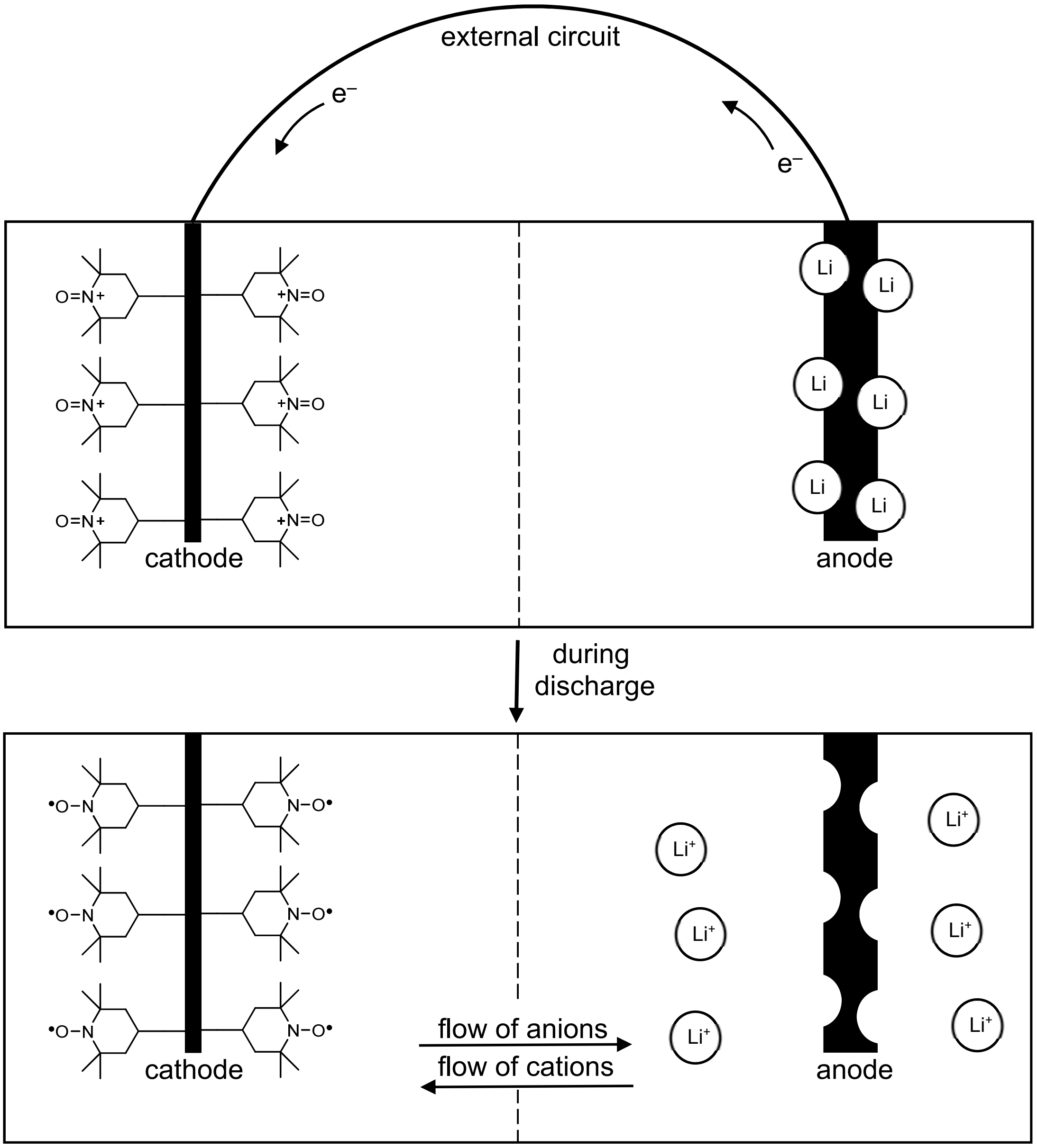
Deduce the structures of **D**, **E**, **F** and **G** and explain the reactions described.

[7]

[Total: 19]

3 An organic radical battery (ORB) is a relatively new type of battery which uses flexible plastics, to provide electrical power. One type of hybrid ORB/Li-ion battery consists of: a cathode made from solid organic polymer containing oxoammonium ion formed from (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) nitroxide radicals; an anode made from graphite with Li atoms inserted between the graphite layers; and an electrolyte of $LiPF_6$ dissolved in organic solvent.

During discharge, Li atoms give up electrons at the anode to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. The anions and cations in the electrolyte move to the anode and cathode respectively. This is illustrated in the following diagram in which  and  are simplified representations of the polymer containing oxoammonium ion and TEMPO nitroxide radicals respectively.



(a) **(i)** Graphite is often mixed in the polymer used for making the cathode electrode.

Suggest a reason for this. [1]

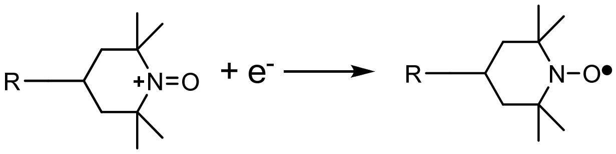
(ii) Calculate the oxidation number of N in the cathode **before** discharge. [1]

(iii) The E_{cell} generated by the hybrid ORB/Li-ion battery under standard conditions is 2.17 V.

Use relevant $E^\ominus$ value from the *Data Booklet* to calculate the electrode potential generated by the cathode half-cell.

[1]

(iv) During discharge, the following reaction occurs at the cathode.



where R represents the organic polymer cathode.

Write an equation for the overall process that occurs during discharge.

[1]

(v) Draw the dot-and-cross diagram of the PF_6^- ion and state its shape.

[2]

(vi) Suggest whether $LiPF_6$ or LiF has a lower melting point. Explain your answer.

[2]

(b) The hybrid ORB/Li-ion battery is a secondary battery, i.e., it is rechargeable.

During charging, 1.22 g of Li is regenerated from Li^+ ions at the cathode.

(i) Calculate the amount of electrons required to form 1.22 g of Li. [1]

Besides the generation of Li, there is a competing side-reaction that occurs at the cathode.

In this side-reaction, ethylene carbonate, $C_3H_4O_3$ undergoes reduction in the presence of Li^+ ions to form ethene and lithium carbonate.

(ii) Write the half-equation for the side-reaction occurring at the cathode.

[1]

A current of 5.0 A is supplied over 2 hours during charging.

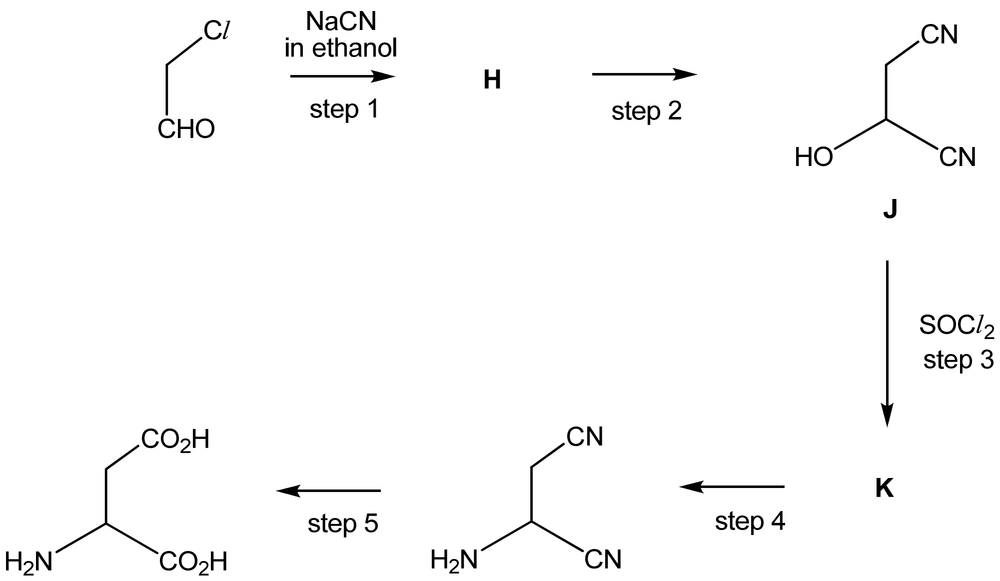
(iii) Use the information given and your answer in **(b)(i)** to calculate the amount of electrons consumed by the side-reaction.

[1]

(iv) Suggest why the battery needs to be replaced after about 1000 charge-discharge cycles.

[1]

(c) Chloroethanal is the starting material in the synthesis of aspartic acid.



(i) Suggest structures for the intermediates **H** and **K**.

[2]

(ii) Suggest reagents and conditions for step 2 and for step 4.

[2]

(iii) The reaction in step 2 produces sample **J**, which does not show optical activity. Explain the observation.

[2]

[Total: 18]

Section B

Answer **one** question from this section

4 **(a)** For many compounds the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy changes of combustion can be used.

The enthalpy change of combustion can be found by a calorimetry experiment in which the heat energy given off during combustion is used to heat a known mass of water and the temperature change recorded.

(i) Define the term *standard enthalpy change of combustion.*

[1]

(ii) Write the equation for the complete combustion of ethanol, CH_3CH_2OH.

[1]

In an experiment to determine the enthalpy change of combustion of ethanol, 0.23 g of ethanol was burned and the heat given off raised the temperature of 100 g of water by 16.3 °C.

(iii) Calculate the heat energy change during the combustion of ethanol.

[1]

(iv) Hence, calculate the enthalpy change on burning 1 mole of ethanol.

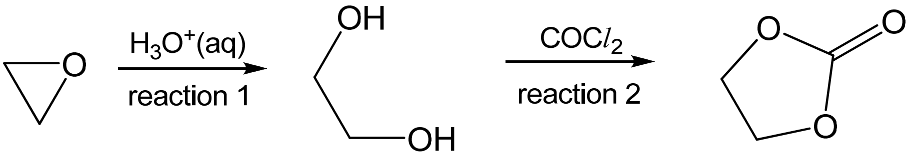
[2]

(v) Suggest one reason why the value for the enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value.

[1]

(b) Epoxides are cyclic ethers commonly used in organic reactions.

Ethylene carbonate can be prepared from an epoxide, oxirane by the following reactions.



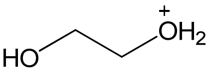
oxirane

ethylene carbonate

(i) Suggest the type of reaction for reaction 2.

[1]

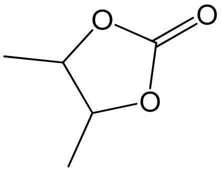
(ii) Reaction 1 is an acid-catalysed reaction that proceeds via a three-step mechanism:

1) Protonation of oxirane by H_3O^+.
2) Ring opening of protonated oxirane due to nucleophilic attack by H_2O to yield an oxonium ion, .
3) Deprotonation of the oxonium ion to yield the product, with the regeneration of H_3O^+.

Suggest the mechanism for Reaction 1.

[3]

Compound **L** can be synthesised from an epoxide in a similar manner as ethylene carbonate.



Compound **L**

(iii) Draw the structure of the epoxide used for synthesising compound **L**.

[1]

(iv) Suggest why compound **L** is able to exhibit cis-trans isomerism.

[1]

(c) A number of isomers with the formula $Fe(H_2O)_6Cl_3$ exist. Their general formula is $[Fe(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.

Each isomer contains a six co-ordinated Fe(III) ion in an octahedral complex. Water molecules not directly bonded with the Fe atom are held in the crystal lattice as water of crystallisation.

(i) Similar to organic compounds, octahedral complexes can also exhibit stereoisomerism depending on the orientation of the ligands.

One such example will be the iron complex when *n* is 2. It can exist in two isomeric forms where only one of them has a dipole moment.

Name the type of isomerism shown by the complex.

[1]

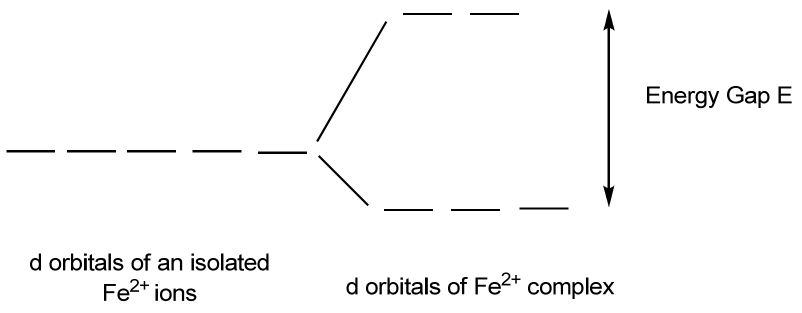
(ii) Draw the structures of the two isomeric forms of the complex.

[2]

(iii) State which isomer has a dipole moment. Explain your answer.

[2]

(iv) The following diagram shows how the d-orbitals are split in an octahedral environment.



When the H_2O ligand is changed to a C*l* ligand, the Fe^{2+} ion changes the electronic configuration from a 'high spin' to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

[2]

(v) State and explain which ligand will result in a larger energy gap, E, between its d-orbitals.

[1]

[Total: 20]

5 Carbonyl compounds are common in our everyday lives. They are mainly used as solvents, perfumes and flavouring agents or as intermediates in the manufacture of plastics and pharmaceuticals.

(a) The characteristic smell of cherries and fresh almonds is due to benzaldehyde.

(i) Benzaldehyde can react with chloromethane to form 3-methylbenzaldehyde. Describe the mechanism for this reaction.

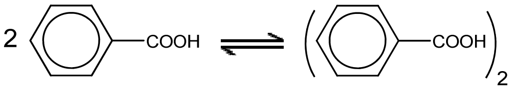
[3]

(ii) Benzene can also react under a similar reaction with chloromethane.

State and explain whether benzene or benzaldehyde would react with chloromethane more readily.

[2]

(b) Benzaldehyde can also react with hot acidified dichromate(VI) to give benzoic acid. In benzene, benzoic acid associates to form dimers.



(i) Draw a diagram to illustrate the bonding in the dimer.

[1]

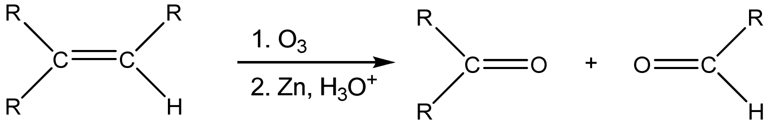
(ii) Predict and explain whether the dimerisation is favoured at a high or low temperature.

[2]

(iii) Suggest why the above equilibrium cannot be established in an aqueous medium.

[1]

(c) Carbonyl compounds can be prepared from alkenes via the ozonolysis reaction as shown below.



An alkene **M**, $C_{11}H_{14}$ was treated with O_3, followed by Zn and H_3O^+ to give **N** C_4H_8O and **P**, C_7H_6O. **N** gives a yellow precipitate with aqueous alkaline iodine while **P** gives a grey precipitate with ammonical silver nitrate solution. In the presence of OH^-, **P** undergoes a reaction to give **Q**, $C_7H_6O_2$ and **S**, C_7H_8O. Both **Q** and **S** react with Na metal, but only **Q** reacts with $NaHCO_3$.

Suggest the structures of **M, N, P, Q** and **S**.

[5]

(d) **T, U, V** and **W** are four consecutive elements in the **fourth** period of the Periodic Table. (The letters are **not** the actual symbols of the elements.)

T is a soft, silvery metal with a melting point just above room temperature. Its amphoteric oxide, $\mathbf{T}_2O_3$, has a melting point of 1900 °C and can be formed by heating **T** in oxygen.

W is a solid that can exist as several allotropes, most of which contain $\mathbf{W}_8$ molecules. **W** burns in air to form $\mathbf{W}O_2$ and $\mathbf{W}O_3$**,** which dissolves in water to form an acidic solution. The acidic solutions react with sodium hydroxide to form the salt $Na_2\mathbf{W}O_3$ and $Na_2\mathbf{W}O_4$ respectively.

(i) Suggest the identities of **T** and **W**.

[2]

(ii) Write equations for the reactions of $\mathbf{T}_2O_3$ with

- hydrochloric acid,
- sodium hydroxide

[2]

(iii) Suggest the structure in $\mathbf{T}_2O_3$.

[1]

(iv) Write an equation for the formation of the acidic solution when $\mathbf{W}O_3$ dissolves in water.

[1]

[Total: 20]

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INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **10 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

This document consists of **xx** printed pages.

Section A

Answer **all** the questions in this section.

1 This question is about the chemistry of ethene and its derivatives.

(a) Ethene is the starting material to form ethanedioic acid.

(i) Suggest the synthetic route for the formation of ethanedioic acid from ethene. [2]

$CH_2CH_2 \rightarrow CH_2(OH)CH_2(OH)$ [1m] → ethanedioic acid

Step 1: cold, KMnO4, NaOH(aq) [✓]

Step 2: $K_2Cr_2O_7$, dil H_2SO_4, heat [✓]

(ii) 0.200 mol of ethene is stored in a 20.0 dm^3 flask with 0.800 mol of ethane at 127^0C.

Calculate the total pressure in the flask. Hence or otherwise, calculate the partial pressure of ethene in the flask. [2]

$P(20.0 \times 10^{-3}) = (0.200 + 0.800)(8.31)(127 + 273)$
$P = 166200$ Pa [1]

Partial pressure of ethene = $0.2/1.0 \times 166200 = 33240$
$= 33.2 \times 10^3$ Pa [1]

(iii) The total pressure that you calculated in **(a)(ii)** is different from the actual pressure exerted. Suggest an explanation for the difference. [1]

There is significant intermolecular forces of attraction present between the gases OR intermolecular forces of attraction between the gases are not negligible [1].

(iv) Ethene reacts with hydrogen in the presence of nickel catalyst to form ethane.

Explain why nickel can be used as a catalyst in this reaction. [2]

Nickel has **available 3d electrons for bond formation** with the reactant molecules (ie. ethene and hydrogen) [1] and **available low lying vacant orbitals or energetically accessible orbitals which can accept electron** pairs from the reactant molecules. [1]

(v) Outline the mode of action of the catalyst in this reaction. [2]

The catalyst is in a solid state and it functions as a **heterogeneous catalyst** **[√]** as it is in a different phase than ethene and hydrogen. Ethene and hydrogen **(reactants) will be adsorbed to the surface of the Ni catalyst.** **[√]** **Bonds in the reactant molecules are weakened** **[√]** which lowers the activation energy. New bonds are then formed between adjacent reactant molecules to form ethane (product). **The product formed will be desorbed from the surface of the Ni catalyst.** **[√]**

(b) Dissolving 4.82×10^{-5} mol calcium ethanedioate, CaC_2O_4, in 1 dm^3 of water forms a saturated solution.

(i) Write an expression for the solubility product of calcium ethanedioate and state its units. [1]

$K_{sp}(CaC_2O_4) = [Ca^{2+}][C_2O_4^{2-}]$ unit: $mol^2\ dm^{-6}$ [1]

(ii) Calculate the solubility product of calcium ethanedioate.

[1]

$$Ksp = (4.82 \times 10^{-5})^2$$
$$= 2.32 \times 10^{-9} \quad [1]$$

[units not nec. as already stated in (i)]

(iii) 50.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ and 50.0 cm^3 of 0.300 mol dm^{-3} $Na_2C_2O_4$ are mixed together. Determine if CaC_2O_4 will be precipitated out.

[2]

For precipitation to occur, IP of CaC_2O_4 must exceed Ksp of CaC_2O_4
Since the volume used is the same, the new concentration is halved the original concentration.

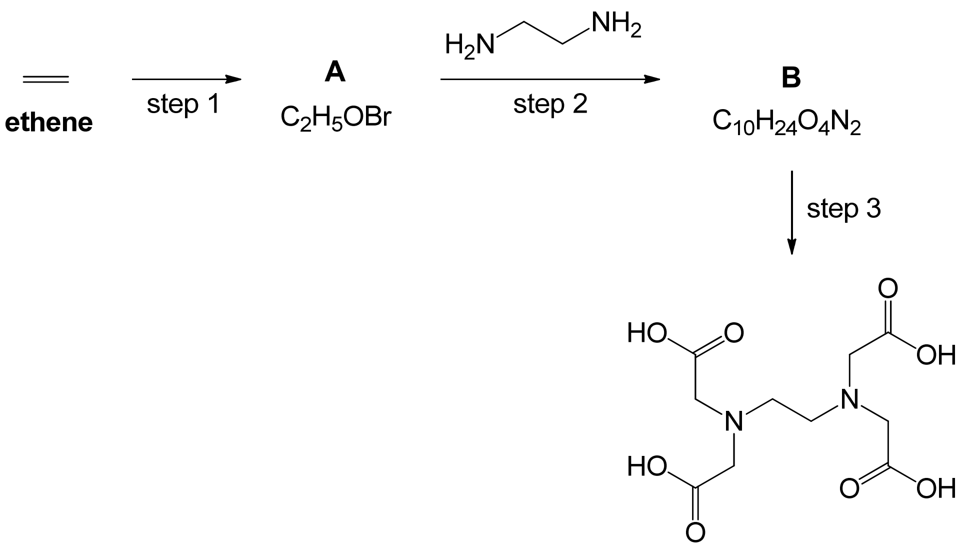
New $[Ca^{2+}] = 0.100 / 2 = 0.05$ [✓]

New $[C_2O_4^{2-}] = 0.300 / 2 = 0.15$ [✓]

IP of $CaC_2O_4 = (0.05)(0.15) = 7.50 \times 10^{-3}$ [✓]

Since IP > Ksp, CaC_2O_4 will ppt out. [✓][ECF with student's Ksp value from (ii)]

(c) Synthesis of the unionised form of EDTA (H_4Y) can be carried out in the laboratory using ethene as the starting material.

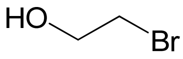


unionised form of EDTA (H_4Y)

(i) Draw the structures of **A** and **B**.

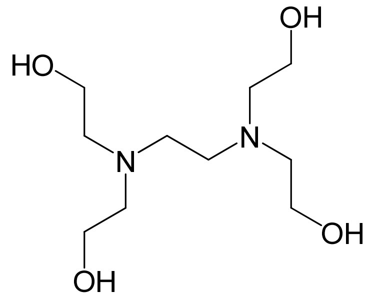
[2]

A:



[1]

B:



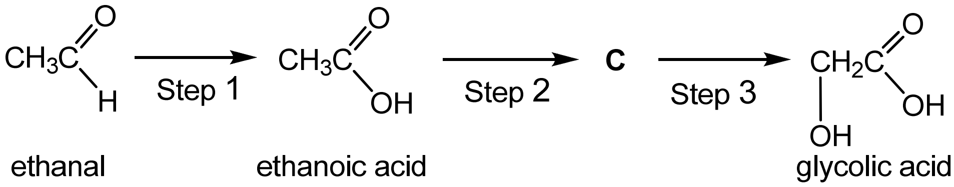
[1]

(ii) Suggest appropriate reagents and conditions for step 3.

[1]

Step 3: dilute H_2SO_4, $KMnO_4$(aq)/$K_2Cr_2O_7$(aq), heat under reflux [1] (followed by careful addition of NaOH(aq))

(d) Ethene can be used to form ethanal. Ethanal in turn is used to synthesize glycolic acid via the reaction shown below.

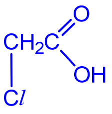


(i) Identify the intermediate **C** and state the reagent and condition for Step 3.

[2]

Step 3: NaOH(aq), heat under reflux; followed by aq. HCl [1]

C:



[1]

(ii) Explain the difference in acidity between glycolic acid and ethanoic acid.

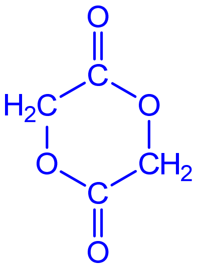
[2]

In glycolic acid, the electron withdrawing –OH [✓] group reduces the negative charge on $–COO^-$ [✓] of the conjugate base of glycolic acid, thus making the anion of glycolic acid is more stable that the ethanoate anion [✓]. Hence, glycolic acid is a stronger acid [✓].

(iii) Two molecules of glycolic acid can react with one another under suitable conditions to form a neutral compound with the loss of two water molecules.

Suggest a possible structure for the compound formed.

[1]



[1]

(iv) Suggest a simple chemical test to distinguish between ethanoic acid and glycolic acid.

[2]

Test: $K_2Cr_2O_7$, dil H_2SO_4, heat [1]
Ethanoic acid: orange $K_2Cr_2O_7$ turns green [✓]
Glycolic acid: orange $K_2Cr_2O_7$ remains [✓]

OR
Test: $KMnO_4$, dil H_2SO_4, heat
Ethanoic acid: purple $KMnO_4$ remains
Glycolic acid: purple $KMnO_4$ decolorised. Effervescence observed. gas produced forms white ppt with $Ca(OH)_2$

[Total: 23]

2 Iron is the fourth most common element in the Earth's crust. It is a d-block element which is known to exhibit different characteristics from the s-block elements. Since ancient times, iron has been widely employed in a variety of applications.

(a) **(i)** One well-known property of iron and its compounds is the ability to catalyse reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I^- and $S_2O_8^{2-}$, to form I_2 and SO_4^{2-} ions.

Using relevant $E^\ominus$ values from the *Data Booklet*, explain why iron(II) chloride can be used as a catalyst for this reaction.

[2]

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + SO_4^{2-}$

Ecell = +2.01 – (0.77)
= +1.24 V (reaction is energetically feasible) [1]

$2\,I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$
Ecell = +0.77 – (+0.54)
= +0.23 V (reaction is energetically feasible) [1]

(ii) A sample of iron was vapourised, ionised and passed through an electric field. Analysis of deflection occurring at the electric field region revealed that a sample of $^{32}S^{2-}$ ions would be deflected by +20° towards the positive potential.

What is the angle, and direction of deflection for a sample of $^{56}Fe^{3+}$ ions passing through the same electric field?

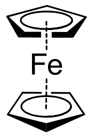
[2]

Angle of deflection of $^{32}S^{2-}$ = 20
20 = k (-2 / 32)
k = - 320

Angle of deflection of $^{56}Fe^{3+}$ = (-320) (3 / 56)
= -17.1˚ [1 for final answer; 1m for indication of direction]

or 17.1° [1m] towards the negative potential [1m]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange solid which is known to exhibit anti-cancer activity. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



ferrocene

(i) State the oxidation number of Fe in ferrocene. [1]

+2

(ii) Suggest why ferrocene is a coloured complex. [2]

There is partially filled 3d orbitals in Fe^{2+}. [√]

In the presence of ligands, 3d orbitals of iron are split into 2 groups with small energy gap (d–d splitting). [√]

Some light energy is used to promote an electron [√] from a d-orbital of lower energy to a d-orbital of a higher energy [√].

(Colour observed is complementary to the colour absorbed.)

(iii) Light of a longer wavelength is lower in energy than light of a shorter wavelength. The following table shows the spectral colours and the corresponding wavelengths.

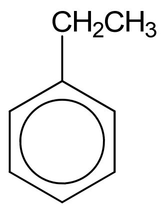
Colour	**Wavelength / nm**
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

Given that aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$. [2]

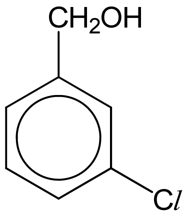
Water causes a smaller split between the 3d orbitals. [1]

With water as the ligand, electromagnetic waves with energy corresponding to red is absorbed which has a lower energy than blue, which is absorbed when $C_5H_5^-$ is the ligand. [1]

(c) Ethylbenzene is used to synthesize (3-chlorophenyl)methanol which is used as a general solvent for inks, paints, lacquers, epoxy resin coatings and as a degreasing agent.



ethylbenzene

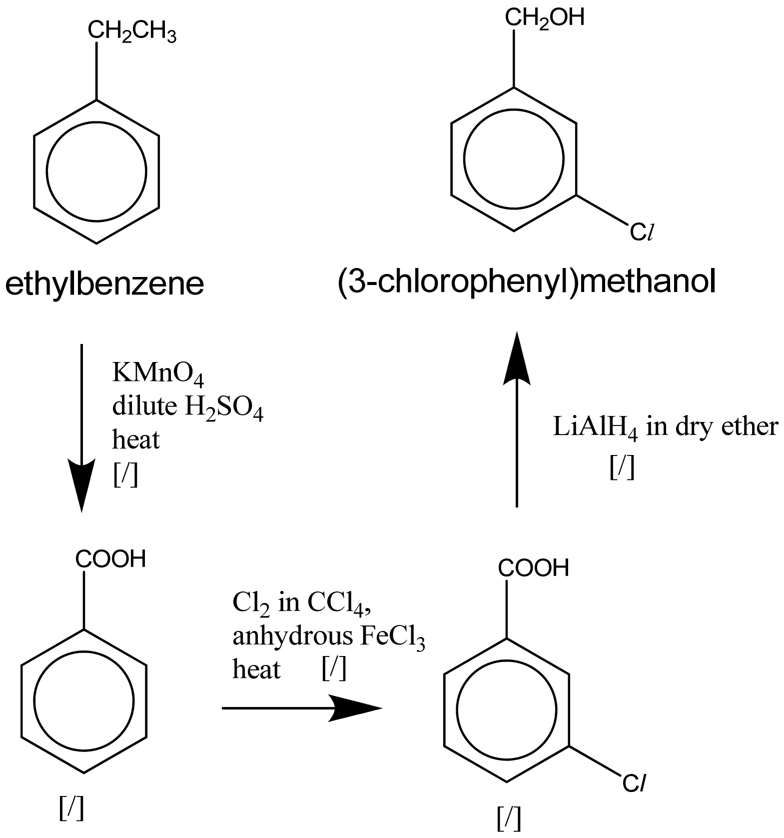


(3-chlorophenyl)methanol

Starting with ethylbenzene, outline a three-step reaction scheme to obtain (3-chlorophenyl)methanol. Your answer should include clearly the reagents and conditions in each step, and the structures of all intermediates formed.

[3]

Ans:



5 [√] – 3m
3 to 4 [√] – 2m
2 [√] – 1m

(d) **D** is an achiral organic compound with the molecular formula C_2H_7NO. It can be formed from the reaction between a primary amide and lithium aluminium hydride. In the presence of a suitable catalyst, 1 mole of **D** reacts with 1 mole of benzoic acid to form **E,** $C_9H_{11}NO_2$. However, 1 mole of **D** requires 2 moles of benzoyl chloride to react completely to form **F,** $C_{16}H_{15}NO_3$ and copious white fumes. 2 moles of **D** can also react with gaseous PCl_5 to form a cyclic **G**, $C_4H_{10}N_2$, which contains a 6-membered ring.

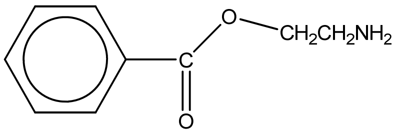
Deduce the structures of **D**, **E**, **F** and **G** and explain the reactions described.

[7]

Info	Deduction
D is formed from reaction between primary amide and LiAlH4	**D** contains a primary amine [√]
1 mol **D** reacts with 1 mol of benzoic acid to form **E,** $C_9H_{11}NO_2$	• **D** undergoes condensation / nucleophilic acyl substitution [√] • **E** is an ester [√] • **D** contains alcohol [√]
1 mol **D** require 2 mol benzoyl chloride to react completely to form Compound **F,** $C_{16}H_{15}NO_3$ and copious white fumes.	• **D** undergoes condensation/ nucleophilic acyl substitution [√] • Copious white fumes are HCl [√] • **F** contains an amide [√] and an ester [√]
2 mol **D** reacts with gaseous PCl_5 to form a cyclic Compound **G**, $C_4H_{10}N_2$	• **D** undergoes nucleophilic substitution [√] • **G** contains an amine [√]
8 - 10 [√] – 3m 5 - 7 [√] – 2m 2 – 4 [√] – 1m	

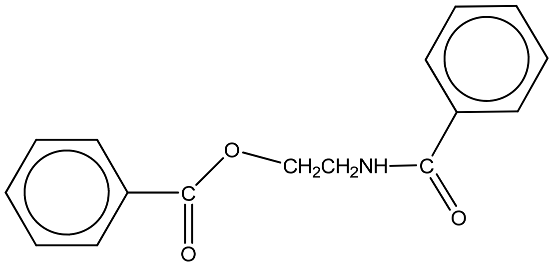
D (C_2H_7NO) : $NH_2CH_2CH_2OH$ [1]

Compound **E** ($C_9H_{11}NO_2$) :



[1]

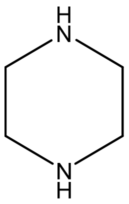
Compound **F** ($C_{16}H_{15}NO_3$) :



[1]

ECF for structure E and F based on wrong structure D, $H_2NCH(OH)CH_3$.

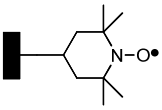
Compound **G** ($C_4H_{10}N_2$) :

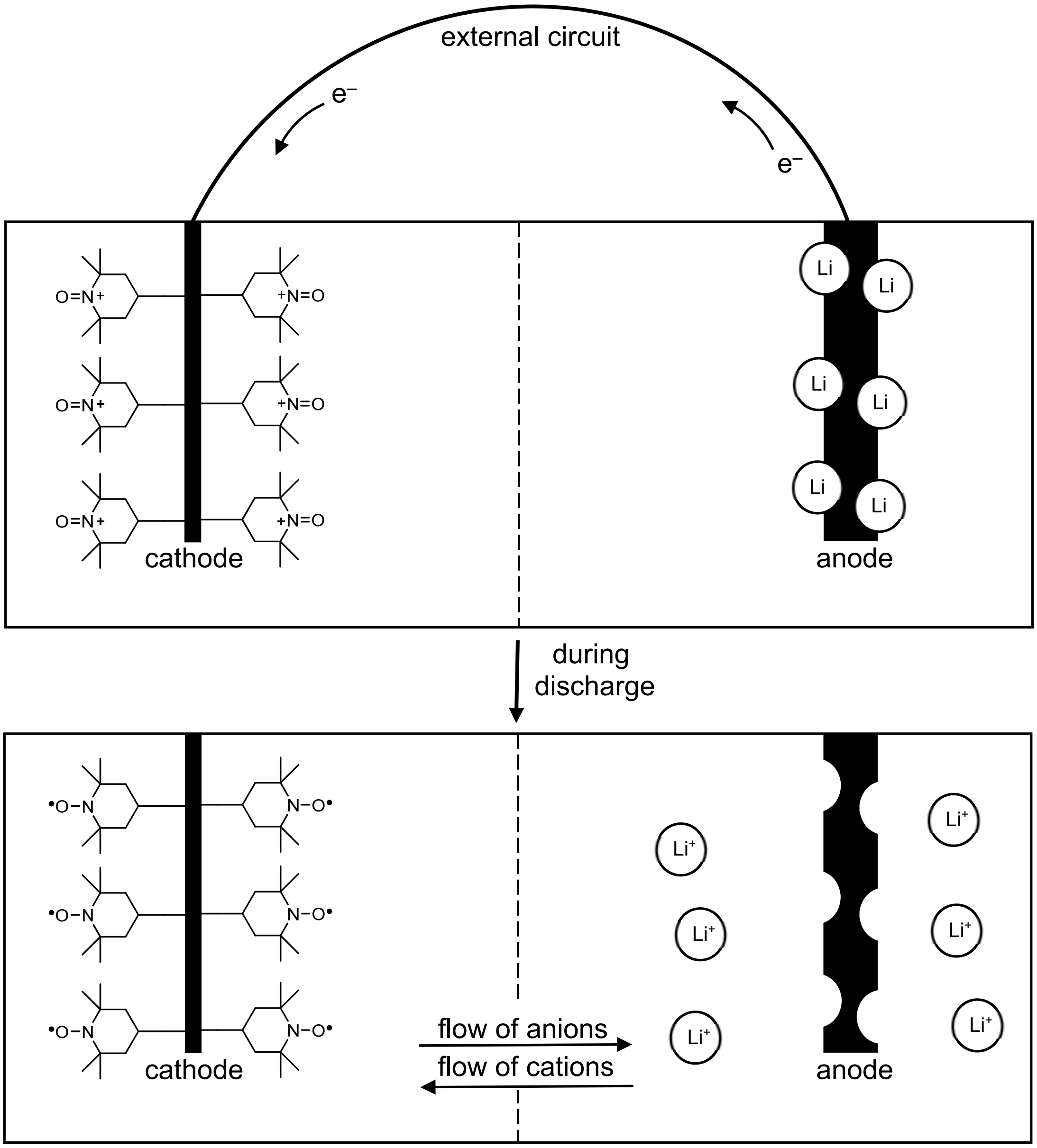


[1]

[Total: 19]

3 An organic radical battery (ORB) is a relatively new type of battery which uses flexible plastics, to provide electrical power. One type of hybrid ORB/Li-ion battery consists of: a cathode made from solid organic polymer containing oxoammonium ion formed from (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) nitroxide radicals; an anode made from graphite with Li atoms inserted between the graphite layers; and an electrolyte of $LiPF_6$ dissolved in organic solvent.

During discharge, Li atoms give up electrons at the anode to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. The anions and cations in the electrolyte move to the anode and cathode respectively. This is illustrated in the following diagram in which and  are simplified representations of the polymer containing oxoammonium ion and TEMPO nitroxide radicals respectively.



(a) **(i)** Graphite is often mixed in the polymer used for making the cathode electrode.

Suggest a reason for this. [1]

To increase the electrical conductivity of the electrode
Or (good) conductor of electricity [1]

(ii) Calculate the oxidation number of N in the cathode **before** discharge. [1]

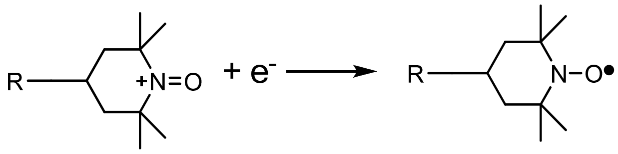
Oxidation number of N is +1 [1]

(iii) The E_{cell} generated by the hybrid ORB/Li-ion battery under standard conditions is 2.17 V.

Use relevant $E^{\ominus}$ value from the *Data Booklet* to calculate the electrode potential generated by the cathode half-cell. [1]

$$\begin{aligned} E_{cell} &= E_{red} - E_{ox} \\ +2.17 &= E_{red} - (-3.04) \\ &= -0.87\ \text{V} \end{aligned}$$
[1, with correct working and sign]

(iv) During discharge, the following reaction occurs at the cathode.

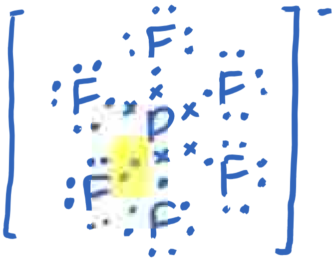


where R represents the organic polymer cathode.

Write an equation for the overall process that occurs during discharge. [1]

Li + → + Li^+ [1]

(v) Draw the dot-and-cross diagram of the PF_6^- ion and state its shape. [2]



[1, check for dative bond and overall charge]

Shape: **Octahedral [1]**

(vi) Suggest whether $LiPF_6$ or LiF has a lower melting point. Explain your answer. [2]

$LiPF_6$. [1, conditional provided student considered LE)
PF_6^- has a **larger anionic radius** [✓] than F^-, giving rise to a **lower magnitude of LE**[✓] (since L.E. $\propto \left|\dfrac{q_+ \times q_-}{r_+ + r_-}\right|$). Hence, $LiPF_6$ has a lower ionic bond strength and less energy is required to overcome the ionic bond, giving rise to lower mp.

(b) The hybrid ORB/Li-ion battery is a secondary battery, i.e., it is rechargeable.

During charging, 1.22 g of Li is regenerated from Li^+ ions at the cathode.

(i) Calculate the amount of electrons required to form 1.22 g of Li. [1]

Amount of Li formed = 1.22 / 6.9 = 0.1768 mol

$Li+ + e \rightarrow Li$

Amount of electrons consumed = 0.1768 = 0.177 mol [1].

Besides the generation of Li, there is a competing side-reaction that occurs at the cathode.

In this side-reaction, ethylene carbonate, $C_3H_4O_3$ undergoes reduction in the presence of Li^+ ions to form ethene and lithium carbonate.

(ii) Write the half-equation for the side-reaction occurring at the cathode. [1]

$C_3H_4O_3 + 2Li^+ + 2e \rightarrow C_2H_4 + Li_2CO_3$ [1]

A current of 5.0 A is supplied over 2 hours during charging.

(iii) Use the information given and your answer in **(b)(i)** to calculate the amount of electrons consumed by the side-reaction. [1]

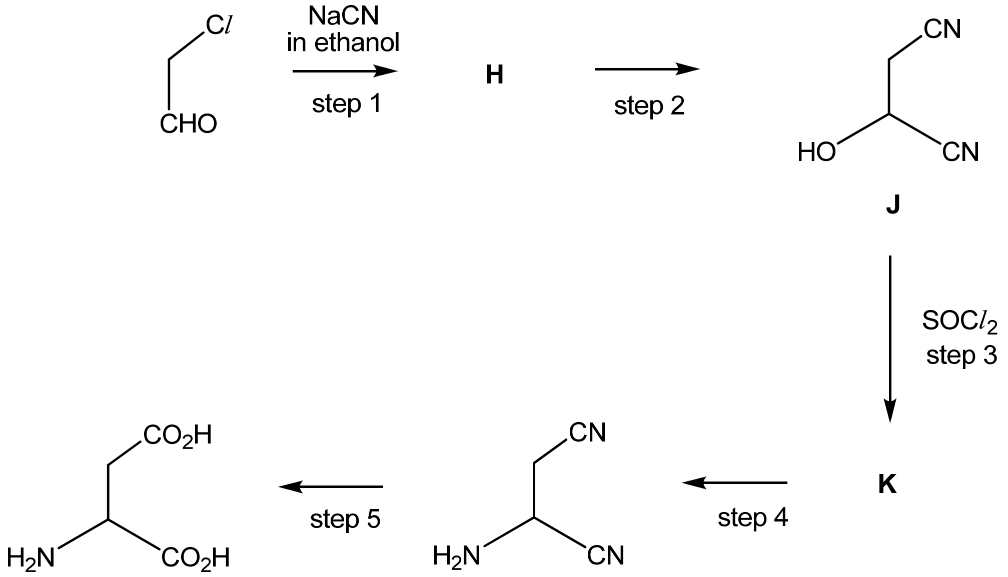
Amount of electrons supplied = (5.0) (2 x 3600) / 96500 = 0.3731 mol [✓].

Hence, amount of electrons consumed by side-reaction
= 0.3731 – 0.1768
= 0.196 mol [✓, **allow ecf from (i)**].

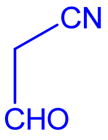
(iv) Suggest why the battery needs to be replaced after about 1000 charge-discharge cycles. [1]

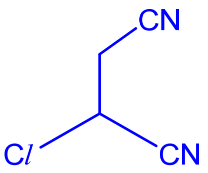
Some of the **Li ions are depleted** / **not all the Li metal is regenerated** during charging **due to the side-reaction** [1].

(c) Chloroethanal is the starting material in the synthesis of aspartic acid.



(i) Suggest structures for the intermediates **H** and **K**. [2]

H:  **[1]**

K:  **[1]**

(ii) Suggest reagents and conditions for step 2 and for step 4. [2]

Step 2: HCN, trace NaOH(aq)/NaCN, cold **[1]**

Step 4: excess, concentrated ethanolic NH_3, heat in sealed tube **[1]**

(iii) The reaction in step 2 produces sample **J**, which does not show optical activity. Explain the observation. [2]

The **nucleophile, CN^-, has equal chances of attacking either above or below the plane of the electron-deficient carbonyl carbon in compound H** **[1]**. Thus, the product mixture contains 50% of each of the enantiomer, forming a **racemic mixture**[√]. Hence, the **optical activity of the 2 enantiomers cancels out**[√]. Thus, sample **J** produced does not show optical activity.

[Total: 18]

Section B

Answer **one** question from this section

4 **(a)** For many compounds the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy changes of combustion can be used.

The enthalpy change of combustion can be found by a calorimetry experiment in which the heat energy given off during combustion is used to heat a known mass of water and the temperature change recorded.

(i) Define the term *standard enthalpy change of combustion.* [1]

Standard enthalpy change of combustion, ΔH_c^θ, of a compound is the enthalpy change (heat evolved) when **1 mole of the substance** is **completely burnt in oxygen** under standard conditions of 298K and 1 bar. [1]

(ii) Write the equation for the complete combustion of ethanol, CH_3CH_2OH. [1]

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$[1] (ss not required)

In an experiment to determine the enthalpy change of combustion of ethanol, 0.23 g of ethanol was burned and the heat given off raised the temperature of 100 g of water by 16.3 °C.

(iii) Calculate the heat energy change during the combustion of ethanol. [1]

Heat change = $mc\Delta T$
= $(100)(4.18)(16.3)$
= 6813.4

= 6810 J[1]
(no mark awarded if unit given is wrong)

(iv) Hence, calculate the enthalpy change on burning 1 mole of ethanol. [2]

Amount of ethanol = 0.23 / (2x12.0 + 6.0 + 16.0)
= 5.00×10^{-3} mol

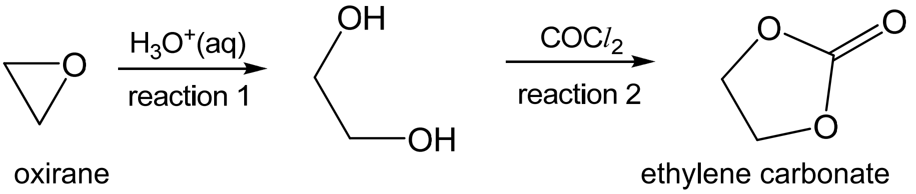
Enthalpy change = $-(6813.4/5.00 \times 10^{-3})$ [1m; ECF from (iii)]
= $-1362680 \text{ J mol}^{-1}$
= $-1360 \text{ kJ mol}^{-1}$ [1m include unit & sign]

(v) Suggest one reason why the value for the enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value. [1]

Heat loss to the surrounding. / Incomplete combustion/ Ethanol is volatile and evaporated./ Ethanol is impure. / Not all energy is absorbed by the water.
(Any answer 1 mark)

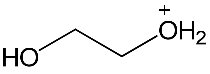
(b) Epoxides are cyclic ethers commonly used in organic reactions.

Ethylene carbonate can be prepared from an epoxide, oxirane by the following reactions.

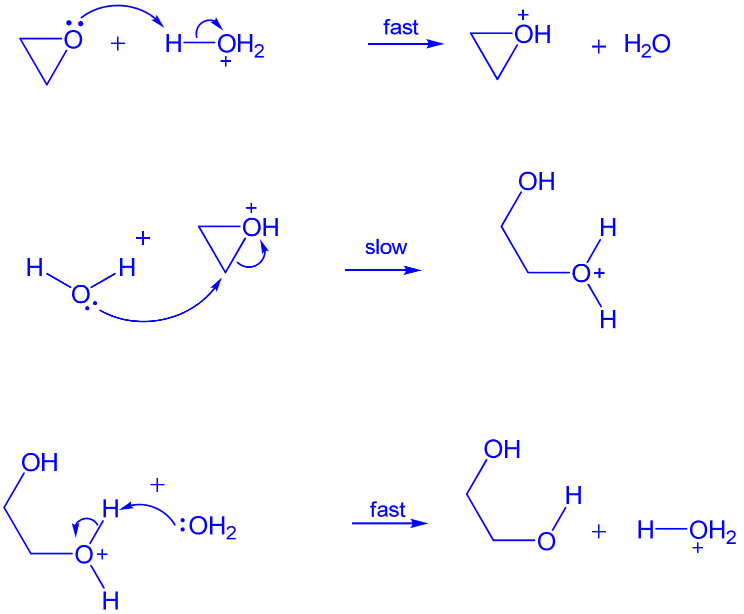


(i) Suggest the type of reaction for reaction 2. [1]
Condensation/ nucleophilic acyl substitution [1]

(ii) Reaction 1 is an acid-catalysed reaction that proceeds via a three-step mechanism:

1) Protonation of oxirane by H_3O^+.
2) Ring opening of protonated oxirane due to nucleophilic attack by H_2O to yield an oxonium ion,  .
3) Deprotonation of the oxonium ion to yield the product, with the regeneration of H_3O^+.

Suggest the mechanism for Reaction 1.
[3]

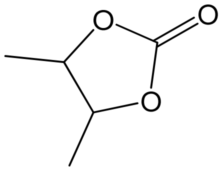


✓ - correct half-arrows and lone pairs for step 1
✓ - formation of H_2O in step 1
✓ - correct structure for protonated epoxide in step 1
✓ - correct half-arrows and lone pair for step 2
✓ - correct half-arrows and regeneration of H_3O^+ for step 3

(fast & slow labels not marked for)

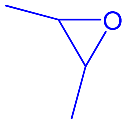
3m – all 5 ✓ ; 2m – 3 to 4 ✓ ; 1m – 2 ✓

Compound **L** can be synthesised from an epoxide in a similar manner as ethylene carbonate.



Compound **L**

(iii) Draw the structure of the epoxide used for synthesising compound **L**. [1]



[1]

(iv) Suggest why compound **L** is able to exhibit cis-trans isomerism. [1]
Restricted C-C bond rotation [1] due to **ring strain/ rigidity of ring**
(and both C atoms of the ring is attached to 2 different groups or atoms)

(c) A number of isomers with the formula $Fe(H_2O)_6Cl_3$ exist. Their general formula is $[Fe(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.

Each isomer contains a six co-ordinated Fe(III) ion in an octahedral complex. Water molecules not directly bonded with the Fe atom are held in the crystal lattice as water of crystallisation.

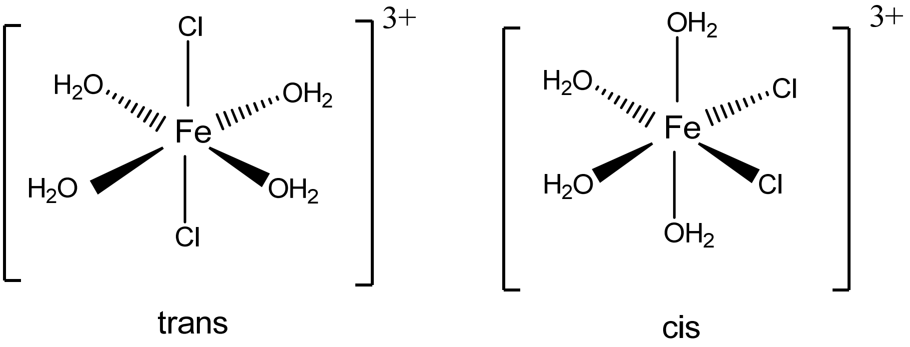
(i) Similar to organic compounds, octahedral complexes can also exhibit stereoisomerism depending on the orientation of the ligands.

One such example will be the iron complex when *n* is 2. It can exist in two isomeric forms where only one of them has a dipole moment.

Name the type of isomerism shown by the complex [1]

Cis- Trans isomerism

(ii) Draw the structures of the two isomeric forms of the complex. [2]

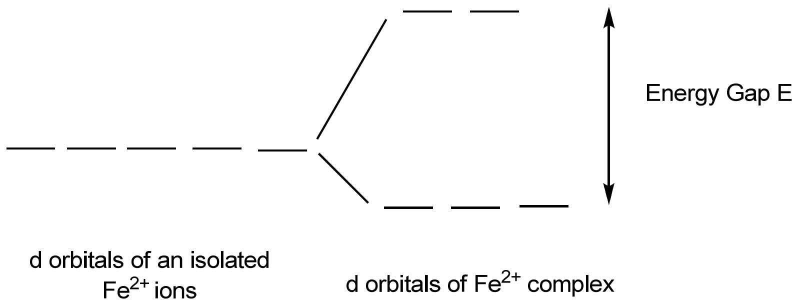


[1 mark each] (labelling of cis-trans not required)

(iii) State which isomer has a dipole moment. Explain your answer. [2]

Cis isomer has a dipole moment. [1] (student need not mention "cis". Marks are awarded as long as student identify the correct isomer)
Cl^- on the same side of the complex/ overall dipole moment does not cancel out.[1]

(iv) The following diagram shows how the d-orbitals are split in an octahedral environment.



When the H_2O ligand is changed to a C*l* ligand, the Fe^{2+} ion changes the electronic configuration from a 'high spin' to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

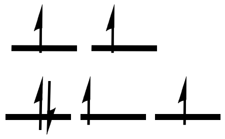
In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

[2]

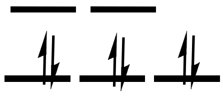
Fe^{2+} : $3d^6$

'High spin' state



[1]

'Low spin' state



[1]

(v) State and explain which ligand will result in a larger energy gap, E, between its d-orbitals.

[1]

(Complex with) Cl ligand [/]
Electrons will only pair up in the lower orbitals when the energy gap was greater than the interelectronic repulsion between the two electrons in the same orbital. (wttse) [/]

[Total: 20]

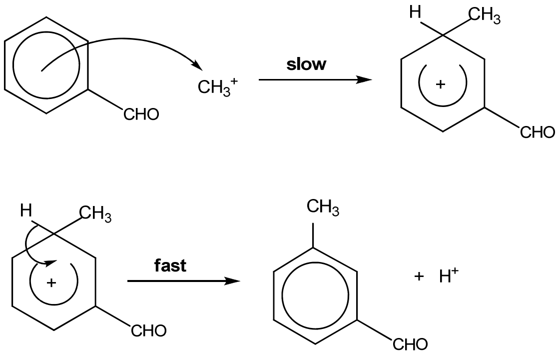
5 Carbonyl compounds are common in our everyday lives. They are mainly used as solvents, perfumes and flavouring agents or as intermediates in the manufacture of plastics and pharmaceuticals.

(a) The characteristic smell of cherries and fresh almonds is due to benzaldehyde.

(i) Benzaldehyde can react with chloromethane to form 3-methylbenzaldehyde. Describe the mechanism for this reaction.

[3]

Electrophilic Substitution **[1]**
$CH_3Cl + FeCl_3 \longrightarrow CH_3^+ + [FeCl_4]^-$



$H^+ + [FeCl_4]^- \longrightarrow FeCl_3 + HCl$
1 [√] for each step

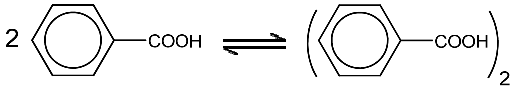
(ii) Benzene can also react under a similar reaction with chloromethane.

State and explain whether benzene or benzaldehyde would react with chloromethane more readily.

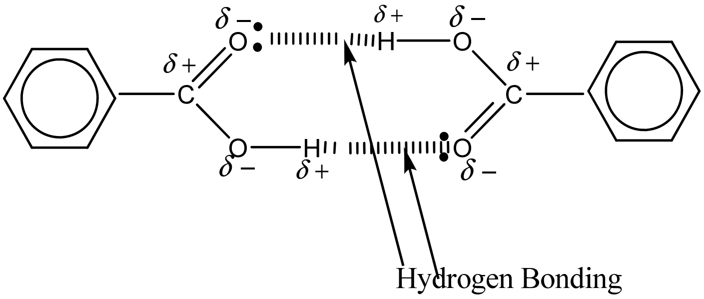
[2]

Benzene would react **more readily [√]** with chloromethane.
Benzaldehyde contains an **electron withdrawing CHO group [√]** which **decreases the electron density of the benzene ring [√]**, making it **less susceptible to electrophilic attacks [√]**.

(b) Benzaldehyde can also react with hot acidified dichromate(VI) to give benzoic acid. In benzene, benzoic acid associates to form dimers.



(i) Draw a diagram to illustrate the bonding in the dimer. [1]



All details included (dipoles, lone pair, hydrogen bonds) – **[1]**

(ii) Predict and explain whether the dimerisation is favoured at a high or low temperature.

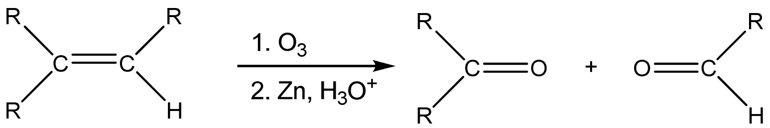
[2]

Low temperature [1, conditional]. At low temperature, the position of equilibrium shifts to the right to favour the **exothermic reaction [1]** to release heat.

(iii) Suggest why the above equilibrium cannot be established in an aqueous medium.
In aqueous medium, **benzoic acid would form hydrogen bonds with the water molecules instead** of forming a dimer, **[1]**

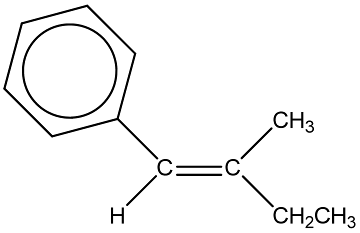
[1]

(c) Carbonyl compounds can be prepared from alkenes via the ozonolysis reaction as shown below.

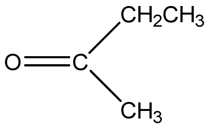


An alkene **M**, $C_{11}H_{14}$ was treated with O_3, followed by Zn and H_3O^+ to give **N** C_4H_8O and **P**, C_7H_6O. **N** gives a yellow precipitate with aqueous alkaline iodine while **P** gives a grey precipitate with ammonical silver nitrate solution. In the presence of OH^-, **P** undergoes a reaction to give **Q**, $C_7H_6O_2$ and **S**, C_7H_8O. Both **Q** and **S** react with Na metal, but only **Q** reacts with $NaHCO_3$.

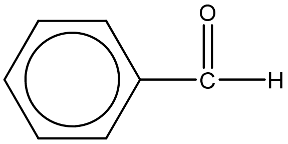
Suggest the structures of **M, N, P, Q** and **S**. [5]



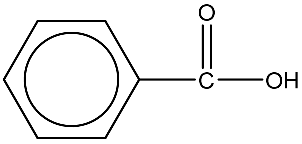
M



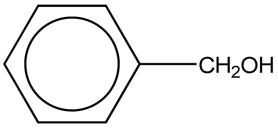
N



P



Q



S

[1] each

(d) **T, U, V** and **W** are four consecutive elements in the **fourth** period of the Periodic Table. (The letters are **not** the actual symbols of the elements.)

T is a soft, silvery metal with a melting point just above room temperature. Its amphoteric oxide, $\mathbf{T}_2O_3$, has a melting point of 1900 °C and can be formed by heating **T** in oxygen.

W is a solid that can exist as several allotropes, most of which contain $\mathbf{W}_8$ molecules. **W** burns in air to form $\mathbf{W}O_2$ and $\mathbf{W}O_3$**,** which dissolves in water to form an acidic solution. The acidic solutions react with sodium hydroxide to form the salt $Na_2\mathbf{W}O_3$ and $Na_2\mathbf{W}O_4$ respectively.

(i) Suggest the identities of **T** and **W**. [2]

T = Ga [1] **W** = Se [1]

(ii) Write equations for the reactions of $\mathbf{T}_2O_3$ with

- hydrochloric acid,
- sodium hydroxide [2]

$\mathbf{T}_2O_3 + 6HCl \rightarrow 2\mathbf{T}Cl_3 + 3H_2O$ [1]

$\mathbf{T}_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na\mathbf{T}(OH)_4$ [1]

(in writing the equations, students can replace **T** with Ga)

(iii) Suggest the structure in $\mathbf{T}_2O_3$. [1]

Giant Ionic Structure [1]

(iv) Write an equation for the formation of the acidic solution when $\mathbf{W}O_3$ dissolves in water. [1]

$\mathbf{W}O_3 + H_2O \rightarrow H_2\mathbf{W}O_4$ [1]

(in writing the equation, students can replace **W** with Se)

[Total: 20]

CHEMISTRY LAB PREPARATION LIST FOR JC2 H2 CHEMISTRY
2018 PRELIM EXAM

APPARATUS NEEDED (PER STUDENT)

S/N	Apparatus	Quantity	Location	Remarks
1	10 cm^3 measuring cylinder	2	Student's bench	Reuse
2	50 cm^3 measuring cylinder	1	Student's bench	Reuse
3	25 cm^3 measuring cylinder	1	Student's bench	Reuse
4	100 cm^3 measuring cylinder	1	Student's bench	Reuse
5	stopwatch	1	Student's bench	Reuse
6	Thermometer (-10°C to +110°C	1	Student's bench	Reuse
7	Glass rod	1	Student's bench	Reuse
8	Wash bottle of distilled water	1	Student's bench	Reuse
9	Pen suitable for labelling glassware	1	Student's bench	Reuse
10	Heat proof mat	1	Student's bench	Reuse
11	Filter Funnel	1	Student's bench	Reuse
12	Test tube rack	1	Student's bench	Reuse
13	Test tube holder	1	Student's bench	Reuse
14	Bunsen burner	1	Student's bench	Reuse
15	Tripod with gauze	1	Student's bench	Reuse
16	Lighter	1	Student's bench	Reuse
17	Spatula	1	Student's bench	Reuse
18	100 cm^3 conical flask	1	Student's bench	Reuse
19	Stand and **bigger clamp**	1	Student's bench	Reuse
20	plastic tub	1	Student's bench	trough for gas collection (minimum capacity 1 dm3)
21	Paper towels		Student's bench	Must change to new one per shift
22	Test tubes	6	Student's bench	Must change to new one per shift
23	Boiling tubes	2	Student's bench	Must change to new one per shift
24	Filter Paper	2-3	Student's bench	Must change to new one per shift
25	Dropping Pipette	5	Student's bench	Must change to new one per shift

* access to a balance weighing

CHEMICALS NEEDED (PER STUDENT)

S/N	Chemical	Concentration	Quantity	Location	Remarks
1	Hydrochloric acid (**FA 1**)	2.0 mol dm^{-3}	70 cm^3		Dilute 170 cm^3 of concentrated (35-37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^3
2	Magnesium (ribbon) (**FA 2**)	about 4 cm length	3 pieces		4 cm Magnesium ribbon supplied in a stoppered container labelled **FA 2** .
3	Sodium thiosulfate (**FA 3)**	0.10 mol dm^{-3}	200 cm^3		Dissolve 24.82g of $Na_2S_2O_3.5H_2O$ in each dm^3 of solution.
4	Hydrochloric acid (**FA 4)**	1.0 mol dm^{-3}	200 cm^3		Dilute 500 cm^3 of 2.0 mol dm^{-3} HC*l* to 1 dm^3 with distilled water.
5	manganese(IV) oxide, MnO_2 (**FA 5**)	-	About 6 g		In a stoppered weighing bottle labelled **FA 5**;
6	sulfuric acid (**FA 6**)	0.5 mol dm^{-3}	40 cm^3		Labelled **FA 6** Cautiously pour 27.5 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water. **Care:** concentrated H_2SO_4 is very corrosive **[MH]**
7	Solid sodium ethanedioate (**FA 7)**	-	about 2 g		In a stoppered bottle labelled **FA 7**
8	manganese(II) sulfate, $MnSO_4$ **FA 8**)	About 0.5 mol dm^{-3}	3 cm^3		dissolving, in deionised water, about 84.5 g of $MnSO_4.H_2O$ in each dm3 of solution. This solution must be stored in a a **stoppered** vial labelled **FA 8**
9	cyclohexene, C_6H_{10}, (**FA 9**)	-	about 1 cm^3		in a **stoppered** vial labelled **FA 9**;
10	bromine water, $Br_2(aq)$ (**FA 10**)	-	about 2 cm^3		in a **stoppered** vial labelled **FA 10**.

STANDARD BENCH REAGENTS

Hazard	Label	Identity	Notes (hazards given in this column are for the raw materials)
[MH]	Dilute hydrochloric acid	2.0 mol dm^{-3} HCl	Dilute 170 cm^3 of concentrated (35 – 37%; approximately 11 mol dm^{-3}) hydrochloric acid to 1 dm^{-3}
[C]	Dilute nitric acid	2.0 mol dm^{-3} HNO_3	Dilute 128 cm^3 of concentrated (70% w/v) nitric acid to 1 dm^3
[MH]	Dilute sulfuric acid	1.0 mol dm^{-3} H_2SO_4	Cautiously pour 55 cm^3 of concentrated (98%) sulfuric acid into 500 cm^3 of distilled water with continuous stirring. Make the solution up to 1 dm^3 with distilled water. **Care:** concentrated H_2SO_4 is very corrosive
[C][MH][N]	Aqueous ammonia	2.0 mol dm^{-3} NH_3	Dilute 112 cm^3 of concentrated (35%) ammonia to 1 dm^3
[C]	Aqueous sodium hydroxide	2.0 mol dm^{-3} NaOH	Dissolve 80.0 g of NaOH in each dm^3 of solution. **Care:** the process of solution is exothermic and any concentrated solution is very corrosive.
[MH]	Aqueous barium nitrate	0.1 mol dm^{-3} barium nitrate	Dissolve 26.1 g of $Ba(NO_3)_2$ in each dm^3 of solution.
[N]	Aqueous silver nitrate	0.05 mol dm^{-3} silver nitrate	Dissolve 8.5g of $AgNO_3$ in each dm^3 of solution.
[MH]	Limewater	Saturated aqueous calcium hydroxide, $Ca(OH)_2$	Prepare fresh limewater by leaving distilled water to stand over solid calcium hydroxide for several days, shaking occasionally. Decant or filter the solution.
	Aqueous potassium manganate (VII)	0.02 mol dm^{-3} potassium manganate (VII)	Dissolve 3.16g of $KMnO_4$ in each dm^3 of solution.
	Aqueous Iodine		Dissolve the 2.5g of solid in water containing sufficient potassium iodide to dissolve the iodine, then make up the solution to 1 dm^3 with distilled water.

The following materials and apparatus should be available **FOR EACH STUDENT**.

Red and blue litmus papers, plain filter strips for use with acidified manganate(VII), aluminium foil for testing nitrate/nitrite, wooden splints and the apparatus normally used in the Centre for use with limewater testing for carbon dioxide.

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/04

Paper 4 Practical **14 Aug 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.
An **insert** is printed on **page 21**.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	**7**
2	**21**
3	**27**
Total	**55**

This document consists of **20** printed pages and **2** blank pages.

1 You will find the relative atomic mass, A_r, of magnesium by measuring the volume of hydrogen produced when a known mass of metal reacts with an excess of acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

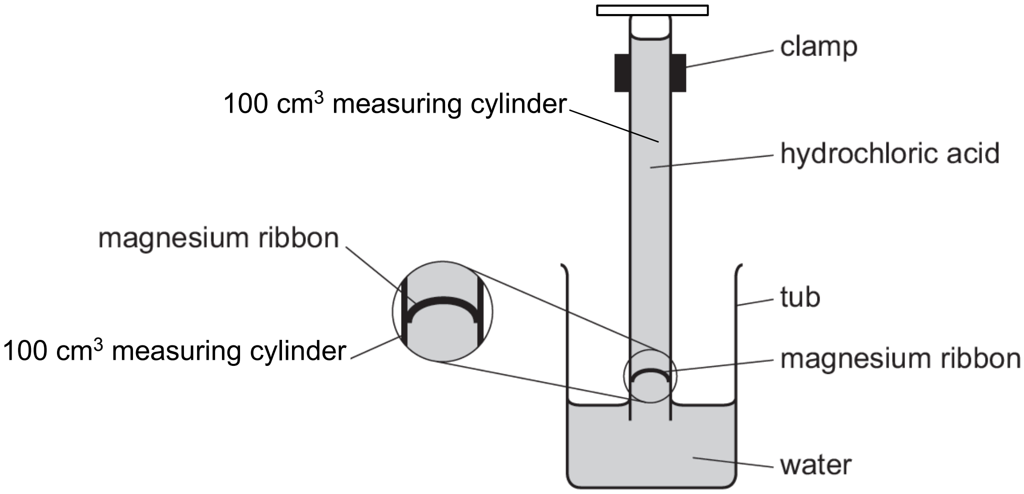
FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

FA 2 is magnesium, Mg.

(a) Method

Read through the whole method before starting any practical work.

- Fill the tub with water to a depth of about 5 cm.
- Weigh the magnesium, **FA 2** and note its mass below.
- Fill the 100 cm^3 measuring cylinder to about 30 cm^3 mark with hydrochloric acid, **FA 1**.
- Gently, with minimal disturbance to the surface of the solution, top up the measuring cylinder containing **FA 1** with distilled water to about 4 to 5 cm above the 100-cm^3 mark.
- Bend the **FA 2** strip into a U-shape.
- Carefully place the **FA 2** strip about half a centimeter into the measuring cylinder so that it is above the liquid and friction holds it in position.
- Hold a piece of paper towel over the open end of the measuring cylinder, invert the measuring cylinder and immediately place it in the tub of water. Remove the paper towel and clamp the measuring cylinder as shown in the diagram.



- The liquid level should now be on the scale of the measuring cylinder. If it is not, repeat the above procedure to set up your experiment again.
- Record the initial reading on the measuring cylinder. Remember that the scale is now upside down.
- Leave the apparatus so that the acid from the measuring cylinder diffuses around the **FA 2** and reacts.
- You should start **Question 2 or Question 3** while waiting for the reaction to complete.
- When all the **FA 2** has reacted, note and record the final reading on the measuring cylinder.
- Calculate the volume of hydrogen produced.

Results

[2]

M1	
M2	

(b) **Calculations**
Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of hydrogen produced.
(Assume that 1 mole of gas occupies 24.0 dm^3 under these conditions.)

(If you are unable to calculate the volume of hydrogen produced in **(a)**, you may assume that the volume of hydrogen produced is 70 cm^3 for the calculation here. Note: this is a hypothetic value.)

Amount of H_2 = ………………………… [1]

M3	

(ii) Use your answer to **(i)** and the mass of magnesium used to calculate the A_r of magnesium.

A_r of Mg = ………………………… [1]

M4	

(c) What would be the effect on the value of the A_r of magnesium calculated if the temperature of the room was much lower than that for your experiment? Explain your answer.

……

……

…… [2]

M5	
M6	

(d) A similar experiment was repeated using aluminium instead. The reaction was much slower. Explain why aluminium took a longer time to react completely.

……

…… [1]

M7	

[Total: 7]

2 Sodium thiosulfate reacts with acid to produce a pale yellow precipitate of sulfur.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(aq) + H_2O(l)$$

You will investigate how the rate of this reaction varies with the concentration of thiosulfate ions.
To do this, you will measure the time taken for a fixed amount of sulfur to be formed.

FA 3 is 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is 1.00 moldm^{-3} hydrochloric acid, HC*l*.

(a) **Experiment 1**

- Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4**.
- Pour the **FA 4** into the **FA 3** in the conical flask and start timing **immediately**.
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert (page **21**) provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 2**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 2

- Use the larger measuring cylinder to transfer 30 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the same measuring cylinder to add 10 cm^3 of distilled water to the conical flask.
- Use the smaller measuring cylinder to add 25 cm^3 of **FA 4** to the mixture in the beaker and start timing **immediately.**
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 3**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 3

Repeat **Experiment 2** using 20 cm^3 of **FA 3**, 20 cm^3 of distilled water and 25 cm^3 of **FA 4**.

Experiments 4 and 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of thiosulfate ions on the rate of the reaction. You should not use a volume of less than 10 cm^3 of **FA 3**.

Results

The relative rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- the reaction time, to the nearest second,
- the relative rate of the reaction, to 3 significant figures, for each of the five experiments

[5]

M8	
M9	
M10	
M11	
M12	

(b) On the grid, plot a graph of rate of reaction (y-axis) against volume of **FA 3** (x-axis).
Circle any points that you consider anomalous and draw a line of best fit to show how the rate of the reaction depends on the volume of **FA 3**. [3]

M13	
M14	
M15	

(c) **Use your graph** to calculate the time that the reaction would have taken if 8 cm^3 of **FA 3** had been used. Show **on the grid** how you obtained your answer.

time = ... [1]

M16	

(d) It has been claimed that the reaction is non-zero order with respect to [$S_2O_3^{2-}$].

State whether you agree or disagree with this claim. Use evidence from your graph to support your answer.

....

....

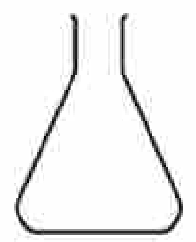
....

....

.... [2]

M17	
M18	

(e) A student broke the 100 cm^3 conical flask when carrying out the experiment and decided to use a petri dish instead. This has a different shape.


Conical Flask


Petri Dish

State and explain what effect this would have on the student's result.

....

....

.... [2]

M19	
M20	

(f) A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

Plan an investigation, based on the experiment described in **2(a)**, to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with

- 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
- 1.00 moldm^{-3} hydrochloric acid, HCl
- the equipment normally found in a school or college laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- an suitable number of experiments you would do, and a reasonable temperature range(minimum and maximum temperatures),
- the apparatus that you would use in addition to that specified in **2(a),**
- the procedure that you would follow and the measurements that you would take.

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.... [4]

M21	
M22	
M23	
M24	

(g) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

....

.... [1]

M25	

[Total: 21]

M26	
M27	
M28	

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added.

Where gases are released, they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

Question 3 consists of two tasks.

In the first task, you are to explore the chemistry of some compounds of an unknown transition element **W** and determine its identities.

FA 5 is a solid sample of a common dioxide of the unknown transition element **W**,
FA 6 is dilute sulfuric acid, H_2SO_4,
FA 7 is a solid sample of sodium ethanedioate, $Na_2C_2O_4$,
FA 8 is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

(a) (i)

Test	Observations
Transfer all of the solid sample of **FA 7** into a small conical flask. Add 25 cm^3 of **FA 6** to this flask. Gently heat the flask until the temperature of the mixture reaches about 60 °C. Swirl the mixture carefully. Place the flask on the heat proof mat. Using a spatula, add **FA 5** to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture. Stop adding **FA 5** to the mixture when you think the reaction is complete.	

Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate is compound **X**. Retain this filtrate for use in **(a)(ii).**	
While you are waiting for (a)(i) to be complete, continue with (c). The colour of the filtrate may change on standing.	

[3]

M29	
M30	
M31	

(a) **(ii)** In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, to separate portions of the filtrate from **(a)(i)** and **FA 8**.

In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

M32	
M33	
M34	

[3]

(b) **(i)** Give **two** conclusions you can draw about the nature of the reaction occurring in **(a)(i).**

In each case, support your conclusion by referring to your observations.

Conclusion **1**……………………………………………………………………...

Evidence……………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

Conclusion **2**……………………………………………………………………...

Evidence……………………………………………………………………………..

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…………………………………………………………………………………… [2]

M35	
M36	

(ii) Explain why you decided to stop the addition of **FA 5** at the point you chose in **(a)(i)**.

You should support your answer by referring to your observations.

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……………………………………………………………………………………. [1]

M37	

(iii) Consider your observations in **(a)(ii).**

Identify the transition metal ion formed in **(a)(i)** and suggest an explanation for the differences between your observations when you added aqueous sodium hydroxide to the filtrate from **(a)(i)**, and to **FA 8**.

Ion present is …………………………………..

Explanation for difference ..……………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………. [1]

M38	

(iv) In **(a)(i)**, the reaction between **FA 5** and **FA 7** occurs under acidic conditions.

Write an ionic equation for this reaction. Use the letter '**W**' to represent the transition metal in this equation.

……………………………………………………………………………………. [1]

M39	

In the second task, you are to perform a series of test to deduce the structure of the unknown hydrocarbon, **FA 9**.

FA 9 is a simple hydrocarbon compound,
FA 10 is bromine water.

(c)

	Test	observations
(i)	Place 5 cm^3 of aqueous sodium hydroxide in a test-tube. Add **1 drop** of **FA 9** to this test-tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	
	Note: Eventually, this reaction will produce a brown MnO_2 precipitate. There is no need for you to wait for this to happen.	
(ii)	Place 5 cm^3 of dilute sulfuric acid in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	
(iii)	Place 5 cm^3 of water in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add **FA 10,** dropwise with shaking, until no further change is seen.	

[3]

M40	
M41	
M42	

Conclusions

(d) Consider the identities of the Mn-containing reactant and eventual product in **(c)(i).**

Suggest a value for the oxidation number of Mn in the coloured ion produced in **(c)(i).** Explain your reasoning.

Oxidation number of Mn………………………………..

Explanation…………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………….. [1]

M43	

(e) Compound **Y** is the main organic product in **(c)(i)**, when **FA 9** reacts with $KMnO_4$ under alkaline conditions. The molecular formula of **Y** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation must be supported by evidence from your observations in **(c)**.

Molecular formula of **FA 9** is ……………………………………………………

Explanation…………………………………………………………………

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…………………………………………………………………………………..

…………………………………………………………………………………..

……………………………………………………………………………… [2]

M44	
M45	

(ii) Draw the structural formulae for **FA 9** and compound **Y**.

Explain how you deduced the structure of **FA 9**.

Structure of **FA 9**	Structure of **Y**

Explanation…………………………………………………………………

…………………………………………………………………………………..

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…………………………………………………………………………………..

……………………………………………………………………………… [2]

M46	
M47	

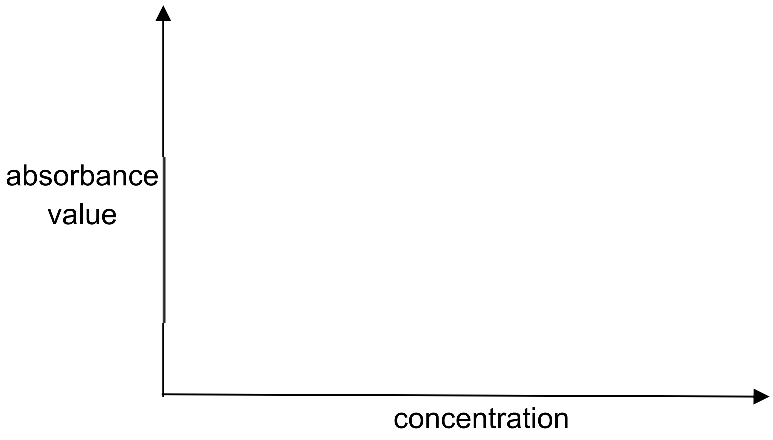
(f) **Planning**

Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion. A few cm^3 of the solution is placed inside a machine, known as a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an *absorbance value.* The more concentrated the solution, the higher the absorbance value, i.e., the absorbance value is directly proportional to the concentration of the solution.

This technique can be used to determine the concentration of a solution of aqueous $\mathbf{W}O_4^-$. A series of known, but different, concentration of solution containing $\mathbf{W}O_4^-$ is prepared. A spectrometer is used to measure the absorbance of each solution. A graph of absorbance against concentration is then plotted. This graph is known as a calibration line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of $\mathbf{W}O_4^-$ in the unknown solution can be determined.

(i) Sketch the calibration line for the graph of absorbance against concentration that you would expect to obtain.



[1]

M48	

(ii) Using the information given above, you are required to write a plan to determine the concentration of **W**O_4^- in a solution of **Z**.

You may assume that you are provided with:

- solution **Z**, of unknown **W**O_4^- concentration less than 2 mol dm^{-3};
- a standard solution containing 5.00 mol dm^{-3} of **W**O_4^-;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 100.0 cm^3 of 2.00 mol dm^{-3} aqueous **W**O_4^-;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- how the calibration line would be used to determine the concentration of **W**O_4^- in solution **Z**.

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.... [7]

M49	
M50	
M51	
M52	
M53	
M54	
M55	

[Total: 21]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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INSERT

Please detach the insert from the question paper for use in **Question 2**.

Innova junior college Innova junior

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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CLASS		INDEX NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

14 Aug 2018

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.
An **insert** is printed on **page 21**.

At the end of the examination, fasten all your work securely together.
The number of marks is given in the brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	**7**
2	**21**
3	**27**
Total	**55**

This document consists of **20** printed pages and **2** blank pages.

1 You will find the relative atomic mass, A_r, of magnesium by measuring the volume of hydrogen produced when a known mass of metal reacts with an excess of acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

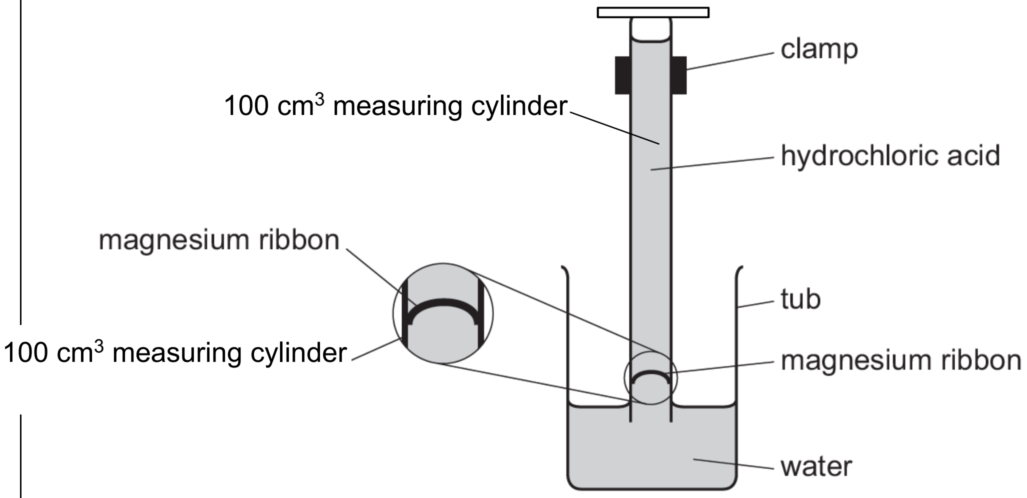
FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

FA 2 is magnesium, Mg.

(a) **Method**

Read through the whole method before starting any practical work.

- Fill the tub with water to a depth of about 5 cm.
- Weigh the magnesium, **FA 2** and note its mass below.
- Fill the 100 cm^3 measuring cylinder to about 30 cm^3 mark with hydrochloric acid, **FA 1**.
- Gently, with minimal disturbance to the surface of the solution, top up the measuring cylinder containing **FA 1** with distilled water to about 4 to 5 cm above the 100-cm^3 mark.
- Bend the **FA 2** strip into a U-shape.
- Carefully place the **FA 2** strip about half a centimeter into the measuring cylinder so that it is above the liquid and friction holds it in position.
- Hold a piece of paper towel over the open end of the measuring cylinder, invert the measuring cylinder and immediately place it in the tub of water. Remove the paper towel and clamp the measuring cylinder as shown in the diagram.



- The liquid level should now be on the scale of the measuring cylinder. If it is not, repeat the above procedure to set up your experiment again.
- Record the initial reading on the measuring cylinder. Remember that the scale is now upside down.
- Leave the apparatus so that the acid from the measuring cylinder diffuses around the **FA 2** and reacts.
- You should start **Question 2 or Question 3** while waiting for the reaction to complete.
- When all the **FA 2** has reacted, note and record the final reading on the measuring cylinder.
- Calculate the volume of hydrogen produced.

Results

Mass of Mg used /g	0.069
Initial reading on measuring cylinder / cm^3	10.0
Final reading on measuring cylinder / cm^3	85.0
Volume of H_2 produced /cm^3	75.0

M1 mass of magnesium, initial and final readings and **volume of hydrogen** with **unambiguous headings** and **correct unit.**
M2 mass recorded to 3d.p. and readings recorded to nearest 0.5 cm^3.

[2]

M1	
M2	

(b) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of hydrogen produced.
(Assume that 1 mole of gas occupies 24.0 dm^3 under these conditions.)

(If you are unable to calculate the volume of hydrogen produced in **(a)**, you may assume that the volume of hydrogen produced is 70 cm^3 for the calculation here. Note: this is a hypothetic value.)

M3 Correct calculation moles H_2 = volume collected / 24000 mol

Amount of H_2 = 75/24000
= 3.125×10^{-3}
= 3.13×10^{-3} mol

Amount of H_2 = ... [1]

M3	

(ii) Use your answer to **(i)** and the mass of magnesium used to calculate the A_r of magnesium.

M4 Correctly calculation using $A_r = \dfrac{\text{mass used}}{\text{amount of } H_2}$

Ar = 0.0690/ 3.125×10^{-3}
= 22.08
= 22.1

A_r of Mg = ... [1]

M4	

(c) What would be the effect on the value of the A_r of magnesium calculated if the temperature of the room was much lower than that for your experiment? Explain your answer.

....

		.... [2]	**M5** **M6**	
		M5 Volume (gas) measured/**or** moles/amount gas/H_2 would have been less **M6** *correct link betw Ar and amt/vol i.e* A_r greater (conditional: must follow from smaller **moles** of H_2/Mg) **or** **M5** Use correct molar volume for new room temperature **M6** A_r unchanged (but must follow from V_m smaller)		
	(d)	A similar experiment was repeated using aluminium instead. The reaction was much slower. Explain why aluminium took a longer time to react completely.		
		.... [1]	**M7**	
		M7 Aluminium has a protective **oxide layer** Or Al is **less reactive** than Mg. Hence, slower.		
		[Total: 7]		

2 Sodium thiosulfate reacts with acid to produce a pale yellow precipitate of sulfur.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(aq) + H_2O(l)$$

You will investigate how the rate of this reaction varies with the concentration of thiosulfate ions.
To do this, you will measure the time taken for a fixed amount of sulfur to be formed.

FA 3 is 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is 1.00 moldm^{-3} hydrochloric acid, HC*l*.

(a) **Experiment 1**

- Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4**.
- Pour the **FA 4** into the **FA 3** in the conical flask and start timing **immediately**.
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert (page **21**) provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 2**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 2

- Use the larger measuring cylinder to transfer 30 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the same measuring cylinder to add 10 cm^3 of distilled water to the conical flask.
- Use the smaller measuring cylinder to add 25 cm^3 of **FA 4** to the mixture in the beaker and start timing **immediately.**
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 3**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 3

Repeat **Experiment 2** using 20 cm^3 of **FA 3**, 20 cm^3 of distilled water and 25 cm^3 of **FA 4**.

Experiments 4 and 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of thiosulfate ions on the rate of the reaction. You should not use a volume of less than 10 cm^3 of **FA 3**.

Results

The relative rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- the reaction time, to the nearest second,
- the relative rate of the reaction, to 3 significant figures, for each of the five experiments

Expt No	Volume of **FA 3** / cm^3	Volume of water / cm^3	Reaction time/ s	Rate of reaction/ s^{-1}
1	40.0	0.0	27	37.0
2	30.0	10.0	36	27.8
3	20.0	20.0	60	16.7
4	25.0	15.0	43	23.3
5	10.0	30.0	136	7.35

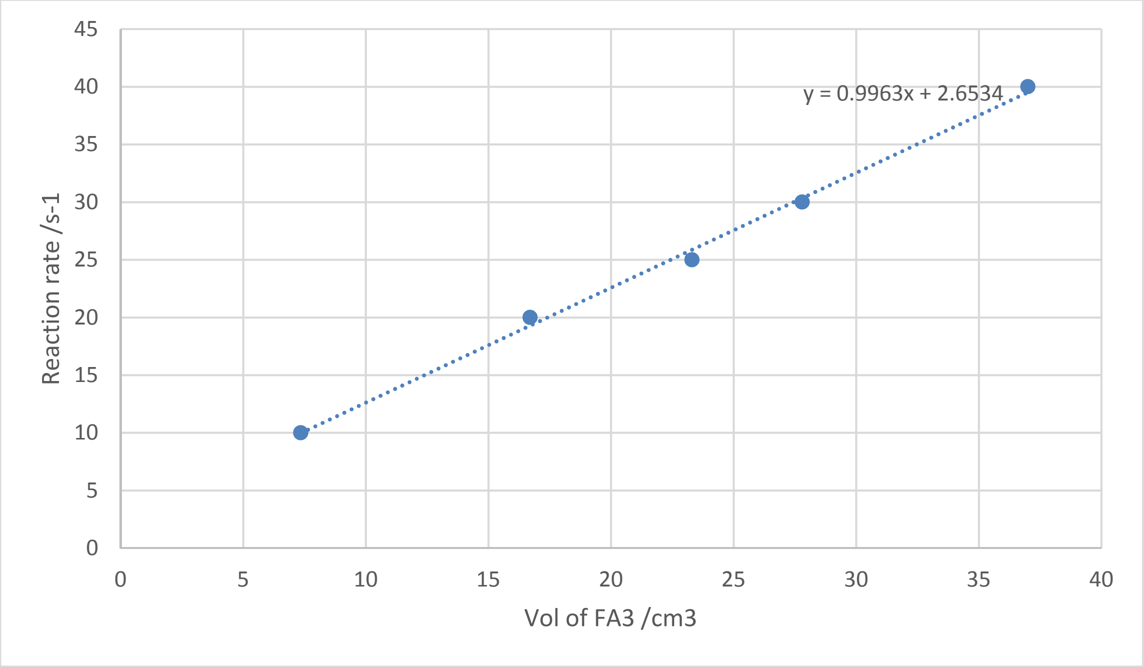
M8– Table that shows volume of FA 3, volume of water, time and rate for 5 experiments. Correct unit for all data: volume(cm^3), time(s), rate(s^{-1})
M9 – all times recorded to the nearest second **(whole number)**, all volume to 1 dp
M10 – Two additional experiments with volume FA 3 not less than 10 cm^3, not more than 40 cm^3 and no volume $\leq$ 2cm^3 close to another volume. Volume of water chosen so that FA 3 + water = 40 cm^3 for the additional experiments. 40cm3, 30cm3, 20cm3 must be present in the table.
M11 – Correctly calculates rate for all experiments and shown to 3 sf.
M12 – Award if candidate's (time for FA3 = 20)/(time for FA3 = 40) is between 1.90 and 2.40.

M8	
M9	
M10	
M11	
M12	

[5]

	(b)	On the grid, plot a graph of rate of reaction (y-axis) against volume of **FA 3** (x-axis). Circle any points that you consider anomalous and draw a line of best fit to show how the rate of the reaction depends on the volume of **FA 3**. [3]

M13	
M14	
M15	



M13 – scales that cover more than half the space in both directions and axes labelled correctly with units.
M14 – points plotted correctly. Points must be within half a small square of the correct position.
M15 – line of best fit drawn which ignores anomalous results identified by the candidate

(c) **Use your graph** to calculate the time that the reaction would have taken if 8 cm^3 of **FA 3** had been used. Show **on the grid** how you obtained your answer.

M16 – correct line drawn within 1 small square (horizontal line must be shown) and correctly calculates (1000/ rate)

When 8 cm3 of FA3 is used,
Reaction rate = 10.6

Reaction time = 1000/10.6
= 94.3s

time = ... [1]

M16	

(d) It has been claimed that the reaction is non-zero order with respect to $[S_2O_3^{2-}]$.

State whether you agree or disagree with this claim. Use evidence from your graph to support your answer.

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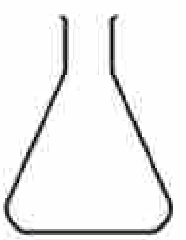
.... [2]

M17	
M18	

Agree or disagree (conditional) **M17**
discuss shape of graph/ gradient compared to zero order or finding $t_{½}$ to prove first order and thus is non-zero. **M18**

(e) A student broke the 100 cm^3 conical flask when carrying out the experiment and decided to use a petri dish instead. This has a different shape.



Conical Flask

Petri Dish

State and explain what effect this would have on the student's result.

....

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.... [2]

M19	
M20	

The time recorded will be **longer. M19** **(Conditional; provided understanding that more sulfur is required is shown in explanation)**
More sulfur is required to be formed in order to cover the mark. **M20**

(f) A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

Plan an investigation, based on the experiment described in **2(a)**, to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with

- 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
- 1.00 moldm^{-3} hydrochloric acid, HC*l*
- the equipment normally found in a school or college laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- an suitable number of experiments you would do, and a reasonable temperature range(minimum and maximum temperatures),
- the apparatus that you would use in addition to that specified in **2(a),**
- the procedure that you would follow and the measurements that you would take.

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.... [4]

1. Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 beaker.
2. Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4** into another 100 cm^3 beaker.
3. Place both of them in a water bath set at 30°C/ Heat and maintain both solution at 30°C.
4. Ensure that both solutions have reached 30°C by using a thermometer to measure their initial temperature.
5. Pour the **FA 4** into the beaker containing **FA 3** and start timing immediately.
6. Stir the mixture in the beaker once and place the beaker on top of the printed insert provided.
7. Look down through the solution in the beaker at the print on the insert.
8. Stop timing as soon as the precipitate of sulphur makes the print on the insert just invisible.
9. Record the reaction time to the nearest second.
10. Repeat the experiment with the same volume of **FA 3** and **FA 4** used but at temperature 35°C, 40°C, 45°C, 50°C and 55°C.

M21– at least 5 experiments (not repeats of the same expt)
M22 – experiments covering at least a 25°C range (no greater than 100°C)
M23 – Maintaing the volumes of both reagents to be the same for all experiment. (Marks can be awarded if students repeat same experiment but volume is kept the same) ;
M24– Indication of **changing** and **maintaining** temperature either via direct heating or water bath.

(g) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

....

.... [1]

		Reference to “hot” apparatus/ sulfur dioxide evolved/ HCl acid (ignore any reference to possible effects) **with** use of **heat proof(thick)** gloves/ use of tongs/ use of fume cupboard. **M25** Spillages and goggles not accepted.
		Shows working in **all** calculations in **1(b)(i) and (ii)**, **2(c).** All calculations must be relevant although they may not be complete or correct. *Any calculation not attempted loses this mark.* **M26** Shows appropriate significant figures (3 ~~or 4 sf~~) in **all** final answers in **1(b)(i)**, **2(c)** and 1 dp in **1(b)(ii)** *Any calculation not attempted loses this mark.* **M27** Shows correct and appropriate units in **all** answers in **1(b)(i) (mol)**, **2(c)(s).** *Any calculation not attempted loses this mark.* **M28**
		[Total: 21]

M21	
M22	
M23	
M24	

M25	

M26	
M27	
M28	

3 **Qualitative Analysis**

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added.

Where gases are released, they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

Question 3 consists of two tasks.

In the first task, you are to explore the chemistry of some compounds of an unknown transition element **W** and determine its identities.

FA 5 is a solid sample of a common dioxide of the unknown transition element **W**,
FA 6 is dilute sulfuric acid, H_2SO_4,
FA 7 is a solid sample of sodium ethanedioate, $Na_2C_2O_4$,
FA 8 is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

(a)	**(i)**	Test	Observations
		Transfer all of the solid sample of **FA 7** into a small conical flask. Add 25 cm^3 of **FA 6** to this flask.	
		Gently heat the flask until the temperature of the mixture reaches about 60 °C.	White solid $Na_2C_2O_4$ dissolves (completely). [/]
		Swirl the mixture carefully. Place the flask on the heat proof mat.	
		Using a spatula, add **FA 5** to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture.	Effervescence/ bubbles after each addition. [/] $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$ Gas produced white ppt in $Ca(OH)_2$ [/] Temperature of mixture rises (even though no heat is applied) [/]
		Stop adding **FA 5** to the mixture when you think the reaction is complete.	Temperature rise stops/ Temperature falls / mixture starts to cool/

Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate is compound **X**. Retain this filtrate for use in **(a)(ii).**	effervescence much less vigorous on addition of more **FA 5**. (reaction is complete)[/] 4 - 5[/] – 3 mark 2 - 3[/] – 2 mark 1[/] – 1 mark **M29, M30, M31**

M29	
M30	
M31	

While you are waiting for (a)(i) to be complete, continue with (c).
The colour of the filtrate may change on standing.

[3]

(a) **(ii)** In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, to separate portions of the filtrate from **(a)(i)** and **FA 8**.

In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

Test	Filtrate	**FA 8**
To a 1 cm depth of filtrate from **(a)(i)**in a test tube, add **NaOH(aq) (dropwise),** with shaking, until in **excess**.	A light brown ppt is formed and the ppt is insoluble in excess NaOH(aq) [/]. On standing, the ppt turns brown. [/]	A off-white ppt is formed and the ppt is insoluble in excess NaOH(aq) [/]. On standing, the ppt turns brown. [/]
	$Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_2$ $Mn(OH)_2 \rightarrow Mn(OH)_3$	

[3]

M32	
M33	
M34	

Both procedure 1 mark (Students can combine both procedure into one) The procedure should describe the addition of a **small volume**/ (dropwise addition), and the addition of an **excess**, of NaOH (aq), both with shaking, to separate samples. **M32**	2[/] – **M33** 4[/] – **M33, M34**

(b) **(i)** Give **two** conclusions you can draw about the nature of the reaction occurring in **(a)(i).**

In each case, support your conclusion by referring to your observations.

Conclusion **1**……………………………………………………………………..

Evidence…………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………………

Conclusion **2**…………………………………………………………………………..

Evidence……………………………………………………………………………..

……………………………………………………………………………………………

…………………………………………………………………………………… [2]

M35	
M36	

Conclusion 1: the reaction is exothermic.
Evidence: the temperature increased, (without further heating), as **FA 5** was added. **M35**

Conclusion 2: It is a redox reaction
Evidence: Positive limewater test shows that CO_2 is evolved because $C_2O_4^{2-}$ is oxidised (by **FA 5**) **M36**

(ii) Explain why you decided to stop the addition of **FA 5** at the point you chose in **(a)(i)**.

You should support your answer by referring to your observations.

……………………………………………………………………………………………

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……………………………………………………………………………………………

…………………………………………………………………………………… [1]

Either a convincing explanation based on the cessation of effervescence/bubbles (on addition of more **FA 5)**

OR

A convincing explanation based on the temperature stops rising/starts to fall/remain constant (on addition of more **FA 5)** **M37**

(iii) Consider your observations in **(a)(ii).**

Identify the transition metal ion formed in **(a)(i)** and suggest an explanation for the differences between your observations when you added aqueous sodium hydroxide to the filtrate from **(a)(i)**, and to **FA 8**.

Ion present is …………………………………..

Explanation for difference ……………………………………………………….

			…………………………………………………………………………………… …………………………………………………………………………………… [1]	M37
			Ion present is Mn^{2+} Some Mn^{2+} in the filtrate is partially oxidised on standing/ in air (to Mn^{3+}, hence resulting in formation of $Mn(OH)_3$.) **M38**	
		(iv)	In **(a)(i)**, the reaction between **FA 5** and **FA 7** occurs under acidic conditions. Write an ionic equation for this reaction. Use the letter '**W**' to represent the transition metal in this equation.	
			…………………………………………………………………………………… [1]	M38
			$\mathbf{W}O_2(s) + 4H^+(aq) + C_2O_4^{2-}(aq) \rightarrow \mathbf{W}^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$ Accept: $2\mathbf{W}O_2(s) + 8H^+(aq) + C_2O_4^{2-}(aq) \rightarrow 2\mathbf{W}^{3+}(aq) + 4H_2O(l) + 2CO_2(g)$ **M39**	M39

	In the second task, you are to perform a series of test to deduce the structure of the unknown hydrocarbon, **FA 9**. **FA 9** is a simple hydrocarbon compound, **FA 10** is bromine water.			
	(c)	**(i)**	Test	observations
			Place 5 cm^3 of aqueous sodium hydroxide in a test-tube. Add **1 drop** of **FA 9** to this test-tube. Add aqueous potassium manganate(VII)**,** dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	(Purple KMnO4 decolourises) Solution turns green/ blue green [/] Colour deepens as more drops added. [/]
			Note: Eventually, this reaction will produce a brown MnO_2 precipitate. There is no need for you to wait for this to happen.	
		(ii)	Place 5 cm^3 of dilute sulfuric acid in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add aqueous potassium manganate(VII)**,** dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	Purple **FA 6** decolourise. [/] $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ Colourless solution turns progressively darker brown. [/]
		(iii)	Place 5 cm^3 of water in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add **FA 10,** dropwise with shaking, until no further change is seen.	Brown bromine water decolourise. (Brown solution turns yellow) [/] 5[/] – 3 marks 3 -4 [/] – 2 marks 1 -2 [/] – 1 mark **M40, M41, M42**
				[3]
Conclusions				
	(d)	Consider the identities of the Mn-containing reactant and eventual product in **(c)(i).** Suggest a value for the oxidation number of Mn in the coloured ion produced in **(c)(i).** Explain your reasoning.		
		Oxidation number of Mn…………………………….. Explanation…………………………………………………………………………		

		…………………………………………………………………………………………… ……………………………………………………………………………………… [1]	**M43**
		Allow oxidation numbers of +5 or +6 And An explanation along the lines of - The oxidation numbers of Mn in MnO_4^- and in MnO_2 are +7 and +4 respectively. - So, as the reaction in **(c)(i)** involves a change of oxidation number from +7 to +4, The oxidation number of the coloured ion will be between these value. M43	

(e) Compound **Y** is the main organic product in **(c)(i)**, when **FA 9** reacts with $KMnO_4$ under alkaline conditions. The molecular formula of **Y** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation must be supported by evidence from your observations in **(c)**.

Molecular formula of **FA 9** is ……………………………………………………

Explanation……………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

…………………………………………………………………………………

………………………………………………………………………………… [2]

M44	
M45	

Explanations based on the following points

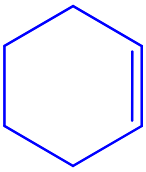
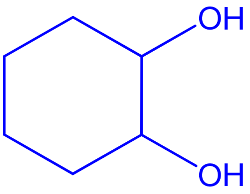
Molecular formula: C_6H_{10} **M44**

- Br_2(aq) decolourised, so C = C present
- Cold alkaline MnO_4^- oxidises C=C to C(OH) – C(OH)/1,2-diol
- Only two O atoms in molecular formula of **Y**, so only one C =C bond.
- So **FA 9** is $C_6H_{12}O_2 - 2 \times OH = C_6H_{10}$

M45 any 2 points mentioned

(ii) Draw the structural formulae for **FA 9** and compound **Y**.

Explain how you deduced the structure of **FA 9**.

Structure of **FA 9**	Structure of **Y**
	

				M46 for both structure correctly drawn
			Explanation…………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… [2]	
			Explanation along the lines of • C_6H_{10} has two double bond equivalents • There is only one C=C bond in the molecule So the compound must be cyclic. **M47(idea along this line)**	

M46	
M47	

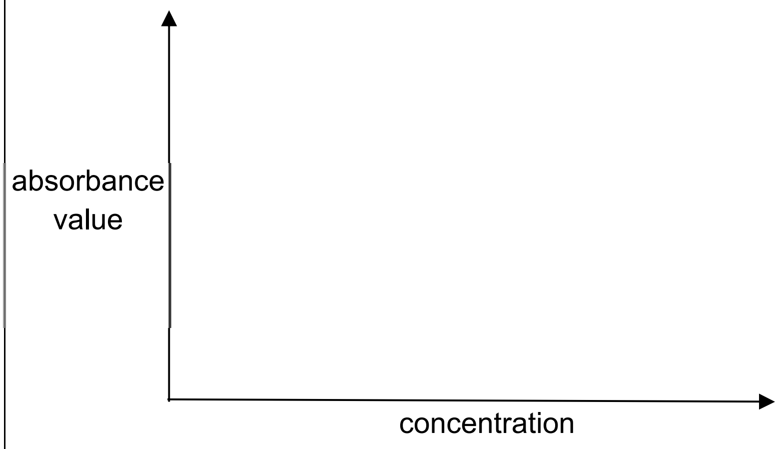
(f) **Planning**

Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion. A few cm^3 of the solution is placed inside a machine, known as a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an *absorbance value.* The more concentrated the solution, the higher the absorbance value, i.e., the absorbance value is directly proportional to the concentration of the solution.

This technique can be used to determine the concentration of a solution of aqueous $\mathbf{WO_4^-}$. A series of known, but different, concentration of solution containing $\mathbf{WO_4^-}$ is prepared. A spectrometer is used to measure the absorbance of each solution. A graph of absorbance against concentration is then plotted. This graph is known as a calibration line.

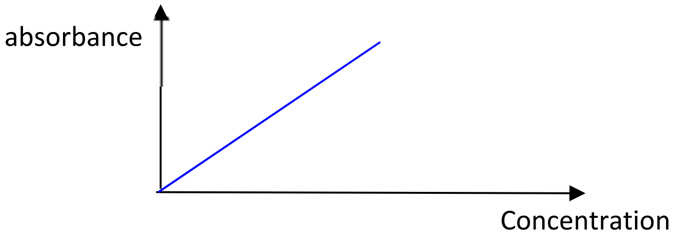
The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of $\mathbf{WO_4^-}$ in the unknown solution can be determined.

(i) Sketch the calibration line for the graph of absorbance against concentration that you would expect to obtain.



[1]

M48	



Correct graph **M48**

(ii) Using the information given above, you are required to write a plan to determine the concentration of **W**O_4^- in a solution of **Z**.

You may assume that you are provided with:

- solution **Z**, of unknown **W**O_4^- concentration less than 2 mol dm^{-3};
- a standard solution containing 5.00 mol dm^{-3} of **W**O_4^-;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 100.0 cm^3 of 2.00 mol dm^{-3} aqueous **W**O_4^-;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- how the calibration line would be used to determine the concentration of **W**O_4^- in solution **Z**.

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.... [7]

M49	
M50	
M51	
M52	
M53	
M54	
M55	

Preparation of 100.0 cm^3 of 2.00 mol dm^{-3} of aqueous **WO_4^-**

Amount of **WO_4^-** in 100cm^3 of 2.00 mol dm^{-3} **WO_4^-** solution
= (100/1000) x 2.00
= 0.200 mol

Volume of 5.00 mol dm^{-3} standard solution required
= 0.2 / 5.00 = 0.04 dm^3 = 40 cm^3

1. Fill the burette with a standard solution containing 5.00 mol dm^{-3} of **WO_4^-**.
2. Run 40.00 cm^3 of the solution into a 100cm^3 volumetric flask.
3. Make up to the mark with deionised water.
4. Stopper, invert and shake the volumetric flask to obtain a homogeneous solution. Label this solution **Q**.

Preparation of a suitable range of diluted solutions

No	Volume of solution Y/ cm^3	Volume of distilled water / cm^3	Concentration of **WO_4^-** prepared/ mol dm^{-3}	Absorban A
1	20	0	2.00	
2	15	5	1.50	
3	10	10	1.00	
4	5	15	0.50	
5	0	20		

Table 2

5. To prepare 1.50 mol dm^{-3} solution, using a burette, measure out 15.00 cm^3 of solution **Q** into a 50 cm^3 beaker.
6. Using another burette, measure out 5.00 cm^3 of deionised water into the same beaker. Stir/ swirl the beaker to obtain a homogeneous solution.
7. Repeat step 5 and 6 with different volumes of solution Y and distilled water to prepare the stated concentrations of dilute solution.

Outline of how results would be obtained

8. Use the spectrometer to measure the absorbance of each of the diluted solutions prepared and record the absorbance in Table 2.
9. Plot a graph of the absorbance against concentration.
10. Draw the calibration line. (Best fit- linear line going through the origin)

Use of calibration line to determine unknown concentration

11. Using the spectrometer, measure and record absorbance of **WO_4^-** from solution **Z**.
12. Using the graph drawn in step 10, read off the corresponding concentration of **WO_4^-** from the calibration line.

Correct volume (40 cm^3) of 5.00 mol dm^{-3} solution used (BOD if student did not show pre-calculation) **M49**

- **40cm^3 if it is 100cm^3 volumetric flask**
- **100cm^3 if it is 250cm^3 volumetric flask(student must mention in the procedure that they will pour out 100cm^3)**

			Correct procedure for preparing 2.00 mol dm^{-3} solution using a volumetric flask (top up to the mark; stopper; invert and shake) **M50** Use of suitable apparatus with stated capacity **M51** - Burette for measuring out 40cm^3 - Volumetric flask - Mention of appropriate apparatus for dilution Correct dilution concept for preparing diluted solutions (ignore use of less accurate apparatus; allow logical, scientifically – sound preparation of concentrations) **M52** - Using solution of known concentration Suitable concentration of diluted solutions (at least 3 more solutions apart from the 2.00 mol dm^{-3} solution prepared, need not prepare 0 mol dm^{-3}; table not required) Students need to calculate out the concentration in their planning. **M53** Measurement of absorbance of various diluted solutions using spectrometer, and plotting of graph of absorbance against concentration. **M54** Measurement of absorbance of solution **Z** and use of the absorbance value to read off the corresponding concentration in the calibration graph (award if students convey the idea in a graphical diagram) **M55**
			[Total: 21]

Qualitative Analysis Notes
[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^- (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^- (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^- (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

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INSERT

Please detach the insert from the question paper for use in **Question 2**.

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JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY **9729/01**

Higher 2

Paper 1 Multiple Choice **13 September 2018**

1 hour

Candidates answer on separate paper.

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** or **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages and **1** blank page.

1 The successive ionisation energies (IE) of two elements, **E** and **J**, are given below:

IE/ kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th	7th	8th
E	550	1065	4138	5500	6910	8760	10230	11800
J	1140	2103	3470	4560	5760	8550	9940	18600

What is the likely formula of the compound that is formed when **E** reacts with **J**?

A $\mathbf{EJ_2}$

B **EJ**

C $\mathbf{E_2J}$

D $\mathbf{E_2J_3}$

2 Carbon, silicon and germanium are Group 14 elements and they all exist in a structure similar to diamond.

The given table shows the bond lengths in these structures.

Element **X**	C	Si	Ge
Bond length **X**–**X** / nm	0.154	0.234	0.244

Which of the following explain why the bond length increases down the group?

1 Degree of orbital overlap decreases down the group.
2 Atomic radius increases down the group.
3 Nuclear charge increases down the group.
4 Electronegativity decreases down the group.

A 1, 2, 3 and 4
B 1 and 2 only
C 1 and 3 only
D 2 and 4 only

3 Which of the following **cannot** be explained by hydrogen bonding?

A the existence of the hydrogen-difluoride anion, HF_2^-
B the difference in volatility between pentan-1-ol and hexan-1-ol
C the difference in melting point between 2-nitrophenol and 4-nitrophenol
D the higher than expected relative molecular mass of ethanoic acid in benzene

4 The percentage by mass of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25%.

What is the mass of magnesium chloride present in 100 g of the mixture?

A 47 g **B** 51 g

C 53 g **D** 56 g

5 When 10 cm^3 of a gaseous hydrocarbon **X** was burned in 70 cm^3 of oxygen, the final gaseous mixture contained 30 cm^3 of carbon dioxide and 20 cm^3 of unreacted oxygen.

What is the formula of hydrocarbon **X**?

[All gaseous volumes are measured under identical conditions.]

A C_2H_6 **B** C_3H_6

C C_3H_8 **D** C_4H_{10}

6 An ion of metal **L** can be oxidised by potassium manganate(VII) in acid solution to form $\mathbf{L}O_3^-$. In an experiment, 1.25×10^{-3} mol of the ion of **L** required 37.5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) for complete reaction.

What is the initial oxidation state of the ion of **L** given that potassium manganate(VII) is reduced to Mn^{2+}?

A +1 **B** +2

C +3 **D** +4

7 Given the following standard enthalpy changes,

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad -394 \text{ kJ mol}^{-1}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad -286 \text{ kJ mol}^{-1}$$

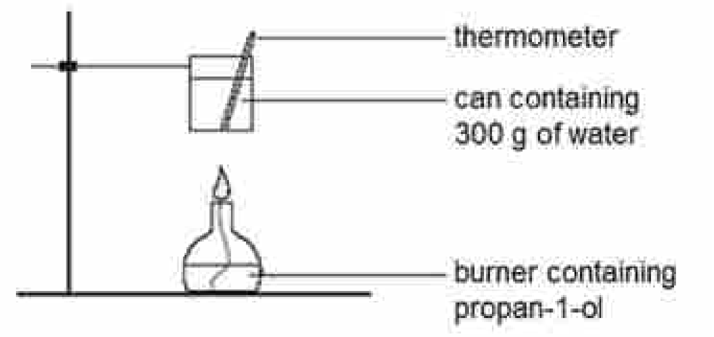
$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad -278 \text{ kJ mol}^{-1}$$

What is the standard enthalpy change of combustion of liquid ethanol, C_2H_5OH?

A –402 kJ mol^{-1} **B** –758 kJ mol^{-1}

C –1368 kJ mol^{-1} **D** –1924 kJ mol^{-1}

8 A student used the set–up below to heat a can containing 300 g of water.



The following data were recorded:

mass of propan–1–ol burnt = m g
change in temperature of water = ΔT °C

Given that:

relative molecular mass of propan–1–ol = 60.0
enthalpy change of combustion of propan–1–ol = –2021 kJ mol^{-1}
specific heat capacity of water = c J g^{-1} K^{-1}

What is the efficiency of this heating process?

A $\dfrac{m \times 2021 \times 1000}{300 \times c \times \Delta T \times 60.0} \times 100\%$

B $\dfrac{m \times c \times \Delta T \times 60.0}{300 \times 2021 \times 1000} \times 100\%$

C $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021} \times 100\%$

D $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$

9 The experimental results obtained for the reaction between **X** and **Y** at constant temperature are given in the table below.

Experiment	[**X**] / mol dm^{-3}	[**Y**] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.3	0.2	4.00×10^{-4}
2	0.6	0.4	1.60×10^{-3}
3	0.6	1.2	1.44×10^{-2}

What is the rate equation for this reaction?

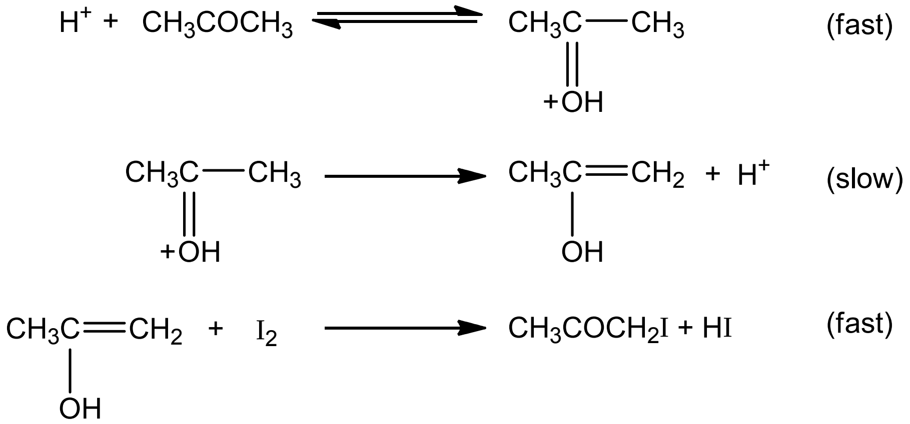
A Rate = $k[\mathbf{Y}]^2$

B Rate = $k[\mathbf{X}]^2$

C Rate = $k[\mathbf{X}]^2[\mathbf{Y}]$

D Rate = $k[\mathbf{X}][\mathbf{Y}]^2$

10 The mechanism for the iodination of propanone in aqueous acid involves the following steps.



Which of the following statements are true?

1 The overall order of the reaction is 1.

2 The acid acts as a catalyst.

3 The rate equation is rate = $k[CH_3COCH_3][H^+]$

4 The rate of the reaction is not affected by a change in the iodine concentration.

A 1, 2 and 4 only

B 2, 3 and 4 only

C 1 and 2 only

D 2 and 3 only

11 The rate of removal of *Aspirin*, a pain-killer drug, from the body is a first order reaction with a half-life of 2.0 h.

How long does it take for 87.5% of *Aspirin* to be removed from the body?

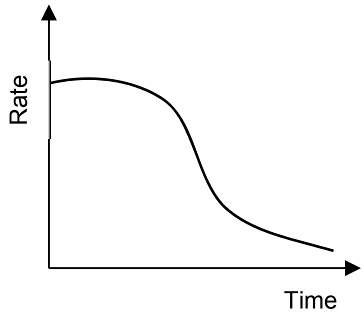
A	6.0 hours	**B**	2.0 hours
C	1.0 hours	**D**	0.4 hours

12 The reaction between potassium manganate(VII) and ethanedioic acid is an example of auto-catalytic reactions, in which one of the products catalyses the reaction.

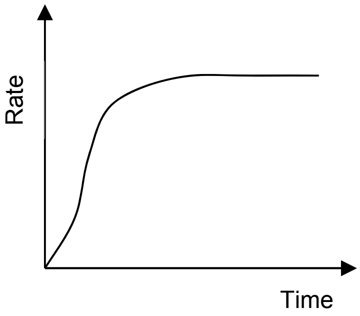
$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H_3O^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 14\ H_2O(l)$$

Which graph correctly represents the kinetics of this reaction?

A



B



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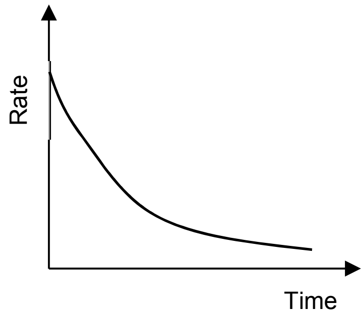

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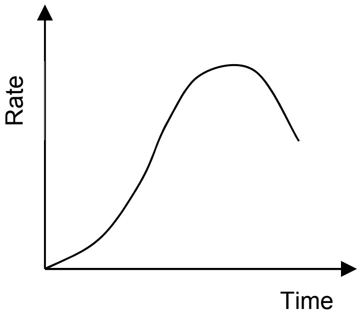
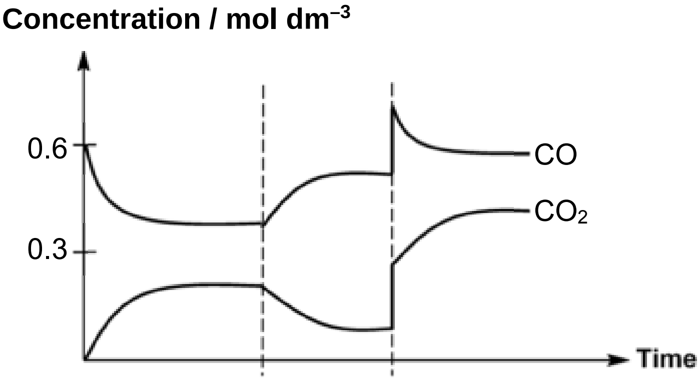


13 At a temperature *T* K, 0.60 mol dm^{-3} of CO and 0.30 mol dm^{-3} of O_2 were introduced into a 5 dm^3 vessel and allowed to reach equilibrium.

$$2\ CO\ (g) + O_2\ (g) \rightleftharpoons 2CO_2\ (g) \qquad \Delta H < 0$$

The graph below shows the changes in the concentration of CO and CO_2 in the system with time. A change was made to the system at time, t_1 and t_2.

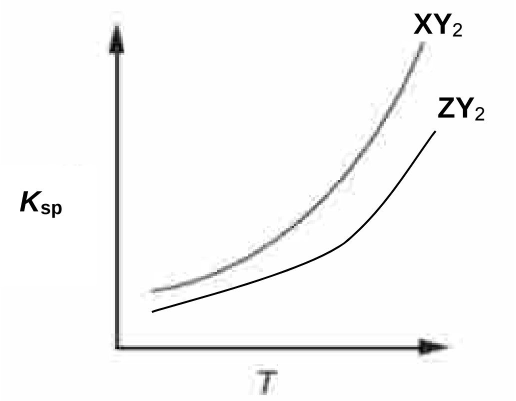


What were the changes made at time, t_1 and t_2?

	t_1	t_2
A	A catalyst was added	Volume of the system is increased
B	The temperature was increased	Volume of the system is decreased
C	Some O_2 was removed	An inert gas was added at constant volume
D	The temperature was decreased	More O_2 was added

14 $\mathbf{XY_2}$ and $\mathbf{ZY_2}$ are sparingly soluble salts containing $\mathbf{Z}^{2+}$, $\mathbf{X}^{2+}$ and $\mathbf{Y}^{-}$ ions.

The solubility product, K_{sp}, of both sparingly soluble salts varies with temperature as shown in the diagram below.



Which conclusions can be drawn from the information?

1 The enthalpy change of solution for both salts is endothermic.

2 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{XY_2}$ decreases the K_{sp} of $\mathbf{XY_2}$.

3 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{ZY_2}$ decreases the solubility of $\mathbf{ZY_2}$.

4 Given a solution with $[\mathbf{X}^{2+}] = [\mathbf{Z}^{2+}]$, $\mathbf{ZY_2}$ is precipitated out first on adding $\mathbf{Y}^{-}$.

A 1 and 3 only

B 3 and 4 only

C 1, 2 and 4 only

D 1, 3 and 4 only

15 A metal object was electroplated with chromium using an aqueous electrolyte of chromium(III) chloride and a graphite electrode. A current of 2.0 A was passed through the electroplating cell for 45 minutes.

What may be derived from the information given above?

1 The object to be electroplated was connected to the negative terminal of the battery.

2 The object increased in mass by 0.97 g.

3 Oxygen gas was evolved at the anode.

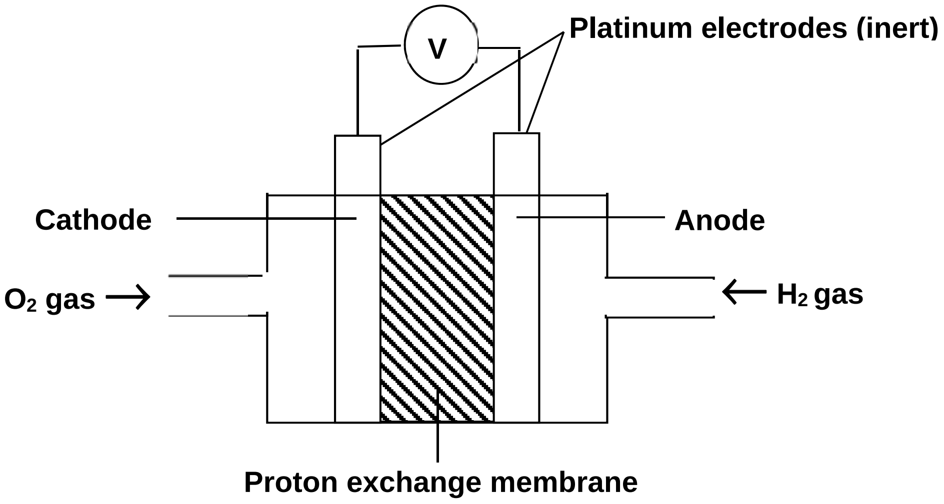
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

16 A hydrogen fuel cell as illustrated below has a typical e.m.f. of 1.23 V.



Which of the following is true regarding the operation of this fuel cell?

1 The e.m.f can be increased by increasing the pressure of oxygen gas to 2 atm.

2 The electrode is platinised to increase the rate of reaction, but e.m.f. is not affected.

3 The proton exchange membrane allows the passage of H^+ ions in order to complete the circuit and maintains electrical neutrality.

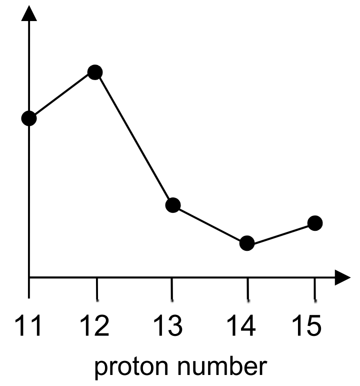
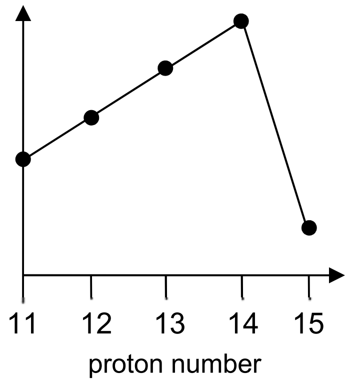
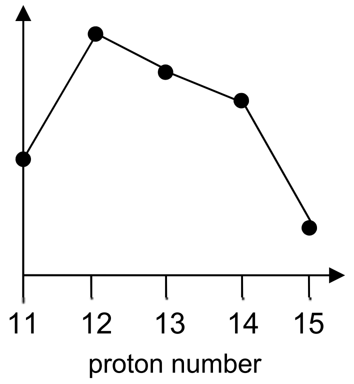
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

17 The following graphs show how three properties of the elements, Na to P, and their compounds, vary with proton number.

		
Graph 1	**Graph 2**	**Graph 3**

What properties are shown by the three graphs?

	Graph 1	Graph 2	Graph 3
A	Melting point of oxide	Melting point of chloride	Electrical conductivity of element
B	Melting point of oxide	Melting point of element	Melting point of chloride
C	Melting point of chloride	Electrical conductivity of element	Melting point of oxide
D	Melting point of chloride	Melting point of element	Melting point of oxide

18 Which property of Group 2 elements (magnesium to barium) or their compounds increases with increasing proton number?

A the stability of the carbonates to heat

B the magnitude of the enthalpy change of hydration of the metal ions

C the acidity of aqueous solutions of the chlorides

D the melting points of the elements

19 For the sequence hydrogen iodide, hydrogen bromide and hydrogen chloride, which of the following properties show a decreasing trend?

1 thermal stability

2 acidity

3 ease of oxidation

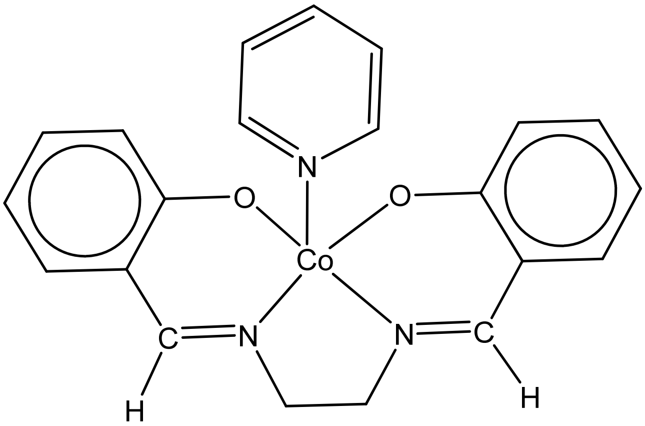
A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

20 The following cobalt complex is known to be the functional model for biological oxygen carrier.



What is the electronic configuration of the cobalt cation in the above complex?

A [Ar] $3d^6$

B [Ar] $3d^7$

C [Ar] $3d^5 4s^2$

D [Ar] $3d^7 4s^2$

21 Transition metals like platinum and rhodium are found in catalytic converters fitted into cars. Which of the following properties best explains the role of transition metals in this use?

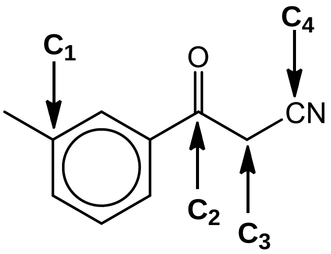
A Transition metals can exhibit variable oxidation states in their compounds as 3d and 4s electrons have similar energies.

B Transition metals form coloured ions due to absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.

C Transition metals have very high melting points because both 3d and 4s electrons are involved in forming strong metallic bond.

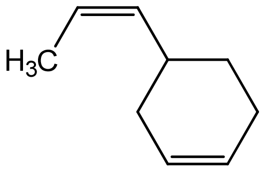
D Transition metals have partially filled 3d orbitals which are available for adsorption of reactant molecules.

22 What is the hybridisation of the various carbon atoms in the following molecule?



	C_1	C_2	C_3	C_4
A	sp^2	sp^3	sp	sp^2
B	sp^2	sp^2	sp^3	sp
C	sp^2	sp^2	sp	sp^3
D	sp^3	sp^2	sp^3	sp

23

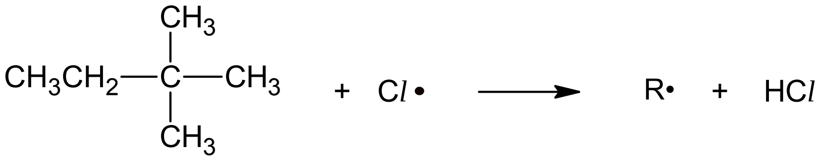


How many stereoisomers does the above molecule have?

A	2	**B**	4
C	6	**D**	8

24 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step, the free alkyl radical R• is formed.



$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + Cl\bullet \longrightarrow R\bullet + HCl$$

How many different forms of R• are possible?

A	1	**B**	2
C	3	**D**	4

25 Which one of the following statements regarding organic reaction mechanisms is **correct**?

1 Electrophilic addition of alkenes involves a carbocation intermediate.

2 Electrophilic substitution of benzene involves an intermediate with 4 π electrons.

3 Nucleophilic substitution of tertiary halogenoalkanes involves a carbocation intermediate.

4 Nucleophilic addition of a carbonyl compound involves an alkoxide intermediate.

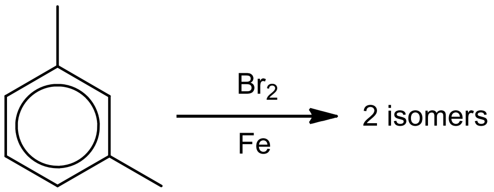
A 1, 2, 3 and 4

B 1 and 2 only

C 2 and 3 only

D 3 and 4 only

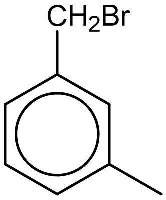
26 When 3-methyltoluene is treated with bromine in the presence of iron filings in the dark, a mixture of two mono-brominated isomers is formed.



3-methyltoluene

What are the structures of these two isomers?

A



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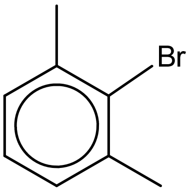

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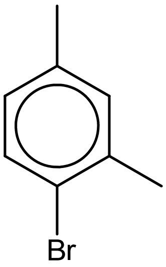

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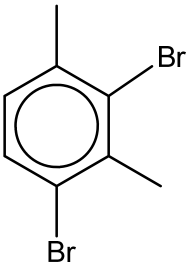

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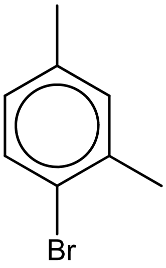

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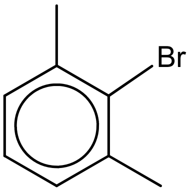

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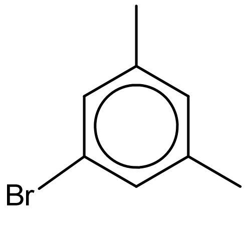

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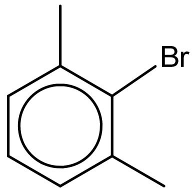


27 When ethyl ethanoate undergoes hydrolysis with dilute sulfuric acid in the presence of $H_2{}^{18}\mathbf{O}$, a mixture of two products is formed. Which of the following pairs correctly gives the structures of the two products?

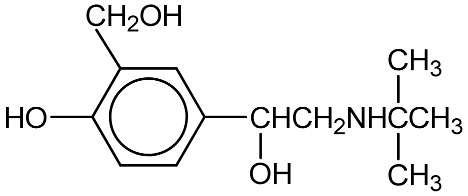
A $CH_3CO^{18}\mathbf{O}H$ and $CH_3CH_2{}^{18}\mathbf{O}H$

B CH_3COOH and $CH_3CH_2{}^{18}\mathbf{O}H$

C $CH_3C^{18}\mathbf{O}OH$ and CH_3CH_2OH

D $CH_3CO^{18}\mathbf{O}H$ and CH_3CH_2OH

28 Albuterol dilates the airways of the lung and is used for treating asthma and other conditions of the lung.



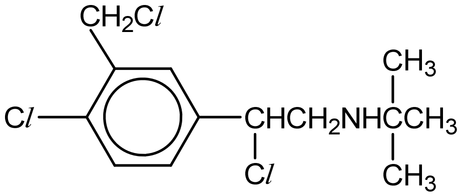
Albuterol

Which of the following statements is true about albuterol?

1 On addition of Na_2CO_3(aq), effervescence of CO_2 is produced.

2 On heating one mole of albuterol with NaOH(aq), one mole of NaOH is used up.

3 On reacting with phosphorus pentachloride,



is one of the products.

A 1 only

B 2 only

C 1 and 3 only

D 2 and 3 only

29 A sample of bromoethane was warmed with ethanolic silver nitrate, and a cream precipitate was observed after about 4 minutes.

Under similar reaction conditions, which one of the following compounds will result in precipitate formation only after 8 minutes?

A iodoethane

B ethanoyl bromide

C bromobenzene

D chloroethane

30 Which of the following gives the correct order of decreasing basic strength?

A $CH_3CH_2NH_2$, NH_3, $(CH_3CH_2)_2NH$

B $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, $C_6H_5NH_2$

C $(CH_3CH_2)_2NH$, NH_3, $C_6H_5NH_2$

D $C_6H_5NH_2$, NH_3, $CH_3CH_2NH_2$

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2018 Paper 1 answer key

1	**A**	2	**B**	3	**B**	4	**C**	5	**C**
6	**B**	7	**C**	8	**D**	9	**A**	10	**B**
11	**A**	12	**D**	13	**B**	14	**D**	15	**A**
16	**A**	17	**D**	18	**A**	19	**C**	20	**B**
21	**D**	22	**B**	23	**B**	24	**C**	25	**A**
26	**C**	27	**D**	28	**B**	29	**D**	30	**C**

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME	

CLASS	**18S**	EXAM INDEX	

CHEMISTRY

9729/02

Higher 2

Paper 2 Structured Questions

29 August 2018
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**13**
2	**13**
3	**11**
4	**10**
5	**17**
6	**11**
Penalty (delete accordingly)	
Lack **3sf** in final ans	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	

This document consists of **20** printed pages.

Answer **all** the questions.

1 Nickel is an important transition metal used in the manufacture of stainless steel alloys. It is first isolated from the mineral ore niccolite by Swedish chemist Axel Fredrik Cronstedt in 1751.

(a) Nickel exists naturally as a mixture of five stable isotopes, each with their own relative isotopic mass. The information about four of these isotopes is given.

isotope	percentage abundance
^{58}Ni	68.1
^{61}Ni	1.14
^{62}Ni	3.63
^{64}Ni	0.93

The relative atomic mass of nickel is 58.7.

Calculate the relative isotopic mass of the fifth isotope of nickel.

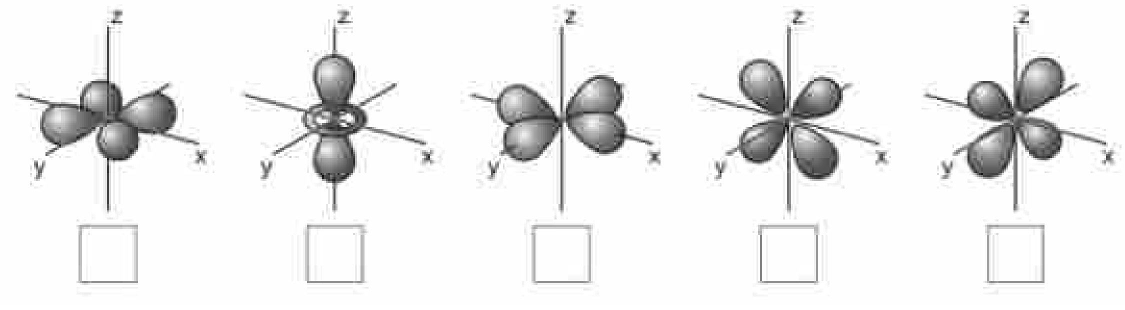
Give your answer to the **nearest whole number**.

[2]

(b) Nickel can form complexes with H_2O ligands.

In a $[Ni(H_2O)_6]^{2+}$ complex, the presence of the H_2O ligands causes the d orbitals to split into two groups at different energy levels.

(i) On the diagram below, tick the box under each of the orbitals of the higher energy level.



[2]

(ii) Explain why a solution of $[Ni(H_2O)_6]^{2+}$ is coloured.

…………………………………………………………………………………..

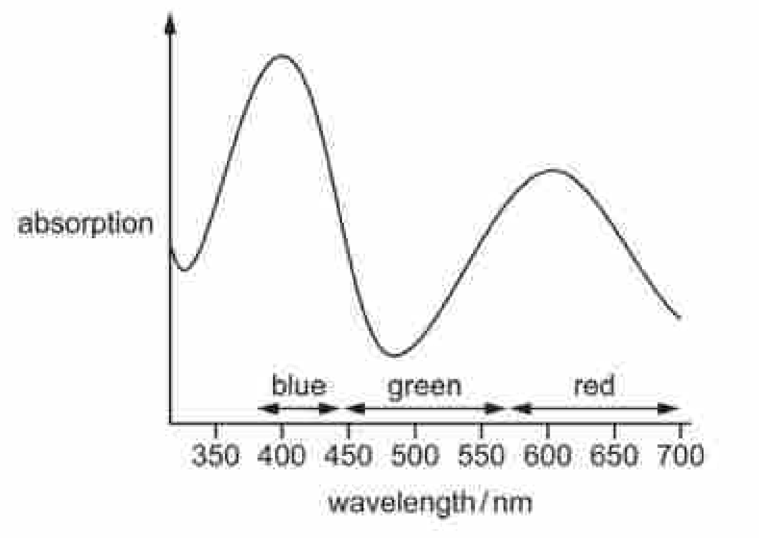
…………………………………………………………………………………..

…………………………………………………………………………………..

…………………………………………………………………………………..

………………………………………………………………………………….. [2]

(iii) The visible spectrum of a solution of $[Ni(H_2O)_6]^{2+}$ is shown below.



State and explain the colour of the solution.

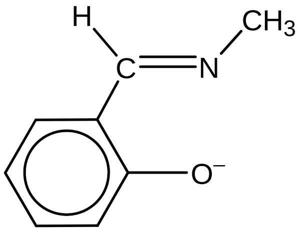
colour of the solution ……………………………….

explanation ……………………………………………………………………….

…………………………………………………………………………………..

………………………………………………………………………………….. [2]

(c) Nickel can form a complex with ligand **X**⁻, which has the structure shown below.



ligand **X**⁻

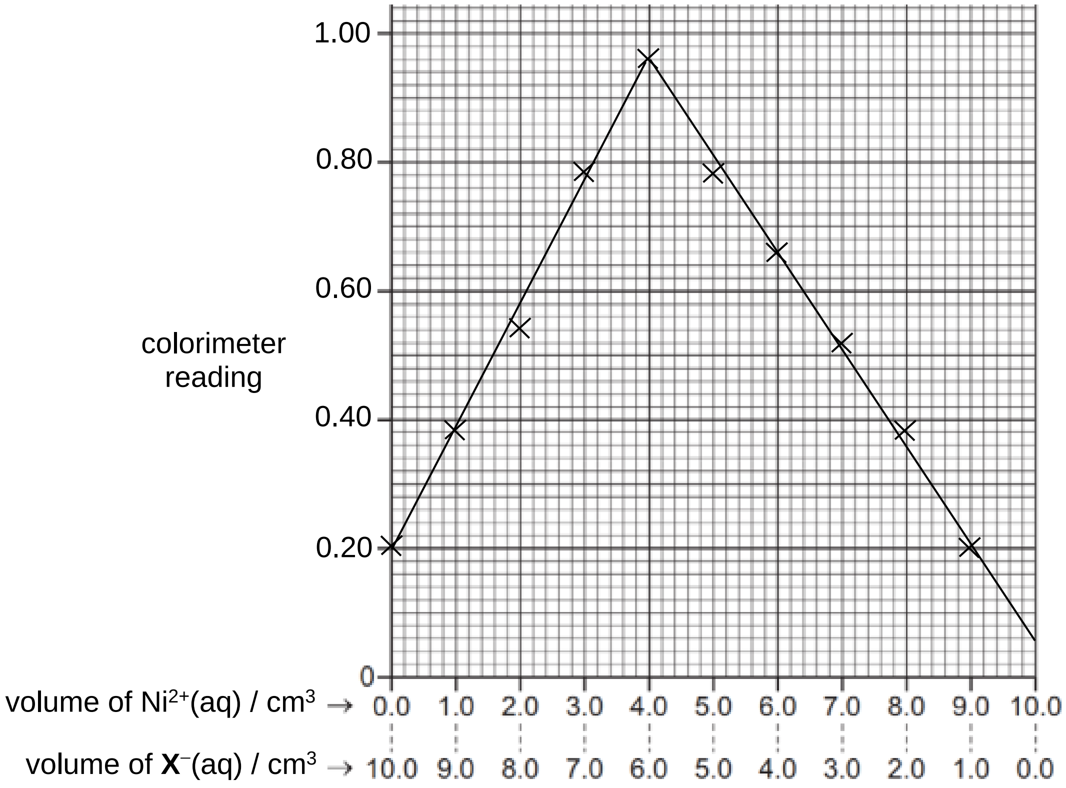
X⁻ is a bidentate ligand. On the structure above, draw circles around the atoms that bind to nickel when **X**⁻ behaves as a ligand. [1]

(d) The formula of a complex can be determined using colorimetry.

In colorimetry, light of a certain wavelength is passed through a complex ion solution. The absorbance of the light is proportional to the intensity of the colour of the solution. The more concentrated the complex ion solution, the more intense its colour and so the higher the absorbance.

An experiment is carried out to determine the formula of the complex formed between nickel and ligand **X**$^-$ having the structure given in **(c)**.

The following graph was obtained when the colour intensities of mixtures of a 3×10^{-3} mol dm^{-3} solution of nickel(II) chloride and a 4×10^{-3} mol dm^{-3} solution containing **X**$^-$ were measured using a colorimeter at room temperature.



Determine the stoichiometry of the complex and suggest its structural formula.

[2]

(e) Like nickel, platinum can also forms complexes in which the central atom is surrounded by four ligands.

A and **B** are isomeric complexes of the same shape with the formula of $Pt(PR_3)_2I_2$.
[The PR_3 ligand has the same shape as NH_3. R is a phenyl group.]

Given that isomer **A** has a dipole moment, draw the structures of **A** and **B**.

isomer **A**

isomer **B**

[2]

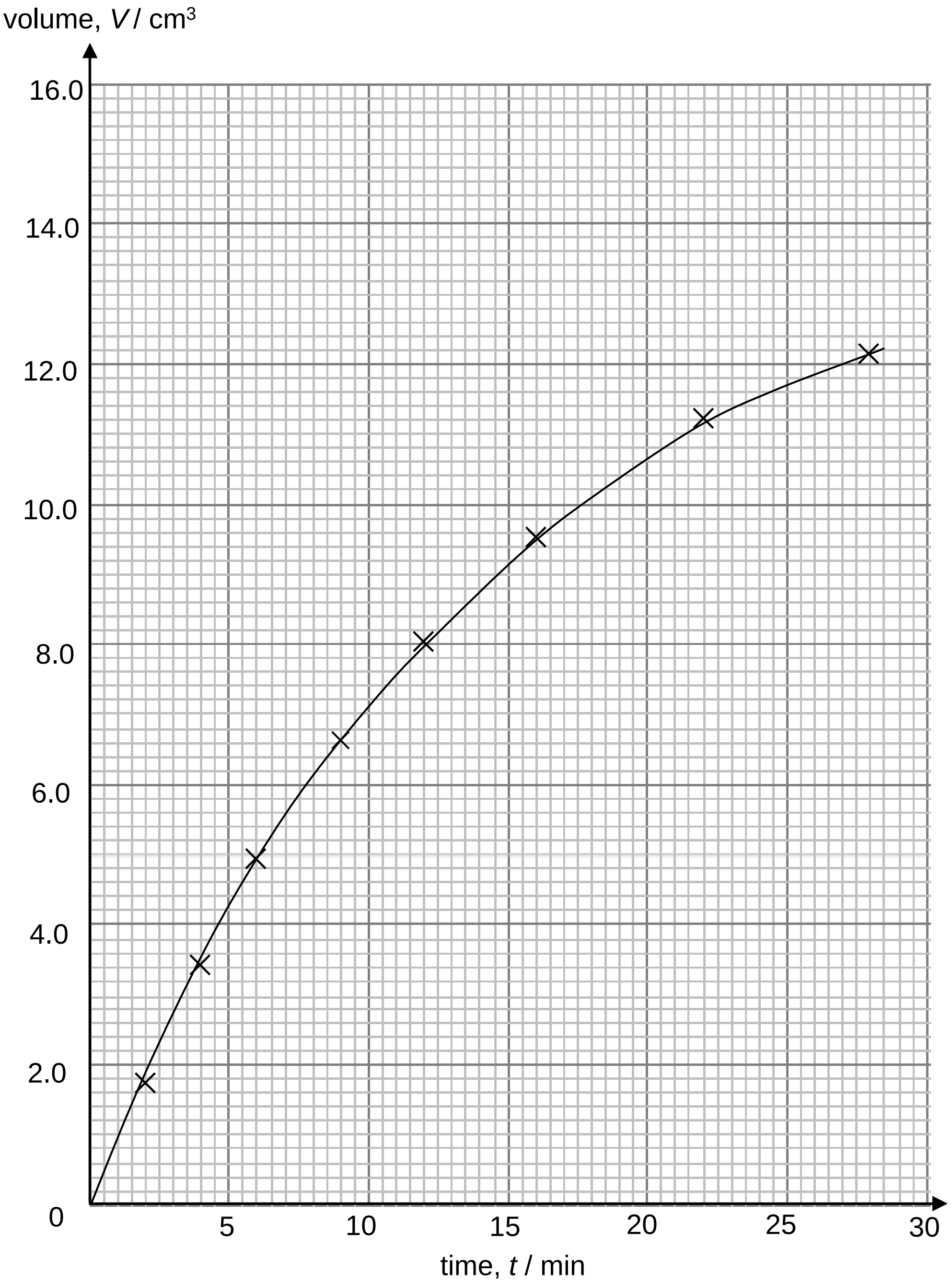
[Total: 13]

2 **(a)** Benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes at 50 °C and 101 kPa, according to the equation below.

$$C_6H_5N_2Cl(aq) \rightarrow C_6H_5Cl(aq) + N_2(g)$$

The progress of the decomposition reaction of a 500 cm^3 sample of $C_6H_5N_2Cl(aq)$ solution was studied by measuring the volume of gas produced over time.

The volume of gas produced, V, after time, t, is proportional to the amount of benzenediazonium chloride that has decomposed. The final volume of gas produced, V_{final}, is 14.6 cm^3 and it is directly proportional to the original concentration of benzenediazonium chloride. The results are recorded in the graph below.



(i) Use the graph to determine the order of the reaction with respect to benzenediazonium chloride.

Show all your working, and draw clearly any construction lines on your graph.

Order of reaction with respect to benzenediazonium chloride: …………….

explanation ……………………………………………………………………….

……………………………………………………………………………………. [2]

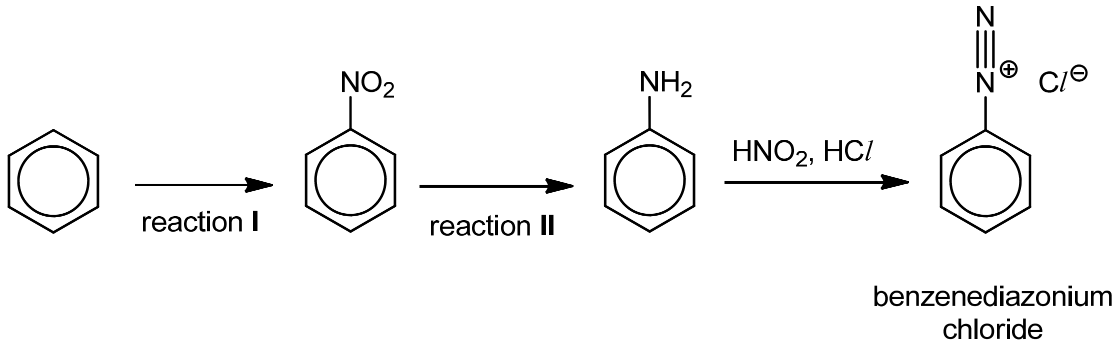
(ii) Calculate the rate constant, stating its units.

[2]

(iii) Assuming nitrogen behaves ideally, calculate the original concentration, in mol dm^{-3}, of benzenediazonium chloride.

[3]

(b) Benzenediazonium chloride is an important intermediate for the production of dyes. The following scheme shows the synthesis of benzenediazonium chloride from benzene.



(i) State the type of reaction and suggest the reagents and conditions for reaction **I**.

type of reaction: ……………………………………………….

reagents: …………………………………………………….

conditions: ………………………………………………….. [3]

In reaction **II**, nitrobenzene is reduced to phenylamine via two steps.

During step 1, granulated Sn and concentrated HC*l* are added to nitrobenzene and the mixture is heated under reflux in a hot water bath for about half an hour. Sn, which acts as the reducing agent, is converted to Sn^{4+} ions.

(ii) Balance the following half-equation for the reduction of nitrobenzene in acid solution to give $C_6H_5NH_3^+$ in step 1.

.... $C_6H_5NO_2$ + ... H^+ + …. e^- → ………………………………………….. [1]

(iii) Hence, by considering electron transfer, write a balanced overall equation for the reaction of nitrobenzene, Sn and concentrated HC*l* in step 1.

…. $C_6H_5NO_2$ + …. Sn + …. HC*l* → ……………………………………………. [1]

Step 2 involves the addition of aqueous sodium hydroxide to the resulting mixture.

(iv) Suggest the purpose of this stage.

…………………………………………………………………………………..

…………………………………………………………………………………..

………………………………………………………………………………….. [1]

[Total: 13]

For Examiner's Use

3 Metals have properties that make them well suited to serve as battery anodes.

They are easily oxidised from their metallic state to produce ions and electrons, where the electrons liberated are conducted throughout the external circuit. The fact that metals are physically strong and easily fashioned into any desired shape adds to their attractiveness as anodes.

Metals commonly employed as anodes in commercial batteries are listed in **Table 3.1**. The tabulated properties give clues as to the ability of each metal to play this role.

Metal	relative atomic mass	density / g cm^{-3}	standard electrode potential, $E^{\ominus}$ / V	electrochemical capacity / A h g^{-1}
lithium	6.9	0.53	–3.04	3.86
sodium	23.0	0.97	–2.71	1.17
magnesium	24.3	1.74	–2.38	2.21
iron	55.8	7.86	–0.44	0.96
zinc	65.4	7.14	–0.76	0.82
lead	207.2	11.3	–0.13	0.26

Table 3.1

(a) Suggest **two** reasons why lithium is the best choice among the metals in **Table 3.1** to be used as a battery anode.

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………… [2]

(b) A schematic diagram of a lithium-ion battery is shown below. Lithium is the anode whereas a paste of iron disulfide (FeS_2) powder mixed with powdered graphite serves as the cathode.

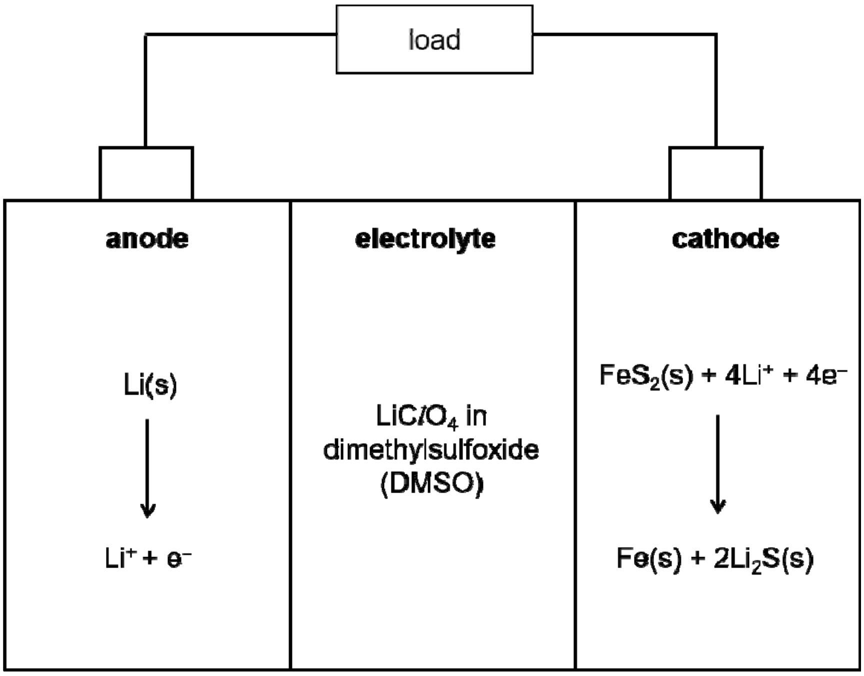


Figure 3.1

(i) On **Figure 3.1**, indicate clearly the direction of electron flow. [1]

(ii) Most batteries use aqueous solutions of ionic salts or ionisable molecules as electrolytes. However, the electrolyte used in this lithium-ion battery must be non-aqueous such as dissolving $LiClO_4$ in dimethylsulfoxide (DMSO), which is an organic solvent. Suggest why.

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(c) Like enthalpy, Gibbs free energy *G* is a state function. Thus, Hess' Law can likewise be applied to calculate the standard Gibbs free energy change of a reaction, $\Delta G^{\ominus}$, from relevant data such as the standard Gibbs free energy changes of formation.

Table 3.2 below lists the standard Gibbs free energy change of formation, $\Delta G_f^{\ominus}$, for some compounds.

species	$\Delta G_f^{\ominus}$ / kJ mol^{-1}
$FeS_2(s)$	–160
$Li_2S(s)$	–439

Table 3.2

(i) Use the data in **Table 3.2** above to show that the standard Gibbs free energy change, $\Delta G_r^{\ominus}$, of the overall cell reaction in the lithium-ion battery is –718 kJ mol^{-1}.

$$4Li(s) + FeS_2(s) \rightarrow Fe(s) + 2Li_2S(s)$$

[1]

(ii) Use the $\Delta G_r^{\ominus}$ value given in **(c)(i)** to calculate the $E^{\ominus}_{cell}$ of this battery.

[2]

(iii) Use your answer in **(c)(ii)** and relevant $E^{\ominus}$ value in **Table 3.1** to calculate the standard electrode potential of the FeS_2(s)/Fe(s) half-cell at the cathode.

[1]

(iv) By using **one** of the phrases *more positive*, *more negative* or *no change*, deduce the effect of increasing [Li^+] on the electrode potential of

- the left-hand electrode (anode) ……………………………………
- The right-hand electrode (cathode) ………………………………….

[2]

(v) Hence deduce whether the overall $E^{\ominus}_{cell}$ is likely to *increase*, *decrease* or *remain the same*, when [Li^+] increases.

…………………………………………………………………………………. [1]

[Total: 11]

4 **(a)** **Figure 4.1** is an incomplete sketch showing the melting points of some of the elements of the Period 3 (sodium to argon). Estimate and indicate, on **Figure 4.1**, the melting points of the four other elements: Mg, A*l*, S and C*l*.

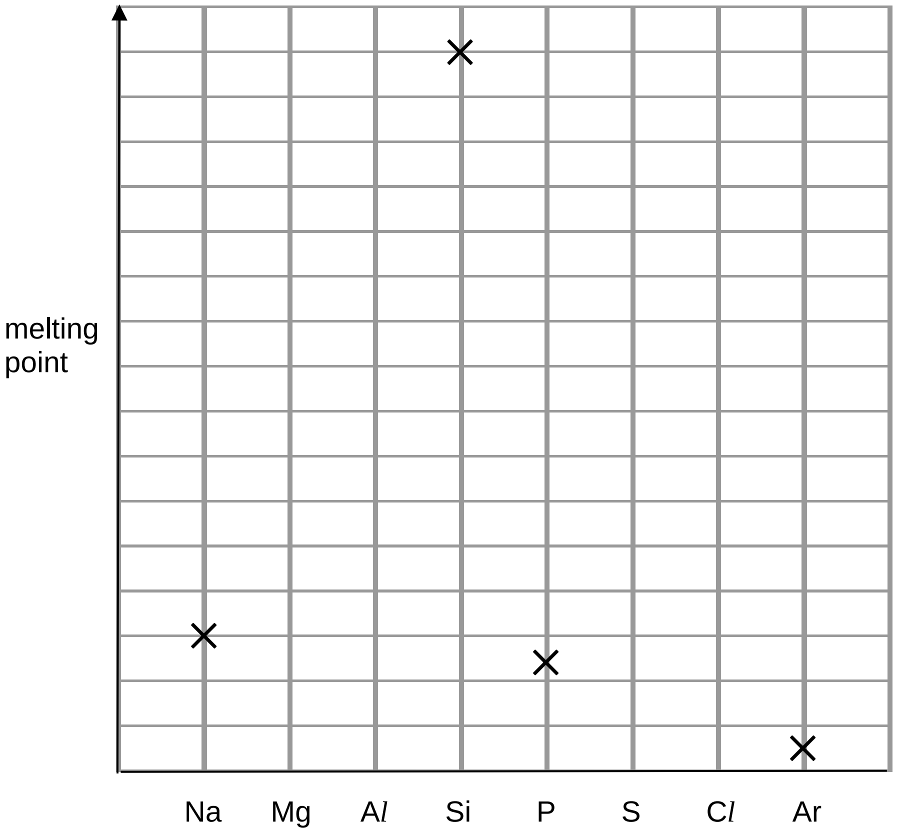
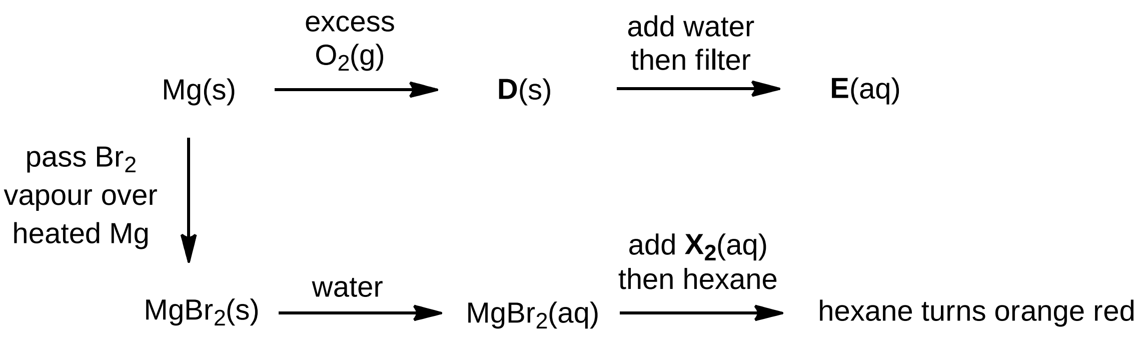


Figure 4.1 [2]

(b) Some reactions of magnesium and its compounds are shown below.



(i) Identify compounds **D** and **E**.

D: ………………….. **E**: ……………………. [2]

(ii) Use appropriate data in the *Data Booklet* to deduce whether $\mathbf{X_2}$ is Cl_2 or I_2.

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………….. [2]

(c) Sodium reacts with water to form aqueous sodium hydroxide.

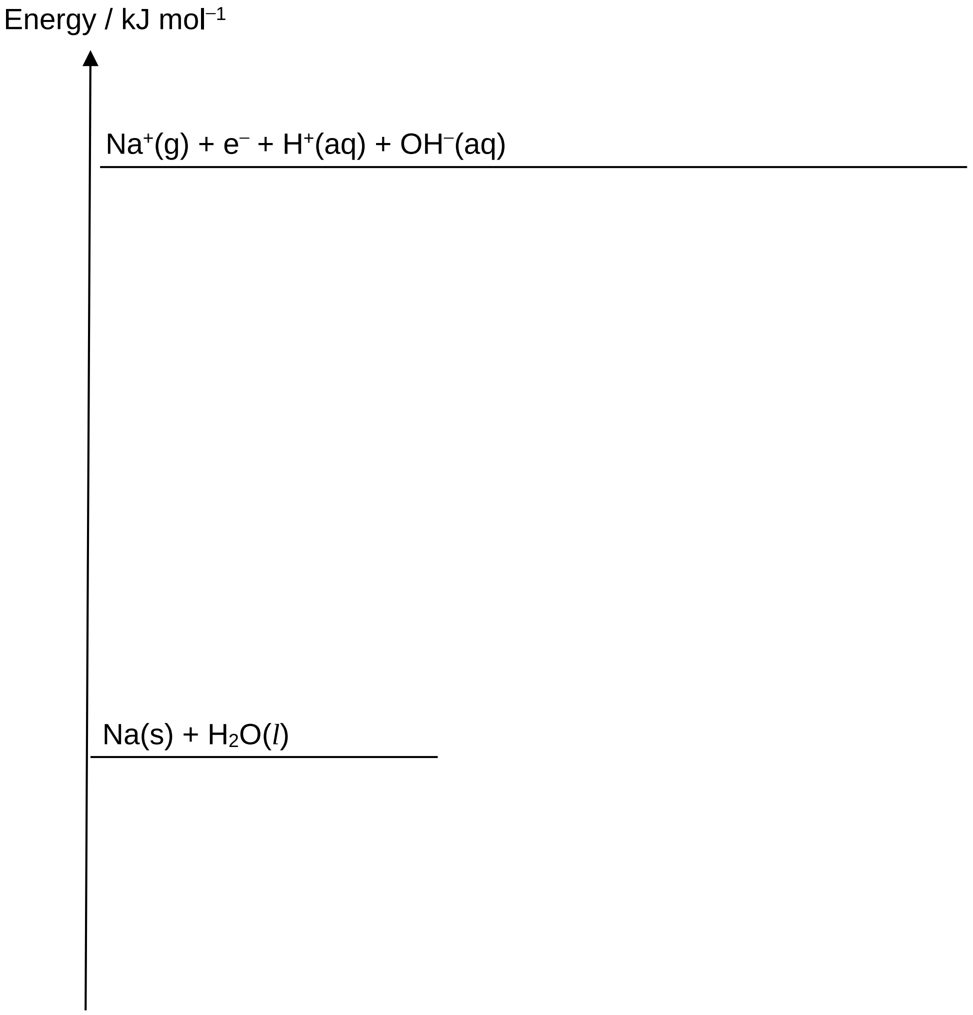
$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) \qquad \Delta H_r$$

On the grid below, draw an energy cycle which can be used to calculate ΔH_r, by incorporating the enthalpy changes in **Table 4.1** and any relevant data from the *Data Booklet*.

Hence, calculate ΔH_r.

	value / kJ mol^{-1}
enthalpy change of atomisation of Na(s)	+107
enthalpy change for $Na^+(g) + H^+(aq) + e^- \rightarrow Na^+(aq) + \tfrac{1}{2}H_2(g)$	–850
enthalpy change for $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	–58

Table 4.1



[4]

[Total: 10]

5 **(a)** But-1-ene reacts with hydrogen bromide to give 2-bromobutane as the major product.

(i) Name and describe the mechanism for this reaction. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.

Name of mechanism: ……………………………………………………

[3]

(ii) With reference to the mechanism you have drawn in **(a)(i)**, explain why the major product is 2-bromobutane rather than 1-bromobutane.

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(iii) 2-bromobutane is chiral. However, the product mixture from this reaction does not rotate plane-polarised light.

With reference to the mechanism you have drawn in **(a)(i)**, explain why this is so.

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………….. [1]

(b) **Figure 5.1** shows a reaction scheme involving 4-bromobutanone.

Compounds **J** and **K** have the following properties:

- Effervescence is seen when reacted with sodium metal.
- No yellow precipitate is formed when mixed with alkaline aqueous iodine.
- A pale cream precipitate slowly forms when excess $HNO_3(aq)$ is added, followed by $AgNO_3(aq)$.

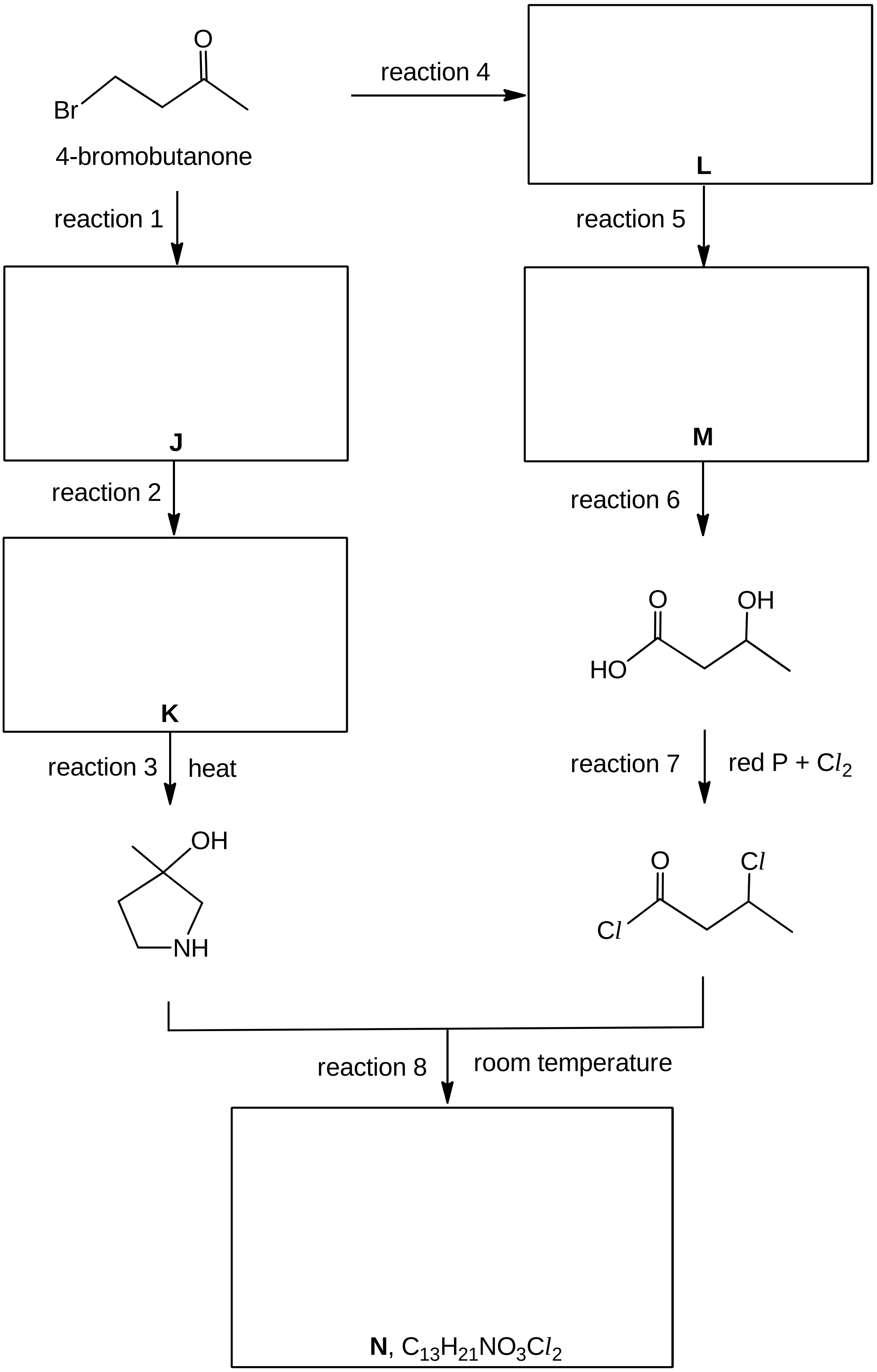


Figure 5.1

(i) Work out the structures for compounds **J**–**N**. Draw their structural formulae in the boxes on the reaction scheme shown in **Figure 5.1**. [5]

(ii) Suggest reagents and conditions for reactions 1, 2, 4, 5 and 6.

reaction 1: …………………………………………………

reaction 2: …………………………………………………

reaction 4: …………………………………………………

reaction 5: …………………………………………………

reaction 6: ………………………………………………… [5]

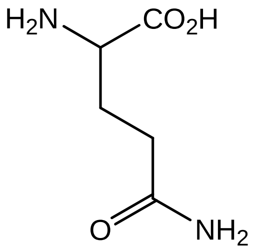
(iii) State the types of reaction for reactions 7 and 8.

reaction 7: …………………………………………………

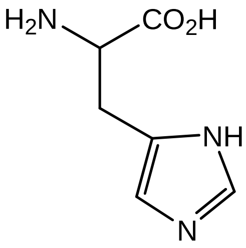
reaction 8: ………………………………………………… [2]

[Total: 17]

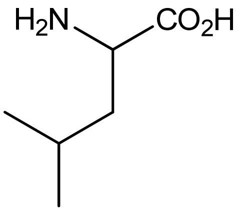
6 A pentapeptide comprises the following five amino acids.



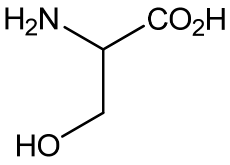
glutamine (gln)
M_r = 146



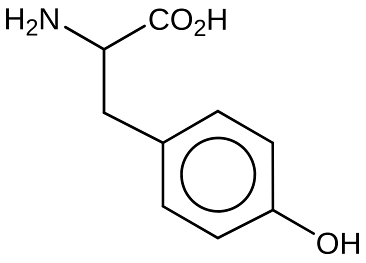
histidine (his)
M_r = 155



leucine (leu)
M_r = 131



serine (ser)
M_r = 105



tyrosine (tyr)
M_r = 181

(a) Calculate the M_r of this pentapeptide. Show your working clearly.

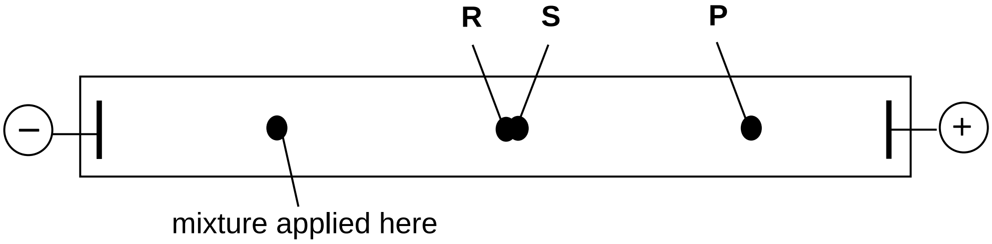
[1]

(b) The pentapeptide was broken down by enzymes to form shorter peptides and individual amino acids. One of the peptides is a dipeptide with the sequence **gln-tyr**.

(i) Draw the structure of the dipeptide at pH 12.

[2]

A mixture of this dipeptide (gln-tyr) and its two constituent amino acids (gln and tyr) was subjected to electrophoresis in a buffer at pH = 12. At the end of the experiment, the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species gln, tyr and gln-tyr.

(ii) Which species is responsible for spot **P**? Explain your answer

spot **P**: …………………….

explanation ………………………………………………………………………

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………….. [2]

(iii) Suggest why the other two species give spots **R** and **S** that are so close together.

……………..…………………………………………………………………………

……………………………………………………………………………………..

…………………………………………………………………………………….. [1]

(c) State a reagent you would use and the observations you would make to distinguish tyrosine (tyr) from glutamine (gln).

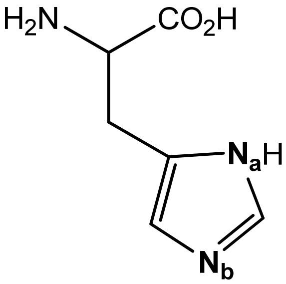
test ……………………………………………

observations ……………………………………………………………………………..

………………………………………………………………………………………………..

……………………………………………………………………………………………… [2]

(d) There are two nitrogen atoms, $\mathbf{N_a}$ and $\mathbf{N_b}$, in the side chain of histidine. However, only one of the nitrogen atoms can act as a Bronsted base.



(i) $\mathbf{N_a}$ and $\mathbf{N_b}$ have the same state of hybridisation. State their state of hybridisation.

……………………………… [1]

(ii) Predict which nitrogen atom, $\mathbf{N_a}$ or $\mathbf{N_b}$, can act as a Bronsted base. Explain your answer.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………….. [2]

[Total: 11]

END OF PAPER

Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 2

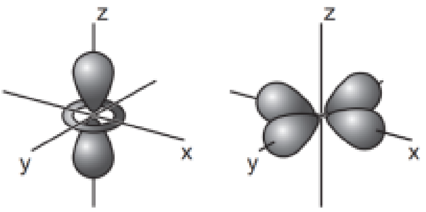
1 **(a)** % abundance of 5th isotope = 100 – (68.1 + 1.14 + 3.63 + 0.93) = 26.2 %

Let relative isotopic mass of 5th isotope be x.

$58.7 = 0.262x + (58 \times 0.681) + (61 \times 0.0114) + (62 \times 0.0363) + (64 \times 0.0093)$

$\therefore\ x = 60$

(b) **(i)**



☑ ☑

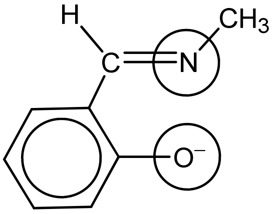
(ii) Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital that is partially filled.

Colour seen is the complement of the colours that are absorbed.

(iii) Colour: Green

Wavelengths corresponding to the blue and red regions are most absorbed (or green region is least absorbed).

(c)



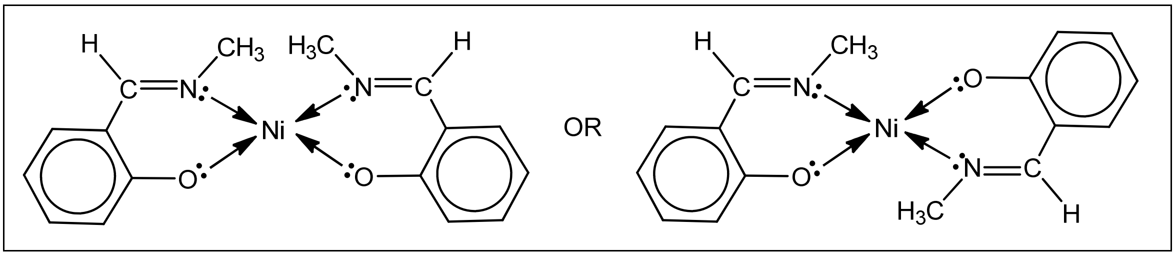
(d) $n(Ni^{2+}) = 4.0 \times 10^{-3} \times 3 \times 10^{-3} = 1.2 \times 10^{-5}$ mol

$n(X^{-}) = 6.0 \times 10^{-3} \times 4 \times 10^{-3} = 2.4 \times 10^{-5}$ mol

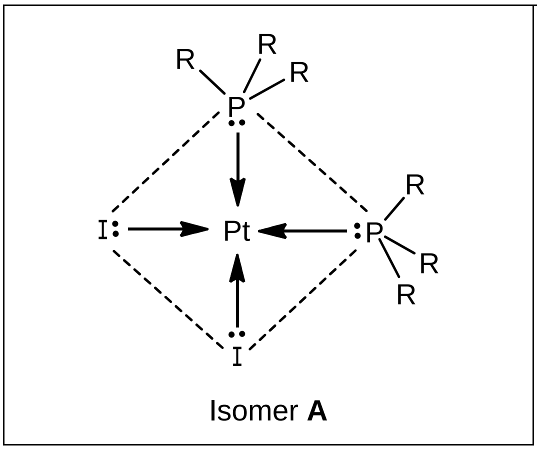
$n(Ni^{2+}) : n(X^{-}) = 1.2 \times 10^{-5} : 2.4 \times 10^{-5} = 1 : 2$

Empirical formula is NiX_2.

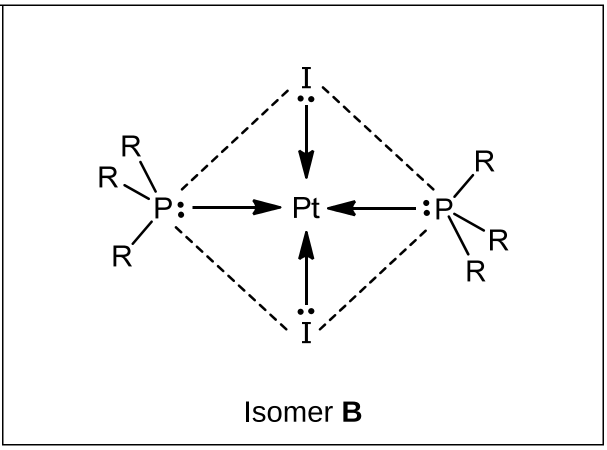
Structural formula of the complex:



(e)

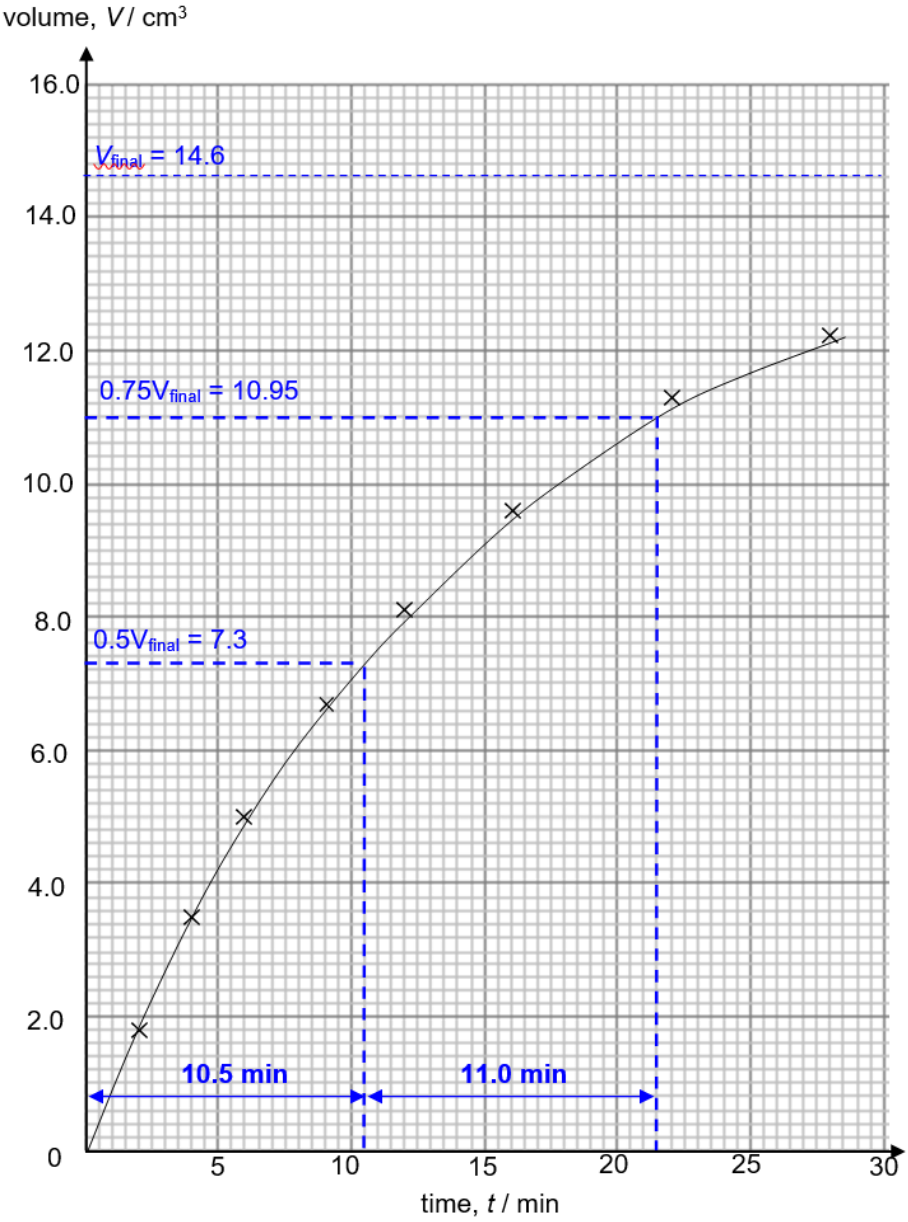


Isomer **A**



Isomer **B**

2 **(a)**



(i) Order of reaction with respect to benzenediazonium chloride: 1

1st $t_{½}$ = 10.5 min; 2nd $t_{½}$ = 11.0 min ⇒ Half-lives are relatively constant.

(ii) Average $t_{½}$ = 0.5 (10.5 + 11.0) = 10.75 min

For overall 1st order reaction, $k = \dfrac{\ln 2}{10.75} = 0.0645\ \text{min}^{-1}$

(iii) $n(N_2) = \dfrac{(101000)(14.7\times10^{-6})}{(8.31)(50+273)} = 0.000549$ mol

= $n(C_6H_5N_2Cl)$ in 500 cm^3 solution

Original [benzenediazonium chloride] = $0.000549\times\dfrac{1000}{500}$ = 0.00110 mol dm^{-3}

(b) **(i)** type of reaction: electrophilic substitution

reagents: concentrated HNO_3

conditions: concentrated H_2SO_4, 50 °C

(ii) $1C_6H_5NO_2 + 7H^+ + 6e^- \rightarrow C_6H_5NH_3^+ + 2H_2O$

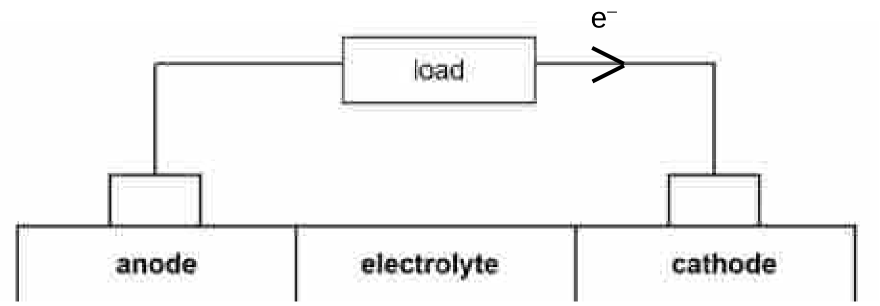
(iii) $2C_6H_5NO_2 + 3Sn + 14HCl \rightarrow 2C_6H_5NH_3Cl + 3SnCl_4 + 4H_2O$

(iv) NaOH will undergo acid-base reaction with $C_6H_5NH_3^+$ (or deprotonate $C_6H_5NH_3^+$) to give $C_6H_5NH_2$.

3 **(a)** Any 2 of the following:

- Li is the lightest/has the lowest density so lithium battery is most portable.
- Li has the most negative $E^{\ominus}$/ is most easily oxidised among the metals and thus gives the largest e.m.f./$E^{\ominus}_{cell}$.
- Li has the largest electrochemical capacity so it can produce the largest amount of electrical charge per unit mass of the metal.

(b) **(i)**



(ii) Li is a reactive metal and will undergo redox reaction with water to produce H_2 gas which may cause explosion.

(c) **(i)**

$$\begin{tikzcd} 4Li(s) + FeS_2(s) \arrow[rr, "\Delta G_r^{\ominus}"] & & Fe(s) + 2Li_2S(s) \\ & 4Li(s) + Fe(s) + 2S(s) \arrow[ul, "\Delta G_f^{\ominus}(FeS_2)"] \arrow[ur, "2\Delta G_f^{\ominus}(Li_2S)"'] & \end{tikzcd}$$

$\Delta G_r^{\ominus} = \Sigma\,(a_i \times \Delta G_f^{\ominus}(\text{products})) - \Sigma\,(a_i \times \Delta G_f^{\ominus}(\text{reactants}))$

$= 2(-439) - (-160)$

$= -718\ \text{kJ mol}^{-1}$ (shown)

(ii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$-718 \times 10^3 = -(4)(96500)(E^{\ominus}_{cell})$

$E^{\ominus}_{cell} = +1.86$ V

(iii) $Li^+ + e^- \rightleftharpoons Li$ $E^{\ominus} = -3.04$ V ---[O]

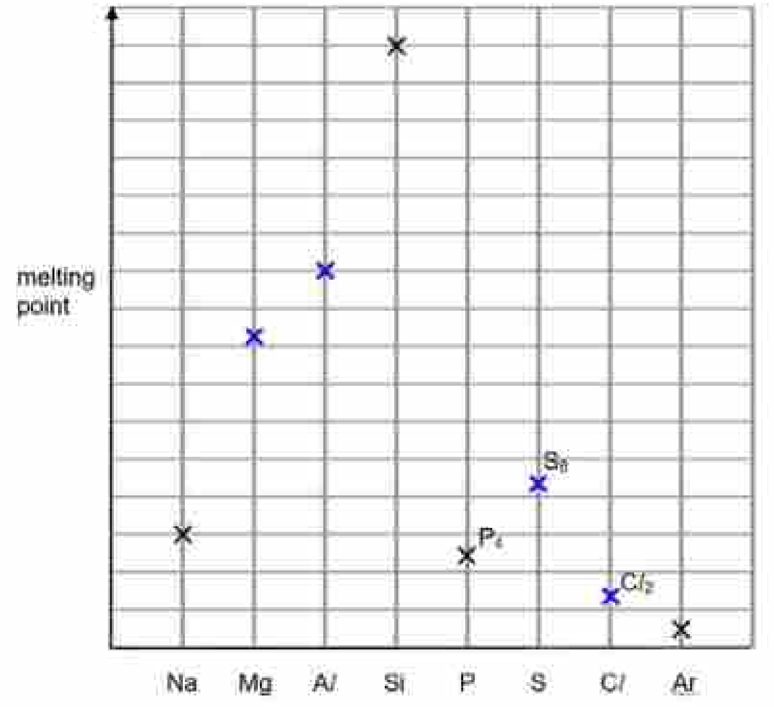
$+1.86 = E^{\ominus}(FeS_2/Fe) - (-3.04)$

$(FeS_2/Fe) = -1.18$ V

(iv)
- the left-hand electrode (anode): more positive
- The right-hand electrode (cathode): more positive

(v) $E^{\ominus}_{cell}$ will remain the same.

4 **(a)**



(b) **(i)** **D**: MgO **E**: $Mg(OH)_2$

(ii) X_2 is Cl_2.

$E^{\ominus}_{cell}$ for reaction of Cl_2 and Br^- = (+1.36) – (+1.07) = +0.29 V > 0 (energetically feasible).

OR

$E^{\ominus}_{cell}$ for reaction of I_2 and Br^- = (+0.54) – (+1.07) = –0.53 V < 0 (energetically not feasible).

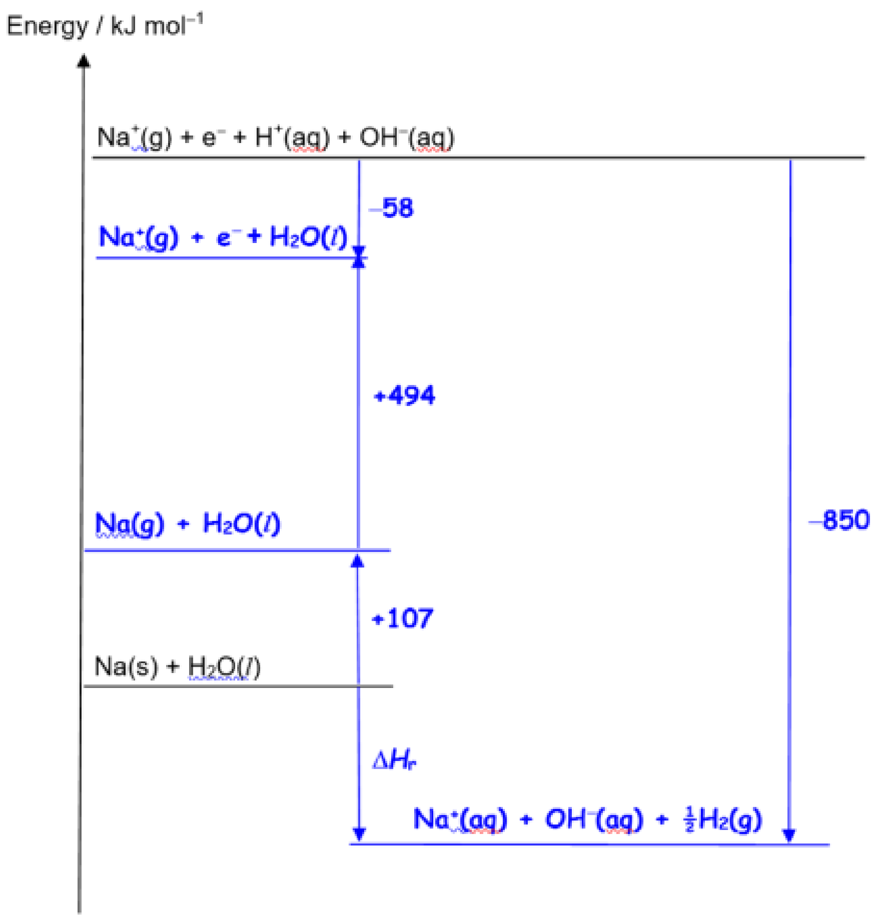
OR

$E^{\ominus}(Cl_2/Cl^-) > E^{\ominus}(Br_2/Br^-)$ so Cl_2 is a stronger oxidising agent than Br_2 and thus can oxidise Br^- to Br_2.

OR

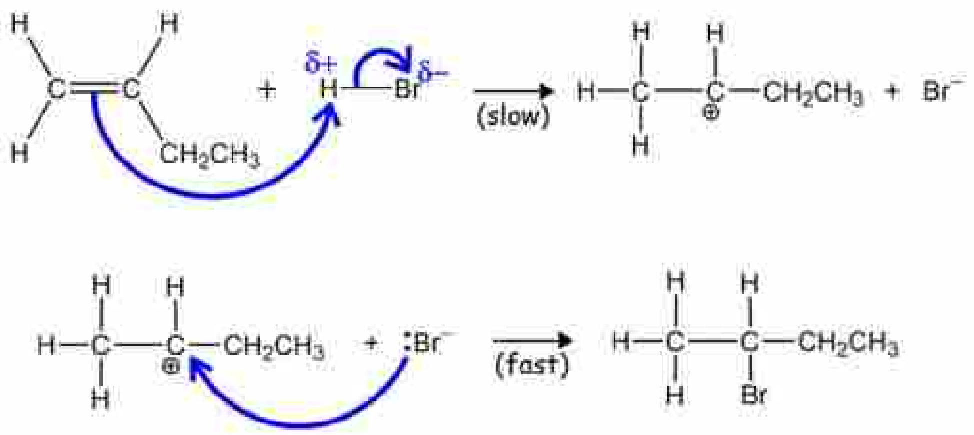
$E^{\ominus}(Br_2/Br^-) > E^{\ominus}(I_2/I^-)$ so I_2 is a weaker oxidising agent than Br_2 and thus cannot oxidise Br^- to Br_2.

(c)



$\Delta H_r = (+107) + (+494) - (-58) + (-850) = -191 \text{ kJ mol}^{-1}$

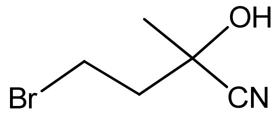
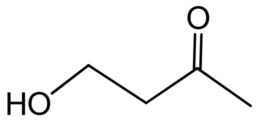
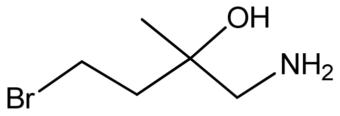
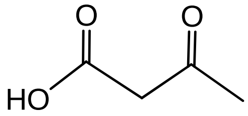
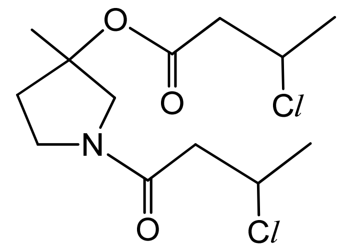
5 **(a)** **(i)** Name of mechanism: electrophilic addition



(ii) In the first step, secondary carbocation, $^{+}CH(CH_3)CH_2CH_3$, (which yields 2-bromobutane) is more stable and thus more readily formed than primary carbocation, $^{+}CH_2CH_2CH_2CH_3$, (which yields 1-bromobutane) as it has one more electron-donating alkyl group which disperses its positive charge more.

(iii) There is equal probability for Br^- to attack either side of the trigonal planar C^+ of carbocation in step 2, forming a racemic mixture.

(b) **(i)**

J: 	**L:** 
K: 	**M**: 
N: 	

(ii) reaction 1: HCN, trace amount of KCN/NaCN

reaction 2: $LiAlH_4$, dry ether OR H_2, Ni, heat

reaction 4: aqueous NaOH/KOH, heat

reaction 5: acidified $K_2Cr_2O_7$/$KMnO_4$, heat

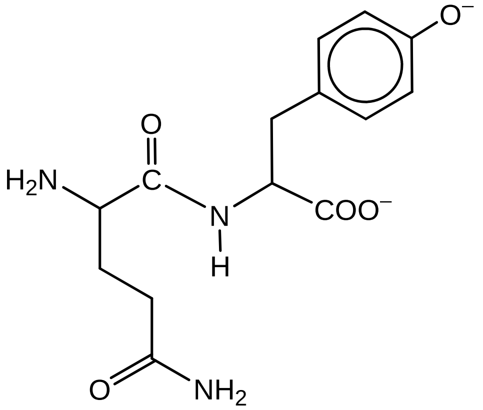
reaction 6: $NaBH_4$, methanol OR H_2, Ni, heat

(iii) reaction 7: nucleophilic substitution

reaction 8: condensation

6 **(a)** $M_r = 146 + 155 + 131 + 105 + 181 - (4 \times 18.0) = 646$

(b) **(i)**



(ii) spot **P**: tyr

Tyrosine has a charge of 2– at pH = 12 and a smaller mass/M_r than gln-tyr. It has the highest $\frac{\text{charge}}{\text{mass}}$ ratio compared to the other two species so it moves the fastest and thus furthest from original position.

(iii) Charge of gln-tyr is twice that of gln and its mass/Mr of is about twice that of gln.

OR

gln and gln-tyr have similar $\frac{\text{charge}}{\text{mass}}$ ratios ($\frac{\text{charge}}{\text{mass}}$ of gln is $\frac{1}{146} = 0.00685$ whereas $\frac{\text{charge}}{\text{mass}}$ of gln-tyr is $\frac{2}{309} = 0.00647$).

(c) test: Br_2(aq)

observations: Tyr decolourises orange Br_2(aq) and forms a white precipitate while gln will not.

OR

test: neutral $FeCl_3$(aq)

observations: Tyr will give a violet colouration while glu will not.

OR

test: NaOH(aq), heat

observations: Gln will give NH_3 gas which turns damp red litmus paper blue while tyr will not.

(d) **(i)** sp^2

(ii) N_b can act as a Bronsted base.

This is because the lone pair of electron on N_a is in an unhybridised p orbital which is parallel to the adjacent π electron systems so it is delocalised into C=C and C=N_b due to p-p orbital overlap. Hence, the lone pair of electrons is not available for protonation.

However, the lone pair (of electron) on N_b is in a sp^2 orbital which is on the same plane as the ring (or not parallel to adjacent π electron system) and hence it will not be delocalised into the adjacent C=C. Thus, the lone pair of electron is available for protonation.

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY
Higher 2

9729/03

Paper 3 Free Response

11 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** Peroxides refer to a class of compounds with an oxygen-oxygen single bond.

Hydrogen peroxide, H_2O_2, is the simplest peroxide. It is commonly used in laboratories for both its oxidising and reducing properties.

Sodium peroxide, Na_2O_2, is prepared by burning sodium in air. This reaction also produces sodium oxide, Na_2O.

Compound	Melting point / ^{o}C
hydrogen peroxide, H_2O_2	−11
sodium peroxide, Na_2O_2	675
sodium oxide, Na_2O	920

(i) Draw the 'dot-and-cross' diagrams for

- hydrogen peroxide, H_2O_2
- sodium peroxide, Na_2O_2. [2]

(ii) Explain the difference in the melting points between

- sodium peroxide (Na_2O_2) and hydrogen peroxide (H_2O_2)
- sodium peroxide (Na_2O_2) and sodium oxide (Na_2O). [2]

(b) The peroxides of the Group 2 elements, MO_2, decompose on heating to produce a single gas and the solid oxide, MO, only.

(i) Write an equation for the thermal decomposition of strontium peroxide, SrO_2. [1]

(ii) Suggest how the temperature at which thermal decomposition of MO_2 occurs varies down Group 2.

Explain your answer. [3]

1 **(c)** Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{=} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{=} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a value of ethanoic acid, CH_3CO_2H, is 4.76.

(i) With reference to the table given, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,
- become larger as n increases. [3]

(ii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid. [1]

(iii) Calculate the pH of a 0.10 mol dm^{-3} solution of $HO_2CCH_2CO_2H$. Ignore the effect of pK_a(2) on the pH. [1]

(iv) Sketch the pH-volume added curve you would expect to obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} $HO_2CCH_2CO_2H$.

Mark clearly the initial pH and the point(s) of maximum buffering capacity. Indicate the volume at equivalence point(s). [3]

(v) The monosodium salts of edible dicarboxylic acids can act as buffers.

Write two equations to show how monosodium butanedioate, $HO_2C(CH_2)_2CO_2Na$, acts as a buffer. [2]

(vi) A solution containing both $HO_2C(CH_2)_2CO_2Na$ and $NaO_2C(CH_2)_2CO_2Na$ forms a buffer solution. The following equilibrium is present in the solution.

$$HO_2C(CH_2)_2CO_2^-(aq) = {}^-O_2C(CH_2)_2CO_2^-(aq) + H^+(aq)$$

By choosing the correct pK_a value given in the table, calculate the pH of a buffer solution made by mixing 100 cm^3 of 0.5 mol dm^{-3} $HO_2C(CH_2)_2CO_2Na$ and 50 cm^3 of 0.3 mol dm^{-3} $NaO_2C(CH_2)_2CO_2Na$. [2]

[Total: 20]

2 Sulfur is the second member of Group 16 in the Periodic Table.

(a) Explain why sulfur has a lower first ionisation energy than phosphorus. [1]

(b) Natural gas, consisting primarily of methane, is available in large amounts and is used as a fuel. However, direct conversion of alkanes such as methane into useful products is challenging owing to their unreactivity.

(i) Give a reason why alkanes are unreactive. [1]

In 2013, scientists discovered that they could selectively convert methane to alkenes using gaseous sulfur, S_2, over a suitable catalyst. This conversion takes place at over 1000 K, where sulfur exists as $S_2(g)$, as shown in **reaction 1**.

(ii) **reaction 1** $2CH_4(g) + S_2(g) \rightarrow C_2H_4(g) + 2H_2S(g)$

Calculate the enthalpy change of **reaction 1** by drawing an energy cycle using the following information.

$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$ $\Delta H_r^{\ominus} = +96.0$ kJ mol^{-1}

$C_2H_4(g) + 3S_2(g) \rightarrow 2CS_2(g) + 2H_2S(g)$ $\Delta H_r^{\ominus} = +91.0$ kJ mol^{-1} [2]

(c) The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen over a catalyst.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) When an equimolar mixture of SO_2 and O_2 is passed over a catalyst at T °C at an initial total pressure of 200 kPa, the percentage conversion of $SO_2(g)$ is 98%.

Calculate the equilibrium partial pressure of each of the three gases and hence, the value of K_p at temperature T °C. [3]

(ii) The table below shows values of K_p for this equilibrium at different temperatures.

temperature / °C	K_p / kPa^{-1}
25	4.0×10^{22}
200	2.5×10^{8}
800	1.3×10^{-3}

Using relevant data from the given table, explain in terms of the position of equilibrium,

- the sign of $\Delta G^{\ominus}$ at 25 °C and
- the sign of ΔH for the forward reaction. [4]

2 **(d)** **(i)** Which of the two gases, SO_2 and O_2, is less ideal? Explain your answer. [1]

(ii) Sketch a graph of volume (V) against temperature (T/ K) for a given mass of an ideal gas at constant pressure. [1]

(e) In the atmosphere, the oxidation of SO_2 to SO_3 can be catalysed by NO_2.

The mechanism for this catalysed oxidation of SO_2 to SO_3 occurs in two steps.

$$\textit{step 1}: \; NO_2(g) + SO_2(g) \xrightarrow{slow} NO(g) + SO_3(g) \qquad \Delta H_{1'} = -88 \text{ kJ mol}^{-1}$$

$$\textit{step 2}: \; NO(g) + \frac{1}{2}O_2(g) \xrightarrow{fast} NO_2(g) \qquad \Delta H_{2'} = -57 \text{ kJ mol}^{-1}$$

Use this information to construct a fully-labelled reaction pathway diagram for the catalysed oxidation of SO_2 to SO_3. Indicate on your diagram, the 'reactants', 'products', $\Delta H_{1'}$, $\Delta H_{2'}$ and the activation energy, E_a, of the reaction. [3]

(f) Oxides of nitrogen are also used in other applications.

One such oxide is N_2O_5, which exists as $[NO_2^+][NO_3^-]$ in solution.

When benzene is added to a solution of N_2O_5 in CCl_4, an excellent yield of nitrobenzene is obtained in the absence of any added catalyst.

(i) Write a balanced equation for the reaction of benzene and N_2O_5. [1]

(ii) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs. [2]

(iii) Compounds **H** has the molecular formula, C_9H_{12}. Mononitration of **H** produces only one organic product. Suggest the structure of **H**. [1]

[Total: 20]

3 **(a)** Copper has the highest electrical conductivity rating among the non-precious metals. The high conductivity of copper is a consequence of its electronic configuration.

(i) State the electronic configuration of Cu atom. [1]

(ii) Explain why copper is regarded as a *transition element*. [1]

(iii) Suggest why copper is **not** usually used for overhead electrical cables despite its superior conductivity. [1]

(b) Electrical wiring is the most important market for the copper industry. To be used in wiring, copper must be at least 99.9% pure. Chalcopyrite, $CuFeS_2$, is the most common copper ore being used to obtain pure copper in a two-step process.

The first step occurs in a furnace where chalcopyrite is heated strongly with silica, SiO_2, and air. The furnace reduces the copper(II) in chalcopyrite to copper.

The reaction occurring in the blast furnace can be represented by the following **unbalanced** equation.

$$CuFeS_2 + SiO_2 + O_2 \rightarrow Cu + FeSiO_3 + SO_2$$

The copper obtained is nowhere near 99.9% pure as it contains nickel and silver as minor impurities to form an alloy.

The second step occurs in an electrolytic cell where the alloy undergoes electrolysis to produce copper at or above 99.9% purity.

(i) Identify the element that undergoes oxidation in the furnace and state the initial and final oxidation numbers of this element. [1]

(ii) In the furnace, the element O is reduced alongside with the element Cu. Using oxidation numbers or otherwise, write a **balanced** equation for the reaction occurring in the furnace. [1]

(iii) Draw a fully labelled diagram of the electrolytic cell where copper purification occurs. [2]

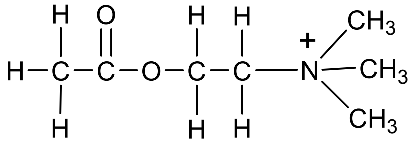
(iv) Explain, by quoting relevant $E^{\ominus}$ values, what happens to the nickel and silver impurities during this purification procedure. [4]

(c) When dilute aqueous ammonia was added to copper(II) sulfate solution, a pale blue precipitate was first observed which dissolved to give a dark blue solution when aqueous ammonia was added in excess. In these reactions, the ammonia can act as a *Bronsted-Lowry base* and as a *Lewis base*.

Illustrate the meaning of *Bronsted-Lowry base* and *Lewis base* using the reactions of aqueous copper(II) ions with ammonia. Write equations to account for the observations noted in these reactions. [4]

3 **(d)** In 2013, scientists suggested that too much copper in our diet may contribute to Alzheimer's disease, a neurological disorder in which death of brain cells causes memory loss and cognitive decline. In patients with Alzheimer's disease, the concentration of acetylcholine, a neurotransmitter essential for processing memory and learning, is found to be lower.

The structure of acetylcholine is shown below.

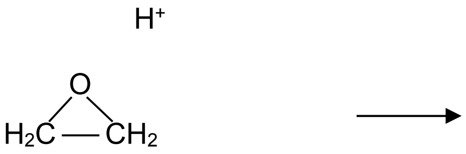


When acetylcholine undergoes hydrolysis in the presence of an enzyme, two products are formed; one of which is a charged species called choline.

(i) Draw the structures of these **two** products. [2]

(ii) As a precursor to the synthesis of acetylcholine, choline is an essential nutrient in our diet. Choline can be produced in a sealed reaction vessel by the reaction of anhydrous trimethylamine, $N(CH_3)_3$, with epoxyethane and HC*l* under moderate pressure.

Copy and complete the diagram below to suggest a mechanism to show how choline is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



epoxyethane [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Thionyl chloride, $SOCl_2$, is a colourless liquid that is primarily used in the chlorination of organic compounds.

(i) Draw the shape of $SOCl_2$. [1]

(ii) Explain which molecule, $SOCl_2$ or $COCl_2$, is expected to have a larger bond angle. [1]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H \rightarrow RCOCl + SO_2(g) + HCl\,(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq). The excess NaOH was titrated with 0.500 mol dm^{-3} HCl(aq). It required 10.8 cm^3 of the HCl(aq) solution to reach the end-point.

(i) Write equations for the complete reactions between

- NaOH and HCl,
- NaOH and SO_2. [2]

(ii) Calculate the total number of moles of NaOH that reacted with the acidic gases, SO_2 and HCl. [1]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl. [1]

(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H. [1]

(v) The R group contains carbon and hydrogen only.

Suggest the structure of RCO_2H. [1]

(c) Using $SOCl_2$ in the initial step, carboxylic acids can be converted into primary amines by the following sequence of reactions.

$$RCO_2H \xrightarrow[\text{step 1}]{SOCl_2} RCOCl \xrightarrow[\text{step 2}]{} \mathbf{D} \xrightarrow[\text{step 3}]{} RCH_2NH_2$$

(i) Identify the structure of **D**. [1]

(ii) Suggest the reagents needed for step 2 and step 3. [2]

(iii) State the *types of reaction* for step 2 and step 3. [1]

4 **(d)** Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- Both angelic acid and **T** exhibit stereoisomerism.
- On treatment with hot acidic $KMnO_4$, angelic acid produces two acidic compounds, **U** and **V**.
- Only **U** gives yellow precipitate with alkaline aqueous iodine.

(i) Suggest structures for **T**, **U**, **V** and angelic acid. Explain the reactions. [6]

(ii) State the types of stereoisomerism shown by angelic acid and compound **T**. [2]

[Total: 20]

5 **(a)** **(i)** Describe the reaction of $SiCl_4$ with water and include any observations you can make. Write an equation for the reaction that occurs. [2]

(ii) Carbon is in the same group as silicon. However, CCl_4 does not react with water. Explain why. [1]

(b) Chlorine-containing organic compounds can also differ in their reactivity towards hydrolysis reactions.

Compounds **A** and **B** are isomers with the molecular formula, C_7H_7Cl. Compound **A** reacts with aqueous NaOH on heating but compound **B** does not.

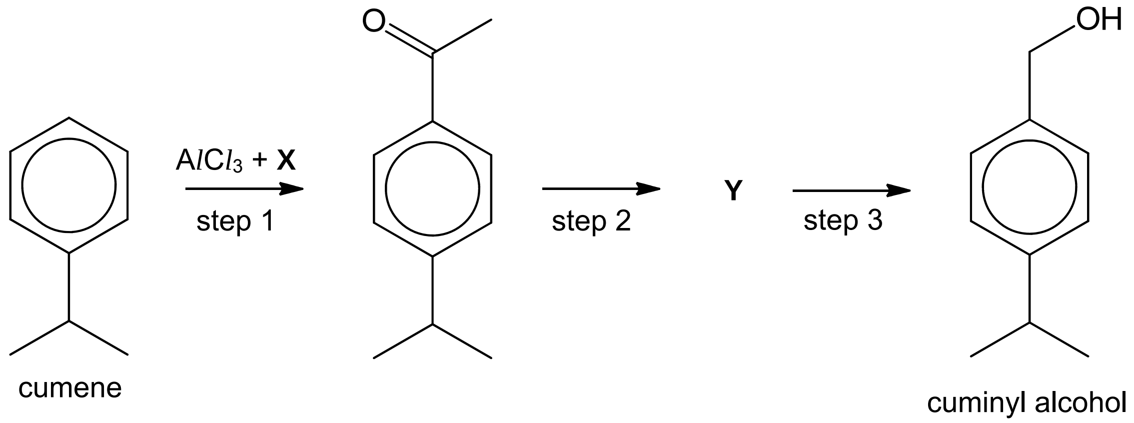
Draw the structures of compounds **A** and **B** and explain the difference in their reactivity towards aqueous NaOH. [2]

(c) Heating tin with hydrochloric acid produces hydrogen gas. Careful removal of water from the resulting product produces white solid $SnCl_2$.

In contrast, passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Using relevant $E^{\ominus}$ from the *Data Booklet*, explain the above observations. [2]

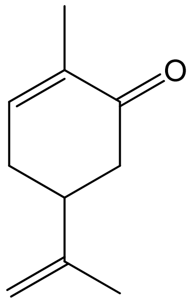
(d) Cumin is a spice used to flavour food. One of the key organic compounds responsible for the smell of cumin is cuminyl alcohol. It can be synthesised from cumene as shown below. Aluminium chloride is used as a catalyst with reagent **X** in step 1.



(i) Suggest the identity of reagent **X**. [1]

(ii) Suggest reagents and conditions for steps 2 and 3 and draw the structure of the intermediate compound **Y**. [3]

5 **(e)** Carvone, an isomer of cuminyl alcohol, is most responsible for the flavour of caraway, dill and spearmint.



carvone

(i) When carvone is treated with $NaBH_4$, compound **M**, $C_{10}H_{16}O$, is produced. Draw the structure of **M** and write an equation to represent this reaction. [2]

(ii) Compound **N** is isomeric with compound **M**.

On treatment with hot concentrated $KMnO_4$, **N** gives two compounds, **P**, C_3H_6O, and **Q**, $C_4H_4O_5$. **P** and **Q** are formed in the mole ratio of 2 : 1.

All three compounds, **N**, **P** and **Q** give an orange precipitate with 2,4-dinitrophenylhydrazine but only **N** forms a silver mirror with Tollens' reagent. One mole of **Q** reacts with two moles of aqueous sodium hydrogencarbonate.

Suggest structures for **N**, **P** and **Q** and explain the observations described above. [7]

[Total: 20]

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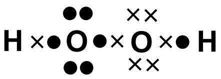
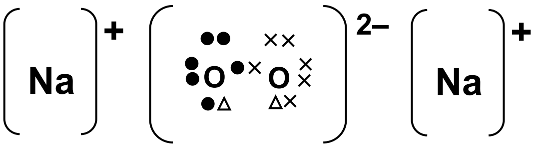
Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 3

1 **(a)** **(i)** H_2O_2 :



[1m]

Na_2O_2 :



Accept:
1) 2 $[Na]^+$

Reject:
1) $[Na]_2^+$
2) electrons are drawn around Na^+

[1m]

(ii) Sodium peroxide has a giant ionic structure while hydrogen peroxide has a simple molecular structure.

More energy is needed to overcome the **strong ionic bonds between Na^+ and O_2^{2-}/oppositely charged ions** (✓)

compared to the **weak intermolecular force in H_2O_2/ hydrogen bonds between H_2O_2 molecules**. (✓)

Hence, sodium peroxide has a higher boiling point than hydrogen peroxide.

Both sodium peroxide and sodium oxide have a giant ionic structure.

While O_2^{2-} and O^{2-} have the same ionic charge, **O_2^{2-}** has a **larger radius/ bigger size than O^{2-}** (✓).

Less energy is needed to overcome the **weaker ionic bonds between Na^+ and O_2^{2-} than that between Na^+ and O^{2-}.** (✓)

Hence, sodium peroxide has a lower boiling point than sodium oxide.

4(✓) : **[2m]** ; 2-3(✓) : **[1m]**

Minus 1m if no comparison of the strength of bonds is made.

(b) **(i)** $SrO_2 \rightarrow SrO + \frac{1}{2}O_2$ or $2SrO_2 \rightarrow 2SrO + O_2$ **[1m]**

(ii) Down the Group, **decomposition temperature increases**. **[1m]**

Down the Group,

① **radius of M^{2+}/cation increases**
② **charge density** of M^{2+} **decreases**

[1m]

③ **polarising power** of M^{2+} **decreases** / **polarisation of O_2^{2-} anion occurs to smaller extent**
④ **less weakening of O–O bond**
⑤ MO_2 becomes **thermally more stable**, higher temperature is needed to decompose.

[1m]

1 (c) (i) pK_a(1) values are all smaller than the pK_a of ethanoic acid

[1m] smaller pK_a implies larger K_a, indicating **dicarboxylic acids are more acidic/ stronger acids** than ethanoic acid

[1m] **–CO_2H group is electron-withdrawing**, **disperse the negative charge** and **stabilise** mono**anion**/ $HO_2C(CH_2)_nCO_2^-$

Or mono**anion**/ $HO_2C(CH_2)_nCO_2^-$ is **stabilised by hydrogen bonding** (especially for malonic acid when n=1)

pK_a(1) values become larger as n increases

[1m] electron-withdrawing **–CO_2H group** is **further away from –CO_2^- / ionising –CO_2H / the other –CO_2H group**

Or intervening **additional electron-donating alkyl groups destabilise anion**

(ii) larger pK_a implies smaller K_a with $HO_2C(CH_2)_nCO_2^-$ being a weaker acid than CH_3CO_2H; it is **more difficult to remove** a positively charged **H^+ from a negatively charged** species/ mono**anion** (electrostatically not favourable) **[1m]**

(iii)

$$[H^+] = \sqrt{K_a \times c}$$

$$= \sqrt{10^{-2.83} \times 0.10}$$

$$= \mathbf{0.0122\ mol\ dm^{-3}}$$

pH = -lg [H^+] = **1.92** **[1m]**

(iv)

The following should be clearly marked and labelled:

(✓) Both axes are labelled with units stated for x-axis.

(✓) Curve starts at pH 1.92 (ecf)

(✓) First maximum buffering capacity at 5 cm^3 and pH 2.83.

(✓) Second maximum buffering capacity at 15 cm^3 and pH 5.69.

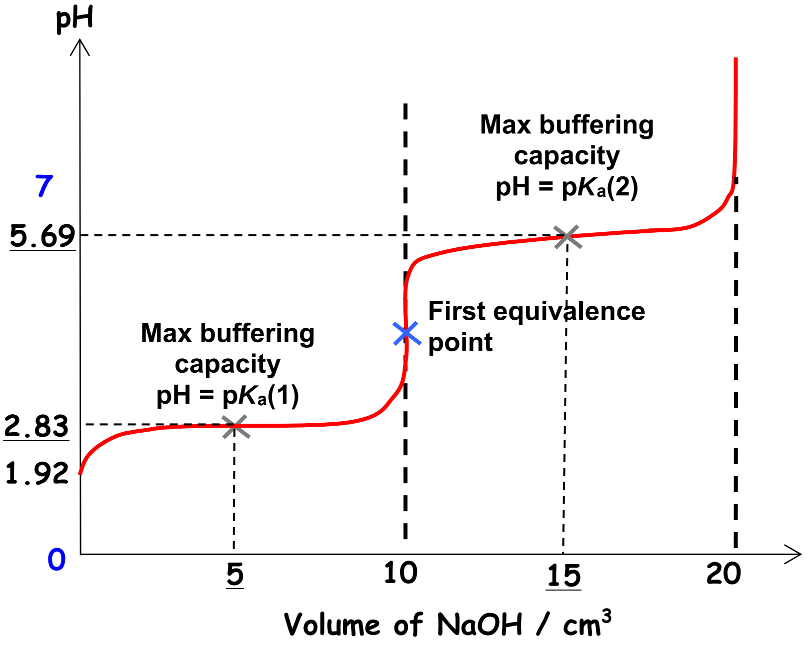
(✓) First equivalence point at 10 cm^3 and graph ends at 20 cm^3

(✓) 2 points of inflection

6(✓) – [3m]

4–5(✓) – [2m]

2–3(✓) – [1m]



(v) **[1m]** $HO_2C(CH_2)_2CO_2Na + H^+ \rightarrow HO_2C(CH_2)_2CO_2H + Na^+$

[1m] $HO_2C(CH_2)_2CO_2Na + OH^- \rightarrow {}^-O_2C(CH_2)_2CO_2Na + H_2O$

allow ionic eqns; reject =

1 (c) (vi) System: Acidic Buffer

$$pH = pK_a + \lg\frac{[salt]}{[acid]} = pK_a + \lg\frac{n(salt)}{n(acid)}$$

$$= 5.61 + \lg\left(\frac{\frac{50}{1000}\times 0.3}{\frac{100}{1000}\times 0.5}\right)$$

$$= \underline{5.09}$$

[1m] quote the correct pK_a (5.61) in working
[1m] pH calculation (ecf from wrong pK_a)

2 (a) Inter-electronic **repulsion between paired 3p electrons** makes it **easier to remove one of the paired** 3p **electrons** than to remove the unpaired 3p electron from phosphorus. [1m]

(b) (i) [1m] Either one of the following:

Very strong C–C and C–H bonds / **high bond energies**

Non-polar / **C and H have similar electronegativities**

(ii)

$$\begin{tikzcd}
2CH_4(g) + S_2(g) \arrow[rr] \arrow[dr, "+3S_2(g)"', "+2(96.0)"] & & C_2H_4(g) + 2H_2S(g) \arrow[dl, "+91.0"', "+3S_2(g)"] \\
& 2CS_2(g) + 4H_2S(g) &
\end{tikzcd}$$

[1m] energy cycle

ΔH for reaction 1 = +2(96.0) – 91.0 = +**101 kJ mol^{-1}** [1m]

(c) (i)

	$2SO_2(g)$ +	$O_2(g)$ ⇌	$2SO_3(g)$	
initial partial pressure /kPa	100	100	0	
	–0.98(100)	**–½(98)**		
eqm partial pressure /**kPa**	**2** (✓)	**51** (✓)	**98** (✓)	**2 (✓): [1m]** **3(✓): [2m]**

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} = \frac{(98)^2}{(2)^2(51)}$$

= **47.1** kPa^{-1} [1m]

(ii) Since **K_p at 25 °C** is much **larger than 1**, the **position of equilibrium** in $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ **lies** very much **to the right** [1m], so the **forward reaction is spontaneous** and **$\Delta G^{\ominus}$ is negative**. [1m]

As **K_p decreases with increasing temperature**, it implies that the **position of equilibrium shifts to the left** [1m] with increasing temperature to absorb some heat. Hence, the backward reaction is endothermic and the **forward reaction is exothermic**, so **ΔH has a negative sign**. [1m]

2 (d) (i) **SO_2** is less ideal.

Either:

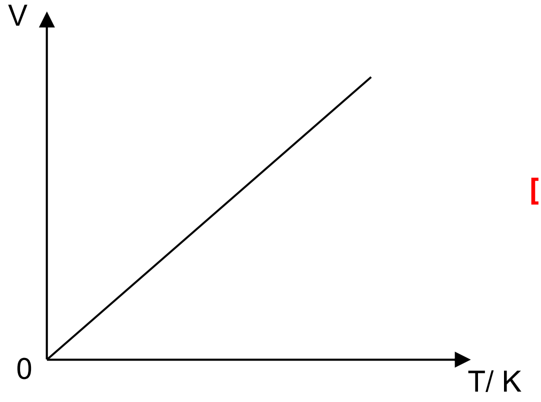
SO_2 has stronger intermolecular forces of attraction between its molecules as it is a **polar molecule / has greater number of electrons per molecule**.

OR

SO_2 is a **larger molecule** than O_2, so the **volume of SO_2 molecules is less negligible compared to the volume of the container/gas**.

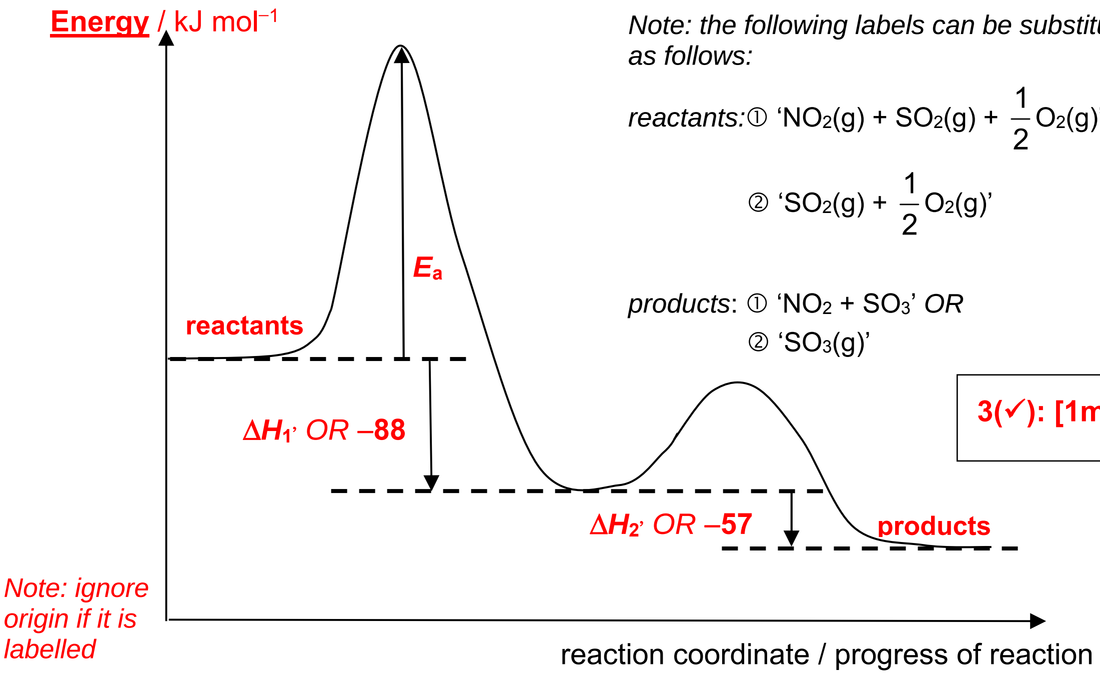
[1m]

(ii)



[1m]

(e)



Note: the following labels can be substituted as follows:

reactants: ① '$NO_2(g) + SO_2(g) + \frac{1}{2}O_2(g)$' *OR*

② '$SO_2(g) + \frac{1}{2}O_2(g)$'

products: ① '$NO_2 + SO_3$' *OR*

② '$SO_3(g)$'

3(✓): [1m]

(✓): *2 humps.*

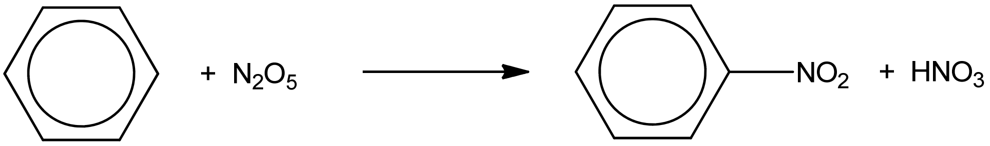
(✓): *label 'reactants', 'products' OR using appropriate formulae (with balanced species)*

(✓): *label y-axis. Ignore x-axis label. Reject if reactants are labelled at '0' level*

[1m] : *Both $\Delta H_{1'}$ and $\Delta H_{2'}$ shown. Ignore direction of arrows.*

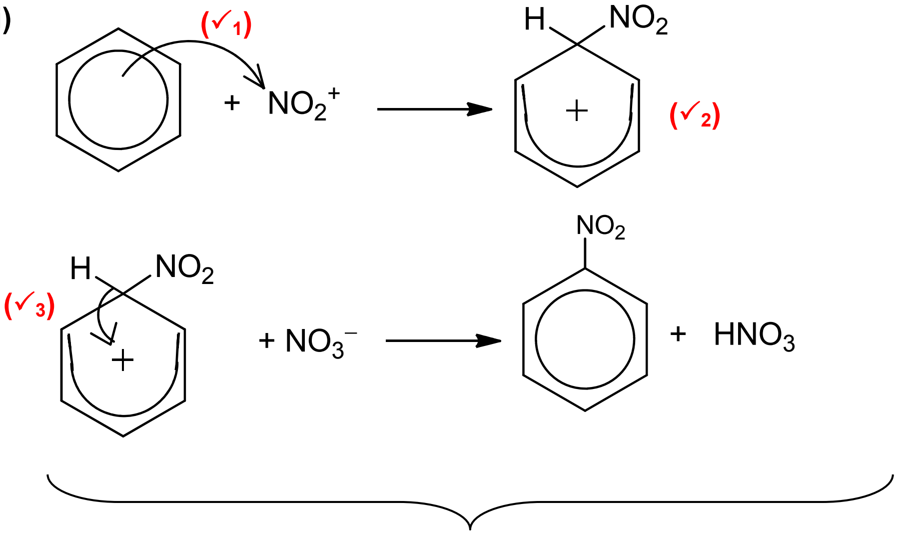
[1m] : *correct labelling of E_a, with $E_{a1} > E_{a2}$. Ignore direction of arrows.*

2 **(f)** **(i)**



[1m]

(ii)



(✓₄): correct products and balanced equation

(✓₁) – *full arrow from π–electron ring of benzene to the N atom of NO_2^+.*

(✓₂) – *correct arenium ion with delocalisation of positive charge over the other 5 carbons.*

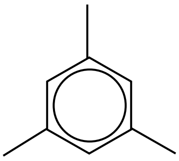
(✓₃) – *full arrow from C–H bond to the (+)ve charge of arenium ion*

(✓₄) – *correct products formed with* ***balanced equation*** *with HNO_3 as the other product*

Note: *Labelling of* ***"slow/fast"*** *step is* ***not*** *required.*

4(✓): [2m]; 2–3(✓): [1m]

(iii) Structure of **H**:



[1m]

3 **(a)** **(i)** Cu: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$** **[1m]**

(**not $3d^9\ 4s^2$** due to the extra stability of $3d^{10}$ and the similar energies of 3d and 4s electron)

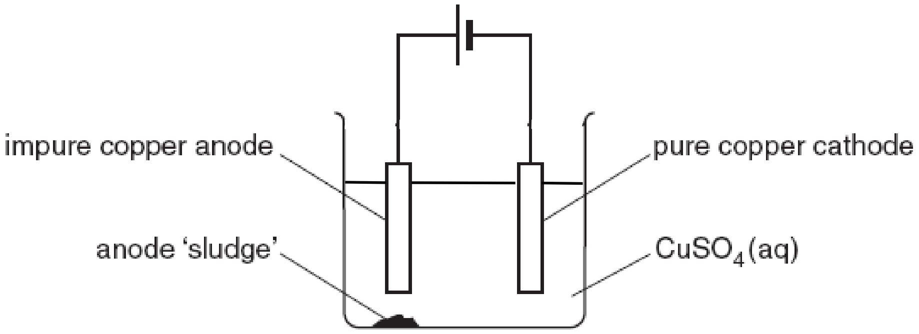
(ii) Copper is a **d-block element** that **forms** one or more **stable ions with incompletely filled d-orbitals**. **[1m]**

(iii) Copper has **high density/** is **too heavy** for overhead use. **[1m]**

(b) **(i)** **S** is oxidised from **–2 to +4** **[1m]**

(ii) $\underline{2}\,CuFeS_2 + \underline{2}\,SiO_2 + \underline{5}\,O_2 \rightarrow \underline{2}\,Cu + \underline{2}\,FeSiO_3 + \underline{4}\,SO_2$ **[1m]**

(iii)



[1m] these labels on the diagram: **impure copper, pure copper, $CuSO_4(aq)$**

[1m] battery with 2 electrodes dipped in a common electrolyte;
battery must show the correct polarity with respect to the impure copper.

(iv) species present:
$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$, $H_2O(l)$, impure Cu (anode) and impurities such as Ag, Ni

$O_2 + 4H^+ + 4e^- \rightleftharpoons \mathbf{2H_2O}$ $E^\ominus = +1.23$ V
$Cu^{2+} + 2e^- \rightleftharpoons \mathbf{Cu}$ $E^\ominus = +0.34$ V
$Ni^{2+} + 2e^- \rightleftharpoons \mathbf{Ni}$ $E^\ominus = -0.25$ V
$Ag^+ + e^- \rightleftharpoons \mathbf{Ag}$ $E^\ominus = +0.80$ V

Note:
The species is more easily oxidised when the $E^\ominus$ is more negative (*or* less positive).

[1m] **quote $E^\ominus$ values for Cu^{2+}/Cu, Ni^{2+}/Ni and Ag^+/Ag**

At the **anode**,
Cu(s) is oxidised to $Cu^{2+}(aq)$ in preference over H_2O as $E^\ominus(Cu^{2+}/Cu)$ is more negative than $E^\ominus(O_2/H_2O)$.
Ni(s) is also **oxidised to Ni^{2+}**(aq) (which goes into the solution) as **$E^\ominus(Ni^{2+}/Ni)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$**. **[1m]**
Ag(s) **is not oxidised** to Ag^+ as **$E^\ominus(Ag^+/Ag)$ is more positive than $E^\ominus(Cu^{2+}/Cu)$**.
∴ **Ag**(s) **is collected as "anode sludge"**. **[1m]**

$\mathbf{2H_2O} + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$V
$\mathbf{Cu^{2+}} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V
$\mathbf{Ni^{2+}} + 2e^- \rightleftharpoons Ni$ $E^\ominus = -0.25$ V

Note:
The species is more easily reduced when the $E^\ominus$ is more positive (*or* less negative).

At the **cathode**,
$Cu^{2+}(aq)$ is reduced to Cu(s) in preference over H_2O as $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(H_2O/H_2)$.

Ni^{2+}(aq) **is not reduced** to Ni(s) **as $E^\ominus(Ni^{2+}/Ni)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$**.
∴ **Ni^{2+}**(aq) **remains in the solution**. **[1m]**

3 (c) [1m] ***Bronsted-Lowry base*** is a **proton/H⁺ acceptor** as illustrated by

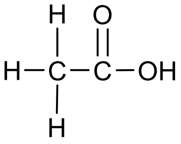
NH_3 accepting a proton/H⁺ from H_2O to form OH^-.
Or $\mathbf{NH_3}(aq) + \mathbf{H_2O}(l) = \mathbf{NH_4^+}(aq) + \mathbf{OH^-}(aq)$

[1m] $\mathbf{Cu^{2+}}(aq) + \mathbf{2OH^-}(aq) \rightarrow \mathbf{Cu(OH)_2}(s)$
pale blue soln pale blue ppt

[1m] $\mathbf{Cu(OH)_2}(s) + \mathbf{4NH_3}(aq) + \mathbf{2H_2O}(l) \rightarrow \mathbf{[Cu(NH_3)_4(H_2O)_2]^{2+}}(aq) + \mathbf{2OH^-}(aq)$
Or $\mathbf{[Cu(H_2O)_6]^{2+}}(aq) + \mathbf{4NH_3}(aq) \rightarrow \mathbf{[Cu(NH_3)_4(H_2O)_2]^{2+}}(aq) + \mathbf{4H_2O}(l)$
dark blue soln

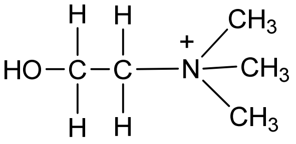
When added in excess, NH_3 acts as a *Lewis base* where N in NH_3 ligand **donates a lone pair** of electrons **to Cu^{2+}**, forming strong dative bonds with Cu^{2+} to give the stable $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex. [1m]

(d) (i)



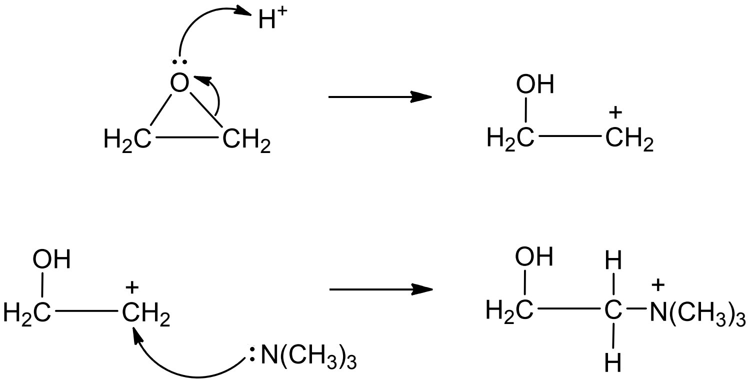
$$H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

[1m] and

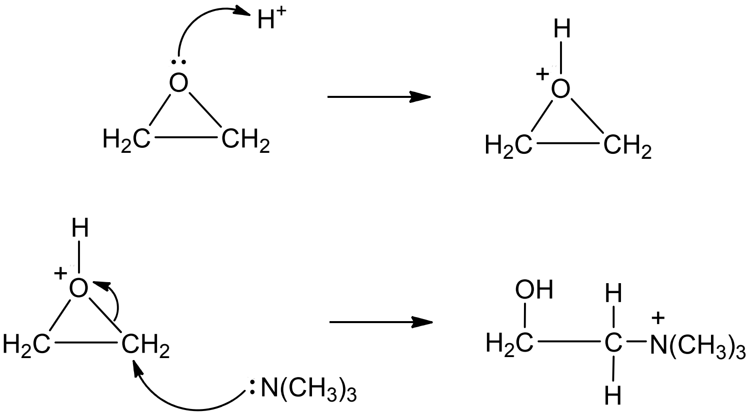


[1m]

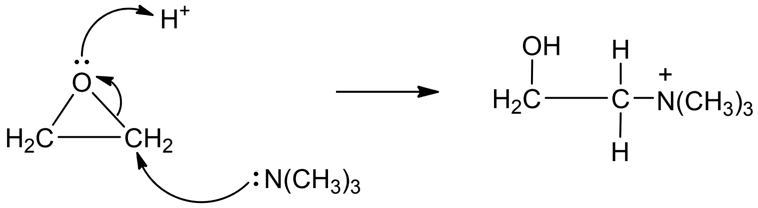
(ii) **Option 1:**



Option 2:

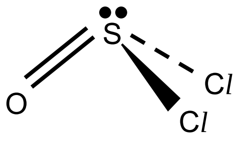


Option 3:

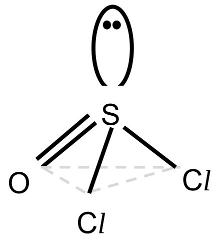


[1m] for each curly arrow with the associated lone pair and any positive charge

4 (a) (i)



or



[1m] illustrate trigonal pyramidal shape.

(ii) **$COCl_2$** will have a larger bond angle. **[1m] bonus**

$COCl_2$ has lesser number/ 3 sets of **electron pairs** (or state **3 bp, 0 lp**) which can be **further apart to minimise repulsion** compared to **$SOCl_2$** that **has 4 electron pairs** (or state **3 bp, 1 lp**). **[1m]**

(b) (i) $NaOH + HCl \rightarrow NaCl + H_2O$ **[1m]**

$2\,NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ **[1m]**

Allow if 2nd eqn is split into 2 eqns: $SO_2 + H_2O \rightarrow H_2SO_3$
$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O$

Reject: $NaOH + SO_2 \rightarrow NaHSO_3$ for NaOH is added in excess

(ii)

$$n(NaOH)\text{ reacted} = \frac{60.0-10.8}{1000}\times 0.500$$

$= \mathbf{0.0246}$ mol **[1m]**

(iii) RCO_2H : $SO_2 + HCl$: $NaOH$
1 : 1 : 3

$$n(RCO_2H) = \frac{0.0246}{3} = \mathbf{0.00820}\text{ mol}$$ **[1m]**

(iv)

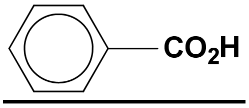
$$M_r\,(RCO_2H) = \frac{1.00}{0.0082} = \mathbf{122}$$ **[1m] no units, 3 s.f., ecf**

(v) RCO_2H: mass units of $-CO_2H = 45$

mass units of $-R = 122 - 45 = 77$

estimated number of C in $-R = 77/12 = 6.4$ (⇒ R contains 6 carbon atoms)

RCO_2H is



[1m]

(c) (i) **$RCONH_2$** **[1m]**

(ii) Step 2: **NH_3**(g) **[1m]** reject (aq)

Step 3: **$LiAlH_4$**, dry ether **[1m]** reject (aq); ignore 'heat'

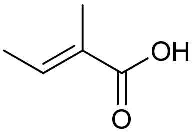
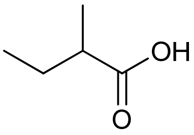
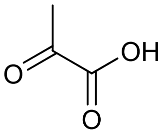
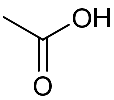
(iii) Step 2: **condensation/ nucleophilic acyl substitution**
Step 3: **reduction**

allow nucleophilic substitution
[1m] each, bonus

4 (d) (i)

Observation	Type of Reaction	Deduction
Angelic acid + H_2 → **T** $C_5H_8O_2$ $C_5H_{10}O_2$	**reduction** (✓)	**Angelic acid** is an **alkene**. (✓)
Angelic acid + $KMnO_4$ → **U** and **V**	**Oxidative cleavage of C=C** /**oxidation** (✓)	**U** and **V** are **carboxylic acids.** (✓)
U + I_2/OH^- → yellow ppt	**Iodoform test/ oxidation** (✓)	**U** has the structure $CH_3{-}\underset{|}{C}{=}O$ (✓)

5-6(✓): [2m]; 3-4(✓): [1m]

angelic acid	T	U	V
			

[1m] for each structure

(ii) angelic acid : **cis-trans isomerism** **[1m]**

compound **T** : **enantiomerism** **[1m]**

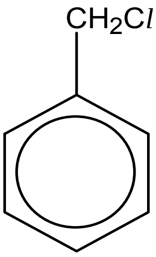
5 (a) (i) **SiC*l*$_4$ reacts with water / hydrolyses** completely in water **to give** a strongly **acidic solution**. **[1m] bonus**

A **white solid/ppt** of SiO_2 will be observed/ **white (or steamy) fumes** of HC*l* will be observed. **[1m]**

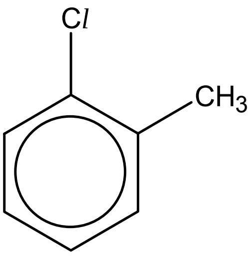
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ **[1m]**

(ii) Unlike silicon, **carbon does not have energetically accessible empty 3d orbitals to accept** a lone pair of **electrons from water** molecules. **[1m]**

(b)



A



B (-CH_3 and C*l* groups can be in any position)

[1m] for both structures of **A** and **B**

For compound **B**, **delocalisation of the lone pair** of electrons **on C*l* into the** π-electron cloud of **benzene ring imparts double bond character to the C–C*l*, strengthening the C–C*l* bond**. Hence, **B** does not react with NaOH(aq). **[1m]**

5 **(c)** $\boxed{2H^+} + 2e^- \rightleftharpoons H_2$ $E^\ominus = 0.00$ V

$Sn^{2+} + 2e^- \rightleftharpoons \boxed{Sn}$ $E^\ominus = -0.14$ V

$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $E^\ominus = +0.15$ V

$\boxed{Cl_2} + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

Reaction between H^+ and Sn:

$E^\ominus_{cell}$ = 0.00 – (–0.14) = +0.14 V > 0 (reaction is energetically feasible) [1m]

Reaction between H^+ and Sn^{2+}:

$E^\ominus_{cell}$ = 0.00 – (+0.15) = –0.15 V < 0

Oxidation of Sn^{2+} to Sn^{4+} by H^+ is NOT energetically feasible.

Reaction between Cl_2 and Sn:

$E^\ominus_{cell}$ = 1.36 – (–0.14) = +1.50 V > 0

Oxidation of Sn to Sn^{2+} by Cl_2 is energetically feasible. [1m]

Reaction between Cl_2 and Sn^{2+}:

$E^\ominus_{cell}$ = 1.36 – (+0.15) = +1.21 V > 0

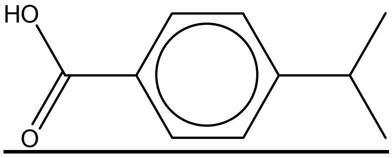
Oxidation of Sn^{2+} to Sn^{4+} by Cl_2 is energetically feasible. **[1m] bonus**

Award max [1m] if three $E^\ominus_{cell}$ values are calculated without any comment.

(d) **(i)** **CH_3COCl** **[1m]**

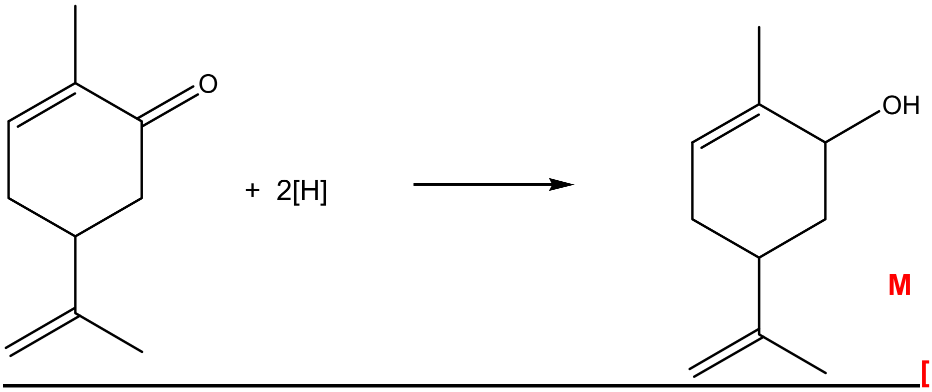
(ii) Step **2**: **alkaline I_2(aq), heat,** followed by H^+(aq) **[1m]**

Step **3**: **$LiAlH_4$, dry ether** **[1m]**

Y: 

[1m]

(e) **(i)**



M **[1m]**

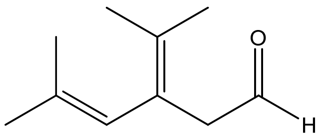
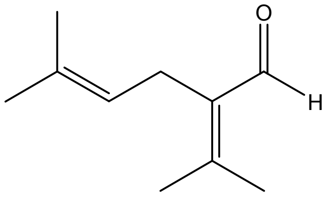
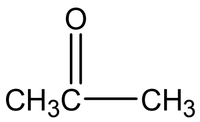
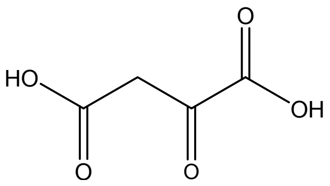
[1m]

5 (e) (ii)

8-9(✓): [4m]
6-7(✓): [3m]
4-5(✓): [2m]
2-3(✓): [1m]

Information from question	Type of reaction	Deduction
N reacts with hot concentrated $KMnO_4$ to give **P** and **Q**	**oxidation** (✓)	**C=C bond in N cleaves** (✓)
N, **P**, **Q** react with 2,4-DNPH	**condensation** (✓)	**N, P and Q contains carbonyl group / contains either aldehyde or ketone groups** (✓)
Only **N** gives silver mirror with Tollens' reagent	**oxidation** (✓)	**N contains** aliphatic **aldehyde group** (✓) **P and Q contain ketone group** (✓)
One mole of **Q** reacts with two moles of $NaHCO_3(aq)$	**acid-carbonate reaction / acid – hydrogen carbonate reaction** (✓)	**Q contains 2 –CO_2H groups** (✓)

[1m] for each correct structure

 or 	 CH_3COCH_3	
N	**P**	**Q**

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME

CLASS **18S**

EXAM INDEX

CHEMISTRY

9729/04

Higher 2

Paper 4 Practical

16 August 2018
2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	**13**
2	**16**
3	**12**
4	**14**
Total	**55**

This document consists of **18** printed pages and **0** blank page.

Answer **all** the questions in the spaces provided.

1 Determination of the A_r of magnesium by a back titration method

FA 1 is an aqueous solution prepared by dissolving 0.215 g of magnesium ribbon in 30.0 cm^3 of 1.00 mol dm^{-3} hydrochloric and made up to 250 cm^3 with deionised water.

FA 2 is aqueous sodium carbonate containing 2.65 g dm^{-3} Na_2CO_3.

In this question, you will titrate **FA 2** with **FA 1** to determine how much hydrochloric acid was left over after the reaction with magnesium.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Using the experimental results, you will determine the A_r of magnesium.

(a) Method

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 1** from the burette into the conical flask until the yellow colour of the solution changes to orange.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points 1 to 5 as necessary until consistent results are obtained.

Results

[5]

(b) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

25.0 cm^3 of **FA 2** requires ……………… of **FA 1** for complete reaction. [1]

(c) **Calculations**

(i) Calculate the amount of sodium carbonate in the 25.0 cm^3 of **FA 2** used in each titration. [A_r: Na, 23.0; C, 12.0; O, 16.0]

Amount of Na_2CO_3 in 25.0 cm^3 of **FA 2** = ………………… [1]

(ii) Use your answer in **(c)(i)** to calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 1**.

[1]

Amount of HC*l* present in 250 cm^3 = …………………

(iii) Calculate the amount of hydrochloric acid that reacted with the magnesium.

Amount of HC*l* that reacted with the magnesium = ………………… [1]

(iv) Hence calculate the relative atomic mass, A_r, of magnesium.

A_r of magnesium = ………………… [1]

(d) The A_r of magnesium given in the Periodic Table is 24.3. Use this value given in the Periodic Table to calculate the percentage error of your A_r value of Mg obtained in **(c)(iv)**.

% error = ………………… [1]

(e) A solution of sodium hydroxide was prepared at the same concentration, in mol dm^{-3}, as **FA 2**. A student repeated the titration but replaced **FA 2** with this sodium hydroxide.

Explain the effect that replacing **FA 2** with this solution of sodium hydroxide would have on the volume of **FA 1** needed for the titration.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………… [2]

[Total: 13]

2 Determination of enthalpy change of formation of magnesium oxide.

FA 3 is magnesium ribbon
FA 4 is magnesium oxide
FA 5 is 2.0 mol dm^{-3} hydrochloric acid

The enthalpy change of formation of magnesium oxide, ΔH_f(MgO), is the enthalpy change when one mole of magnesium oxide is formed from its elements in their standard states under standard conditions.

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) \qquad \Delta H_f(MgO)$$

To cause magnesium and oxygen to react together, they must be heated. The reaction then proceeds in an uncontrolled and highly exothermic fashion. It is not possible to measure this enthalpy change without the use of equipment such as a bomb calorimeter.

You are to perform an experiment by which you will determine this enthalpy change by an indirect route.

Both magnesium and magnesium oxide react exothermically with hydrochloric acid to form magnesium chloride. You will determine the molar enthalpy changes for **reaction 1** and **reaction 2**.

reaction 1 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H_{rxn\,1}$

reaction 2 $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) \qquad \Delta H_{rxn\,2}$

You will then use Hess's Law to determine a value for the enthalpy change of formation of magnesium oxide, ΔH_f(MgO).

(a) Determining the enthalpy change of reaction 1 between FA 3 and FA 5.

Follow the instructions below to determine the maximum temperature change when a known mass of magnesium, **FA 3**, reacts completely with excess **FA 5**. Record all the mass readings in Table 2.1 and all measurements of time and temperature in the space provided below the table.

Method 1

1. Weigh the stoppered weighing bottle labelled **FA 3** and its contents. Record the total mass of weighing bottle and **FA 3**.
2. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
3. Stir the solution in the cup with the thermometer and measure its temperature. Record this temperature in your table in **(a)(i)** (this is the temperature at t = 0 min) and start the stop-watch. Repeat this measurement each minute for 3 minutes and record each temperature.
4. At the fourth minute, carefully add **FA 3** from the weighing bottle to **FA 5** in the cup. Quickly stir the mixture with the thermometer but **do not measure the temperature**.
5. Continue to stir the mixture. Measure and record the temperature at 4½ minutes, then **every half minute** until the temperature reaches a maximum, and then **every minute** until the tenth minute.
6. Empty and wash the Styrofoam cup. Rinse the cup with deionised water and dry it using a paper towel.
7. Reweigh the emptied weighing bottle and record its mass. Calculate and record the mass of **FA 3** used.

(a) **(i)** **Results**

Record the required mass readings in Table 2.1 and in an appropriate format in the space below, record all measurements of time and temperature.

Table 2.1

Mass of weighing bottle with **FA 3** /g	
Mass of empty weighing bottle / g	
Mass of **FA 3** used / g	

Measurements of time and temperature:

[3]

(a) **(ii)** Plot a graph of temperature (y-axis) against time (x-axis) on the grid below. You will use the graph to determine the theoretical temperature change at 4 minutes. The scale for temperature should extend at least 1 °C above your highest recorded temperature.

1. Draw a straight line of best-fit for the points before the fourth minute. Draw a second straight line of best-fit for the points after the fourth minute. Extrapolate both lines to the fourth minute.
2. From your graph, read the minimum and maximum temperature at the fourth minute. Record these values in the spaces below and determine a value for the maximum temperature rise, $\Delta \boldsymbol{T}$, at the fourth minute.

Temperature at 4th minute

minimum = ………... ^{o}C

maximum = ……….. ^{o}C

temperature rise, $\Delta \boldsymbol{T}$ = ……..….. K [4]

(iii) Use your $\Delta \boldsymbol{T}$ from **(a)(ii)** to calculate a value for the molar enthalpy change of **reaction 1** between **FA 3** and **FA 5**, $\Delta H_{\text{rxn 1}}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3]

$\Delta H_{rxn\ 1}$ = …………………… kJ mol^{-1} [2]

(b) Determining the enthalpy change of reaction 2 between FA 4 and FA 5.

A student carried out an experiment to determine the enthalpy change of **reaction 2**, $\Delta H_{\text{rxn 2}}$, using a known mass of **FA 4** that reacts with excess **FA 5**.

The student was provided with five pre-weighed samples of **FA 4**, labelled **v**, **w**, **x**, **y** and **z**, and carried out the experiment according to the following instructions.

Method 2

1. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
2. Stir the solution in the cup with the thermometer. Read and record its temperature. This is the initial temperature of **FA 4**, $\boldsymbol{T}_{\text{initial}}$.
3. Carefully add sample **v** to the **FA 5** in the cup.
4. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record the maximum temperature reached, $\boldsymbol{T}_{\text{max}}$.
5. Wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 with the remaining samples **w**, **x**, **y** and **z**.

The student recorded all masses and temperatures in Table 2.2 below.

Table 2.2

	expt **v**	expt **w**	expt **x**	expt **y**	expt **z**
Mass of **FA 4** added to the cup, **m** / g	0.507	0.503	0.487	0.506	0.476
$\boldsymbol{T}_{\text{initial}}$ / °C	31.2	31.2	31.0	31.1	31.3
$\boldsymbol{T}_{\text{max}}$ / °C	38.7	38.6	38.2	38.2	38.3
Temperature change, $\Delta \boldsymbol{T}$ / °C					
$\dfrac{\Delta \boldsymbol{T}}{\mathbf{m}}$ / °C g^{-1}					

(i) Complete Table 2.2 by calculating values for $\Delta \boldsymbol{T}$ and $\Delta \boldsymbol{T}/\mathbf{m}$. Leave values for $\Delta \boldsymbol{T}/\mathbf{m}$ to 3 significant figures.

(ii) Based on the calculated $\Delta \boldsymbol{T}/\mathbf{m}$ values in Table 2.2, determine an appropriate mean maximum temperature change, $\Delta \boldsymbol{T}_{\text{ave}}$, and mean mass of **FA 4**, $\boldsymbol{m}_{\text{ave}}$.

$\Delta \boldsymbol{T}_{ave}$ = …………………. °C $\boldsymbol{m}_{\text{ave}}$ = …………………… g [2]

(iii) Use your results in **(b)(ii)** to calculate a value for the molar enthalpy change of **reaction 2** between **FA 4** and **FA 5**, $\Delta H_{rxn\ 2}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3; O, 16.0]

$\Delta H_{rxn\ 2}$ = …………………… kJ mol^{-1} [2]

(c) Use your values for $\Delta H_{rxn\ 1}$ and $\Delta H_{rxn\ 2}$, together with the enthalpy change of formation of water, $\Delta H_f(H_2O)$, to calculate a value for the enthalpy change of formation of magnesium oxide, $\Delta H_f(MgO)$.

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f(H_2O) = -286 \text{ kJ mol}^{-1}$$

Note: If you were unable to calculate the enthalpy changes, assume that the value of $\Delta H_{rxn\ 1}$ is –457 kJ mol^{-1} and the value $\Delta H_{rxn\ 2}$ is –141 kJ mol^{-1}.

$\Delta H_f(MgO)$ = ………………… kJ mol^{-1} [2]

(d) Two methods, **Method 1** and **Method 2**, have been used to determine the maximum temperature change, $\Delta \boldsymbol{T}$, of an exothermic reaction. Which method would give a more accurate $\Delta \boldsymbol{T}$? Explain your answer.

………………………………………………………………………………………...

……………………………………………………………………………………….

……………………………………………………………………………………….

[1]

[Total: 16]

3 Planning

The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^{-}\,(aq)$$

The equilibrium constant for the above solubility equilibrium, K_{sp}, is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^{-}(aq)]^2$$

This solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate.

The exact concentration of IO_3^- ions is determined by titration. Excess aqueous KI and aqueous H^+ is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-\,(aq) + 5I^-\,(aq) + 6H^+\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate, $Na_2S_2O_3$ of known concentration.

$$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

(a) Using the information given above, you are required to write a plan to determine the solubility product, K_{sp}, of calcium iodate, $Ca(IO_3)_2$, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$ (M_r = 248.2)
- solid calcium iodate, $Ca(IO_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol dm^{-3}
- aqueous hydrochloric acid, HC*l*, of about 1 mol dm^{-3}
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm^3 of 0.075 mol dm^{-3} aqueous $Na_2S_2O_3$;
- the preparation of about 100 cm^3 of a saturated solution of calcium iodate, $Ca(IO_3)_2$ at 20 °C;
- the essential details of the titration process;
- an outline of how you would use your mean titre value to determine the solubility product of $Ca(IO_3)_2$.

In your calculations, you should let **V** cm^3 be your mean titre and express your final mathematical expression in terms of **V**.

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For Examiner's Use

[8]

(b) The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

Justify, with calculations, that the chosen concentration, 0.075 mol dm^{-3}, of aqueous $Na_2S_2O_3$ solution is appropriate. [M_r of $Ca(IO_3)_2$ = 389.9]

[2]

(c) The experiment described in your plan in **(a)** is repeated using 0.1 mol dm^{-3} aqueous $Ca(NO_3)_2$ solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V).

State and explain how, if at all, the titre values and calculated K_{sp} would be expected to differ from that obtained in **(a)**.

[Assume that both the experiments were carried out under the same conditions.]

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

[Total: 12]

4 Qualitative Analysis

(a) You are provided with solid **FA 6** which contains $S_2O_8^{2-}$ anion and one cation from the ions listed in the *Qualitative Analysis Notes*.

You are to perform the tests described in Table 4.1 to deduce the nature of **FA 6** and to identify the cation present in **FA 6**.

Record your observations in Table 4.1. Your answers should include
- details of colour changes and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.
Marks are not given for chemical equations.
No additional or confirmatory tests for ions present should be attempted.

Table 4.1

Tests	*Observations*
(i) To a spatula measure of **FA 6** in a boiling tube, add 1-2 cm depth of dilute hydrochloric acid and heat cautiously. Retain the solution for **test (ii)**.	
(ii) To the resulting solution from **test (i)**, add barium nitrate(V) solution.	
(iii) To a spatula measure of **FA 6** in a test tube, add 1-2 cm depth of freshly prepared solution of iron(II) sulfate solution and warm.	
(iv) Place a spatula measure of **FA 6** in a boiling tube and add dilute nitric acid to dissolve the solid. Then add 1 cm depth of manganese(II) sulfate solution and 4 drops of silver nitrate(V) solution to act as a catalyst. Heat cautiously to bring the mixture to boiling.	
(v) To a spatula measure of **FA 6** in a boiling tube, add 1 cm depth of aqueous sodium hydroxide. Heat cautiously.	

[5]

(b) **(i)** State, with supporting evidence, the nature of **FA 6**.

nature of **FA 6**: ………………………………………………

evidence: ……………………………………………………………………..

……………………………………………………………………………….

……………………………………………………………………………….

(ii) Identify the cation in **FA 6**. cation: ……………..

(iii) Write the ionic equation, including state symbols, for the reaction that occurs in **test (i)**.

………………………………………………………………………………. [4]

(c) You are provided with an organic solution **FA 7** which contains one functional group.

Care: FA 7 is flammable. Do not use Bunsen burner for heating. Use the hot water provided.

FA 7 gives a positive test with 2,4–dinitrophenylhydrazine.

Devise **two** other confirmatory tests using the **bench reagents provided** to identify the functional group present in **FA 7**.

Carry out the tests and record details of the tests performed and observations made in table 4.2.

Table 4.2

Confirmatory Tests	*Observations*

Functional group present in **FA 7**: …………..……………… [5]

[Total: 14]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no. ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in excess dilute strong acids)

(c) Tests for gases

gas	*test and test results*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME	Mark Scheme		
CLASS	**18S**	EXAM INDEX	

CHEMISTRY

9729/04

Higher 2

Paper 4 Practical

16 August 2018
2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 16 and 17.

Shift
Laboratory

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Mark Scheme:
For calculations, the principle of no double penalty (error carried forward) applies.
For connecting parts, marking from point of first penalty onwards will be based on correct method only.

For Examiner's Use	
1	13
2	16
3	12
4	14
Total	55

This document consists of **17** printed pages and **0** blank page.

Answer **all** the questions in the spaces provided.

1 Determination of the A_r of magnesium by a back titration method

FA 1 is an aqueous solution prepared by dissolving 0.215 g of magnesium ribbon in 30.0 cm^3 of 1.00 mol dm^{-3} hydrochloric and made up to 250 cm^3 with deionised water.

FA 2 is aqueous sodium carbonate containing 2.65 g dm^{-3} Na_2CO_3.

In this question, you will titrate **FA 2** with **FA 1** to determine how much hydrochloric acid was left over after the reaction with magnesium.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Using the experimental results, you will determine the A_r of magnesium.

(a) **Method**

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 1** from the burette into the conical flask until the yellow colour of the solution changes to orange.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points 1 to 5 as necessary until consistent results are obtained.

Results

Titration number	1	2
Final burette reading / cm^3	23.80	47.80
Initial burette reading / cm^3	0.00	24.00
Volume of FA 1 used / cm^3	23.80	23.80
	✓	✓

[1] A proper table with correct headers (must state *'burette'*) and units. (Do not award if any final and initial burette readings are inverted)

[1] All burette readings are recorded to the nearest 0.05 cm^3 + correct computation of titres.

(Do not award if 50 is used as initial burette reading or burette reading is > 50)

[1] Has two uncorrected titres within 0.10 cm^3 + place ✓ under selected titres within 0.10 cm^3. (Do not award if additional titration is performed after consistent titres are obtained.)

Accuracy: Supervisor's titre, V = 23.80 cm^3

(V ± 0.20) cm^3, 23.60 – 24.00 cm^3 [2]

(V ± 0.40) cm^3, 23.40 – 24.20 cm^3 [1]

[5]

(b) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

average volume of FA 1 used = $\dfrac{23.80 + 23.80}{2}$ = $\underline{23.80}$ cm^3

- quotes the selected titres within 0.10 cm^3 in the working
- calculates average titre correctly to 2 d.p.

[1]

25.0 cm^3 of **FA 2** requires $\underline{23.80}$ $\underline{\text{cm}^3}$ of **FA 1** for complete reaction. [1]

(c) **Calculations**

(i) Calculate the amount of sodium carbonate in the 25.0 cm^3 of **FA 2** used in each titration. [A_r: Na, 23.0; C, 12.0; O, 16.0]

$$\text{Amount of } Na_2CO_3 = \underline{\frac{2.65}{106.0} \times \frac{25.0}{1000}} = 6.25 \times 10^{-4} \text{ mol} \quad [1]$$

Amount of Na_2CO_3 in 25.0 cm^3 of **FA 2** = $\underline{6.25 \times 10^{-4}}$ $\underline{\text{mol}}$ [1]

(ii) Use your answer in **(c)(i)** to calculate the amount of hydrochloric acid present in 250 cm^3 of **FA 1**.

Na_2CO_3 : HCl

1 : 2

(25.0 cm^3) (23.80 cm^3)

Amount of HCl in 250 cm^3

$$= \underline{\frac{250}{\text{ans.(b)}} \times (2 \times \text{ans.(c)(i)})}$$

$$= \frac{250}{23.80} \times (2 \times 6.25 \times 10^{-4}) = 0.01313 \text{ mol} \quad [1]$$

[1]

Amount of HCl present in 250 cm^3 = $\underline{0.0131}$ $\underline{\text{mol}}$

(iii) Calculate the amount of hydrochloric acid that reacted with the magnesium.

Amount of HCl reacted with Mg

$$= \underline{\left(\frac{30}{1000} \times 1.00\right) - \text{ans.(c)(ii)}}$$

$$= \left(\frac{30}{1000} \times 1.00\right) - 0.01313 = 0.01687 \text{ mol} \quad [1]$$

Amount of HCl that reacted with the magnesium = $\underline{0.0169}$ $\underline{\text{mol}}$ [1]

(iv) Hence calculate the relative atomic mass, A_r, of magnesium.

A_r of Mg

Mg : HCl

1 : 2

$$= \underline{\frac{0.215}{\left(\frac{1}{2} \times \text{ans.(c)(iii)}\right)}} = \frac{0.215}{\left(\frac{1}{2} \times 0.01687\right)} = 25.49 \quad [1]$$

A_r of magnesium = $\underline{25.5}$ $\underline{\text{(no units)}}$ [1]

(d) The A_r of magnesium given in the Periodic Table is 24.3. Use this value given in the Periodic Table to calculate the percentage error of your A_r value of Mg obtained in **(c)(iv)**.

$$\% \text{ error} = \frac{\left|\text{ans(c)(iv)} - 24.3\right|}{24.3} \times 100\%$$

$$= \frac{\left|25.49 - 24.3\right|}{24.3} \times 100\% = 4.90\ \% \quad [1]$$

% error = 4.90 % [1]

(e) A solution of sodium hydroxide was prepared at the same concentration, in mol dm^{-3}, as **FA 2**. A student repeated the titration but replaced **FA 2** with this sodium hydroxide.

Explain the effect that replacing **FA 2** with this solution of sodium hydroxide would have on the volume of **FA 1** needed for the titration.

Half the volume of FA 1 is required since NaOH and HC*l* react in a mole ratio of 1:1 while Na_2CO_3 and HC*l* react in a mole ratio of 1:2. [1]

[2]

[1] State correct units in 1(b)[cm^3], (c)(i)(ii)(iii)[mol], (c)(iv)[no units] and 1(d)[%]

Any calculation not attempted loses this mark.

[Total: 13]

2 Determination of enthalpy change of formation of magnesium oxide.

FA 3 is magnesium ribbon
FA 4 is magnesium oxide
FA 5 is 2.0 mol dm^{-3} hydrochloric acid.

The enthalpy change of formation of magnesium oxide, ΔH_f(MgO), is the enthalpy change when one mole of magnesium oxide is formed from its elements in their standard states under standard conditions.

$$Mg(s) + \tfrac{1}{2} O_2(g) \rightarrow MgO(s) \qquad \Delta H_f(MgO)$$

To cause magnesium and oxygen to react together, they must be heated. The reaction then proceeds in an uncontrolled and highly exothermic fashion. It is not possible to measure this enthalpy change without the use of equipment such as a bomb calorimeter.

You are to perform an experiment by which you will determine this enthalpy change by an indirect route.

Both magnesium and magnesium oxide react exothermically with hydrochloric acid to form magnesium chloride. You will determine the molar enthalpy changes for **reaction 1** and **reaction 2**.

reaction 1 $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H_{rxn\,1}$

reaction 2 $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) \qquad \Delta H_{rxn\,2}$

You will then use Hess's Law to determine a value for the enthalpy change of formation of magnesium oxide, ΔH_f(MgO).

(a) Determining the enthalpy change of reaction 1 between FA 3 and FA 5.

Follow the instructions below to determine the maximum temperature change when a known mass of magnesium, **FA 3**, reacts completely with excess **FA 5**. Record all the mass readings in Table 2.1 and all measurements of time and temperature in the space provided below the table.

Method 1

1. Weigh the stoppered weighing bottle labelled **FA 3** and its contents. Record the total mass of weighing bottle and **FA 3**.
2. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
3. Stir the solution in the cup with the thermometer and measure its temperature. Record this temperature in your table in **(a)(i)** (this is the temperature at t = 0 min) and start the stop-watch. Repeat this measurement each minute for 3 minutes and record each temperature.
4. At the fourth minute, carefully add **FA 3** from the weighing bottle to **FA 5** in the cup. Quickly stir the mixture with the thermometer but **do not measure the temperature**.
5. Continue to stir the mixture. Measure and record the temperature at 4½ minutes, then **every half minute** until the temperature reaches a maximum, and then **every minute** until the tenth minute.
6. Empty and wash the Styrofoam cup. Rinse the cup with deionised water and dry it using a paper towel.
7. Reweigh the emptied weighing bottle and record its mass. Calculate and record the mass of **FA 3** used.

(a) (i) Results

Record the required mass readings in Table 2.1 and in an appropriate format in the space below, record all measurements of time and temperature.

Table 2.1

Mass of weighing bottle with **FA 3** /g	5.382
Mass of empty weighing bottle / g	5.248
Mass of **FA 3** used / g	0.134

Measurements of time and temperature:

Time / min	Temperature / °C
0	29.6
1	29.6
2	29.6
3	29.6
4	-
$4\frac{1}{2}$	41.6
5	42.0
$5\frac{1}{2}$	41.6
6	41.3
7	40.6
8	40.0
9	39.4
10	38.9

[1] Tabulates all time-temp data in a single table with correct headers and units. If headers have no units, then each reading must have units stated + records all masses consistently to 2/3 d.p. and correctly calculates mass of FA3.

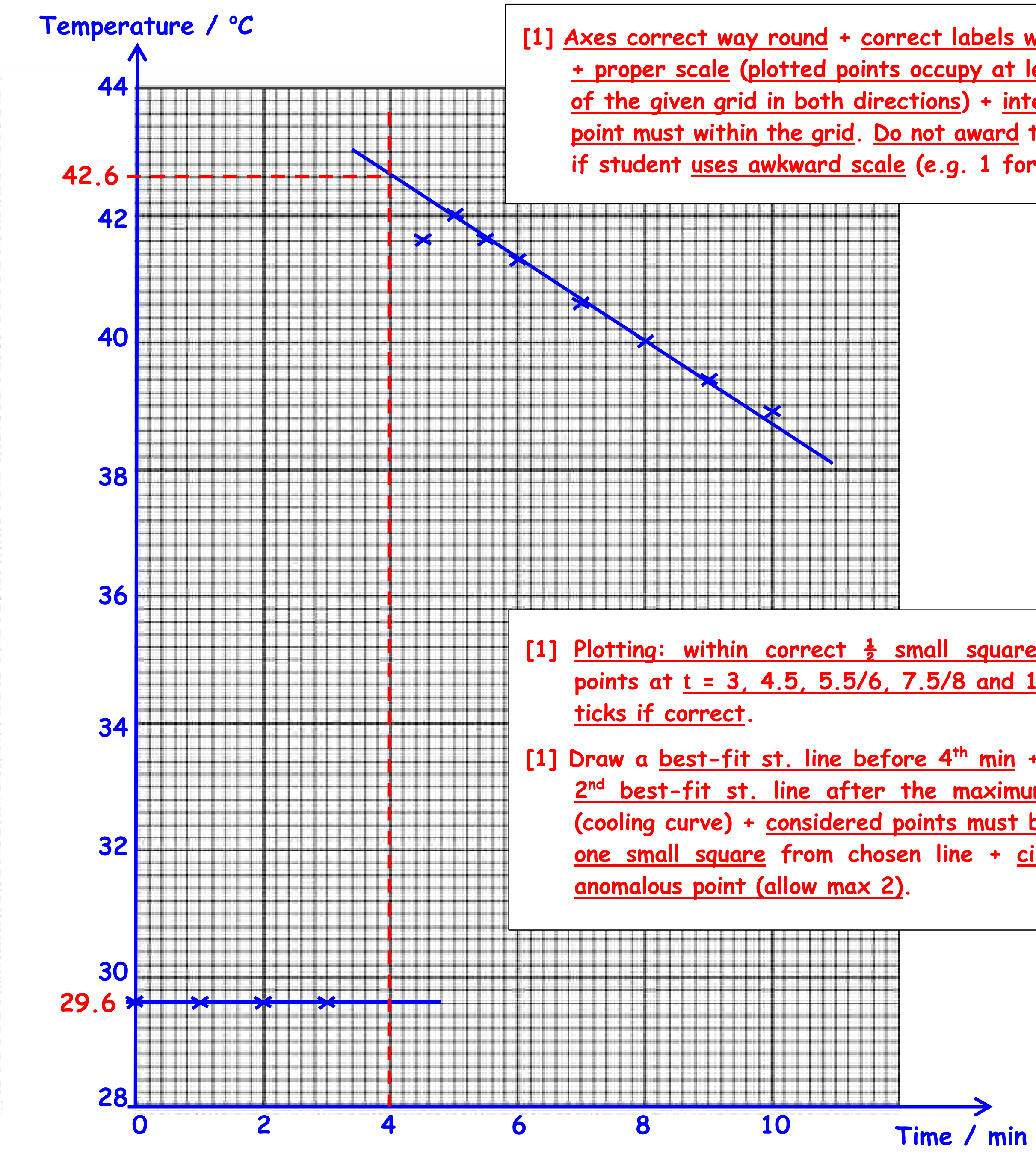
[1] Records all time readings consistently in the same format e.g. "$4\frac{1}{2}$" "5" "$5\frac{1}{2}$" / "4.5" "5.0" "5.5" / "4 min 30 s" "5 min 0 s" + changes from $\frac{1}{2}$ min to 1 min intervals AFTER maximum temp reached + need to have at least one $\frac{1}{2}$ minute reading after the maximum temp.

[1] Records ALL temperature readings to the nearest 0.1 °C (1 d.p.) (using 0.2 °C interval thermometer)

[3]

(a) **(ii)** Plot a graph of temperature (y-axis) against time (x-axis) on the grid below. You will use the graph to determine the theoretical temperature change at 4 minutes. The scale for temperature should extend at least 1 °C above your highest recorded temperature.

1. Draw a straight line of best-fit for the points before the fourth minute. Draw a second straight line of best-fit for the points after the fourth minute. Extrapolate both lines to the fourth minute.
2. From your graph, read the minimum and maximum temperature at the fourth minute. Record these values in the spaces below and determine a value for the maximum temperature rise, ΔT, at the fourth minute.



[1] Axes correct way round + correct labels with units + proper scale (plotted points occupy at least half of the given grid in both directions) + intersection point must within the grid. Do not award this mark if student uses awkward scale (e.g. 1 for 3/7)

[1] Plotting: within correct ½ small square. Check points at t = 3, 4.5, 5.5/6, 7.5/8 and 10; place ticks if correct.

[1] Draw a best-fit st. line before 4th min + draw a 2nd best-fit st. line after the maximum temp. (cooling curve) + considered points must be within one small square from chosen line + circle any anomalous point (allow max 2).

[1] Extrapolates the both straight lines to intersect the vertical line (line may not be drawn) at 4 min + states min temp, max temp and ΔT correctly to the nearest half square or in 1 d.p. (following the precision of thermometer)

Temperature at 4th minute

minimum = 29.6 °C

maximum = 42.6 °C

temperature rise, Δ*T* = 13.0 K [4]

(iii) Use your ΔT from **(a)(ii)** to calculate a value for the molar enthalpy change of **reaction 1** between **FA 3** and **FA 5**, $\Delta H_{rxn\ 1}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3]

Heat evolved = q = mcΔT

$= \underline{(50.0 \times 1.05) \times 3.75 \times 13.0}$ J

= 2559 J = 2.559 kJ [1] (in J or kJ) ignore sign

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \quad \Delta H_{rxn\ 1}$

Mg is limiting, HCl is in excess.

$$\Delta H_{rxn\ 1} = -\frac{2.559}{\left(\frac{0.134}{24.3}\right)} = -464 \text{ kJ mol}^{-1}$$ [1] with -ve sign

$\Delta H_{rxn\ 1}$ = $\underline{-464}$ kJ mol^{-1} [2]

(b) Determining the enthalpy change of reaction 2 between FA 4 and FA 5.

A student carried out an experiment to determine the enthalpy change of **reaction 2**, $\Delta H_{\text{rxn 2}}$, using a known mass of **FA 4** that reacts with excess **FA 5**.

The student was provided with five pre-weighed samples of **FA 4**, labelled **v**, **w**, **x**, **y** and **z**, and carried out the experiment according to the following instructions.

Method 2

1. Use a 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 5** into a Styrofoam cup. Place this cup inside a second Styrofoam cup which is held in a 250 cm^3 glass beaker to prevent it tipping over.
2. Stir the solution in the cup with the thermometer. Read and record its temperature. This is the initial temperature of **FA 4**, T_{initial}.
3. Carefully add sample **v** to the **FA 5** in the cup.
4. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. Record the maximum temperature reached, T_{max}.
5. Wash and carefully dry the Styrofoam cup.
6. Repeat steps 1 to 5 with the remaining samples **w**, **x**, **y** and **z**.

The student recorded all masses and temperatures in Table 2.2 below.

Table 2.2

	expt **v**	expt **w**	expt **x**	expt **y**	expt **z**
Mass of **FA 4** added to the cup, **m** / g	0.507	0.503	0.487	0.506	0.476
T_{initial} / °C	31.2	31.2	31.0	31.1	31.3
T_{max} / °C	38.7	38.6	38.2	38.2	38.3
Temperature change, ΔT / °C	7.5	7.4	7.2	7.1	7.0
$\frac{\Delta T}{m}$ / °C g^{-1}	14.8	14.7	14.8	14.0	14.7

(i) Complete Table 2.2 by calculating values for ΔT and $\Delta T/m$. Leave values for $\Delta T/m$ to 3 significant figures.

[1] correctly computes ΔT to 1 d.p. and '$\Delta T/m$' to 3 s.f.

(ii) Based on the calculated $\Delta T/m$ values in Table 2.2, determine an appropriate mean maximum temperature change, ΔT_{ave}, and mean mass of **FA 4**, m_{ave}.

$$\Delta T_{ave} = \frac{7.5 + 7.4 + 7.2 + 7.0}{4} = 7.3 \text{ (1 d.p.)}$$

$$m_{ave} = \frac{0.507 + 0.503 + 0.487 + 0.476}{4} = 0.493 \text{ (3 d.p.)}$$

[1] correctly calculates both ΔT_{ave} (in 1 d.p.) and m_{ave} (in 3 d.p.) based on 4 consistent values (excludes one anomalous result)

ΔT_{ave} = 7.3 °C m_{ave} = 0.493 g [2]

(iii) Use your results in **(b)(ii)** to calculate a value for the molar enthalpy change of **reaction 2** between **FA 4** and **FA 5**, $\Delta H_{rxn\ 2}$, in kJ mol^{-1}.
Assume that the specific heat capacity of the final solution is 3.75 J g^{-1} K^{-1} and that its density is 1.05 g cm^{-3}. [A_r: Mg, 24.3; O, 16.0]

Heat evolved = $q = mc\Delta T_{ave}$

$= \underline{(50.0 \times 1.05) \times 3.75 \times 7.3}$ J

$= 1437$ J $= 1.437$ kJ [1] (in J or kJ) ignore sign!

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(g) \qquad \Delta H_{rxn\ 2}$$

MgO is limiting, HCl is in excess.

$$\Delta H_{rxn\ 2} = -\underline{\frac{1.437}{\left(\frac{0.493}{40.3}\right)}} = \underline{-117} \text{ kJ mol}^{-1}$$ [1] with -ve sign

$\Delta H_{rxn\ 2}$ = $\underline{-117}$ kJ mol^{-1} [2]

(c) Use your values for $\Delta H_{rxn\ 1}$ and $\Delta H_{rxn\ 2}$, together with the enthalpy change of formation of water, $\Delta H_f(H_2O)$, to calculate a value for the enthalpy change of formation of magnesium oxide, $\Delta H_f(MgO)$.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f(H_2O) = -286 \text{ kJ mol}^{-1}$$

Note: If you were unable to calculate the enthalpy changes, assume that the value of $\Delta H_{rxn\ 1}$ is –457 kJ mol^{-1} and the value $\Delta H_{rxn\ 2}$ is –141 kJ mol^{-1}.

$$\begin{tikzcd}
Mg(s) + \tfrac{1}{2}O_2(g) \arrow[r, "\Delta H_f(MgO)"] \arrow[d, "\Delta H_{rxn\ 1}"', "+2HCl(aq)"] & MgO(s) \arrow[d, "\Delta H_{rxn\ 2}"', "+2HCl(aq)"] \\
MgCl_2(aq) + H_2(g) + \tfrac{1}{2}O_2(g) \arrow[r, "\Delta H_f(H_2O)"] & MgCl_2(aq) + H_2O(l)
\end{tikzcd}$$

[1] correct working (simultaneous eqns or energy cycle)

By Hess's law,

$\underline{\Delta H_f(MgO) = \Delta H_{rxn\ 1} + (-286) - (\Delta H_{rxn\ 2})}$

$= -464 + (-286) - (-117)$ (or $-457 + (-286) - (-141)$)

$= \underline{-633}$ (or $\underline{-602}$) kJ mol^{-1} [1] with sign

$\Delta H_f(MgO)$ = $\underline{-633}$ (3 s.f. or exact value) kJ mol^{-1} [2]

(d) Two methods, **Method 1** and **Method 2**, have been used to determine the maximum temperature change, ΔT, of an exothermic reaction. Which method would give a more accurate ΔT ? Explain your answer.

ΔT obtained by <u>Method 1</u> is more accurate as a <u>cooling correction has been done</u> by the extrapolating the cooling curve to the time of mixing <u>to compensate/account for the heat loss to the surroundings</u>. [1]

[1]

Bonus [1]: <u>shows workings in all calculations</u> + <u>gives all final answers to 3 s.f.</u> in 1(c), 1(d), 2(a)(iii), 2(b)(iii) and 2(c).

[Total: 16]

3 Planning

The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}.

When solid calcium iodate(V) is added to water, a small amount dissolves to form a saturated solution, establishing an equilibrium between the undissolved salt and its aqueous ions.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^-\,(aq)$$

The equilibrium constant for the above solubility equilibrium, K_{sp}, is also known as the solubility product of calcium iodate.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$$

This solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate.

The exact concentration of IO_3^- ions is determined by titration. Excess aqueous KI and aqueous H^+ is first added to a sample of saturated calcium iodate solution to liberate iodine.

$$IO_3^-\,(aq) + 5I^-\,(aq) + 6H^+\,(aq) \rightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine liberated in the resulting mixture is then titrated with sodium thiosulfate, $Na_2S_2O_3$ of known concentration.

$$I_2\,(aq) + 2S_2O_3^{2-}\,(aq) \rightarrow 2I^-\,(aq) + S_4O_6^{2-}\,(aq)$$

(a) Using the information given above, you are required to write a plan to determine the solubility product, K_{sp}, of calcium iodate, $Ca(IO_3)_2$, at 20 °C.

You may assume that you are provided with:

- solid sodium thiosulfate crystals, $Na_2S_2O_3.5H_2O$ (M_r = 248.2)
- solid calcium iodate, $Ca(IO_3)_2$
- aqueous potassium iodide, KI, of about 0.2 mol dm^{-3}
- aqueous hydrochloric acid, HC*l*, of about 1 mol dm^{-3}
- starch indicator
- any other required apparatus normally found in a college laboratory.

Your plan should include details of, including quantities:

- the preparation of 250.0 cm^3 of 0.075 mol dm^{-3} aqueous $Na_2S_2O_3$;
- the preparation of about 100 cm^3 of a saturated solution of calcium iodate, $Ca(IO_3)_2$ at 20 °C;
- the essential details of the titration process;
- an outline of how you would use your mean titre value to determine the solubility product of $Ca(IO_3)_2$.

In your calculations, you should let **V** cm^3 be your mean titre and express your final mathematical expression in terms of **V**.

To prepare 250.0 cm^3 of 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$:

Mass of $Na_2S_2O_3.5H_2O$ required = $\frac{250}{1000} \times 0.075 \times 248.2$ = *4.65 g

1. Weigh accurately *4.65 g of solid $Na_2S_2O_3.5H_2O$ into a weighing bottle using an electronic weighing balance.

[1] weigh correct mass of solid used in 2-3 d.p. (accept a range)

2. Transfer all the weighed solid into a small beaker and dissolve the solid completely with about 50 cm^3 deionised water.
3. Using a filter funnel, carefully transfer the solution and all washings into a 250.0 cm^3 graduated flask. Make up to the graduated mark with deionised water. Stopper and shake the flask well to obtain a homogeneous solution.

[1] accurately prepares 250 cm^3 of standard soln with complete transfer (no loss of $S_2O_3^{2-}$)

To prepare 100 cm^3 of $Ca(IO_3)_2$ saturated solution at 20 °C:

1. Use a 100 cm^3 measuring cylinder to transfer 100 cm^3 of deionised water into a 250 cm^3 conical flask.
2. Using a spatula, add a few tips of solid $Ca(IO_3)_2$ into the conical flask. Stopper the flask and shake the flask for a few minutes. Keep adding more solid $Ca(IO_3)_2$, with shaking after each addition, until some $Ca(IO_3)_2$ solids are left undissolved.

   To ensure that the solution is saturated, shake the flask at intervals and leave the conical flask in a *thermostat controlled water bath set at 20 °C for some time. There must be some solids left undissolved.

[1] correctly prepares a saturated soln of $Ca(IO_3)_2$ at 20 °C (with *)

(allow stirring or swirling in place of shaking)

3. To remove undissolved solids, filter the saturated solution into a clean, dry conical flask using a dry filter funnel and a piece of dry filter paper. [1] dry filtration

Titration procedure:

1. Fill a burette with 0.075 mol dm^{-3} $Na_2S_2O_3(aq)$.
2. Pipette 25.0 cm^3 of the saturated solution into a conical flask.
3. Use a 10 cm^3 measuring cylinder to add to the flask 5 cm^3 of $HCl(aq)$ and 10 cm^3 of $KI(aq)$.

[1] accurately prepares titrant and analyte with min 10 cm^3 of KI & 5 cm^3 of H^+

4. Titrate the liberated I_2 in the mixture with $Na_2S_2O_3(aq)$ from the burette until the solution turns pale yellow. Then add about 1 cm^3 of starch indicator and continue the titration until the dark blue-black colour just disappears/turns colourless at the end-point.
5. Repeat the titration to obtain two consistent titres within 0.10 cm^3 in difference.

[1] correct titration procedure using starch (allow a few drops)

To calculate K_{sp} of $Ca(IO_3)_2$:

Amount of $S_2O_3^{2-}$ required = $\frac{V}{1000} \times 0.075$ = 7.5×10^{-5} V mol

Amount of IO_3^- in 25.0 cm^3 saturated solution

= $\frac{1}{6} \times 7.5 \times 10^{-5}$ V = 1.25×10^{-5} V mol

IO_3^- : I_2 : $S_2O_3^{2-}$
1 : 3 : 6

$[IO_3^-]$ in saturated solution = 1.25×10^{-5} V $\times \frac{1000}{25.0}$ = 5×10^{-4} V mol dm^{-3} [1]

$$\begin{array}{lccccc} & Ca(IO_3)_2\,(s) & = & Ca^{2+}\,(aq) & + & 2IO_3^-\,(aq) \\ \text{eqm conc.} & - & & 2.5\times10^{-4}\ V & & 5\times10^{-4}\ V \end{array}$$

$K_{sp}\,(Ca(IO_3)_2) = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$

$= (2.5\times10^{-4}\ V)(5\times10^{-4}\ V)^2$

$= 6.25 \times 10^{-11}\ V^3$ mol^3 dm^{-9} [1]

[8]

(b) The solubility of calcium iodate(V), $Ca(IO_3)_2$, at 20 °C, is approximately 2.4 g dm^{-3}. Justify, with calculations, that the chosen concentration, 0.075 mol dm^{-3}, of aqueous $Na_2S_2O_3$ solution is appropriate. [M_r of $Ca(IO_3)_2$ = 389.9]

Expected $[IO_3^-]$ in the saturated solution = $\frac{2.4}{389.9} \times 2$ = 0.0123 mol dm^{-3} [1]

Amount of IO_3^- in 25.0 cm^3 = $\frac{25.0}{1000} \times 0.0123$ = 3.08×10^{-4} mol

Amount of $S_2O_3^{2-}$ required = $3.08 \times 10^{-4} \times 6$ = 1.85×10^{-3} mol

Expected titre when 0.075 mol dm^{-3} $Na_2S_2O_3$ is used

= $\frac{1.85 \times 10^{-3}}{0.075}$ = 0.0246 dm^3

= 24.6 cm^3 which is within the capacity of a burette. [1]

[2]

(c) The experiment described in your plan in **(a)** is repeated using 0.1 mol dm^{-3} aqueous $Ca(NO_3)_2$ solution, instead of deionised water, to prepare a saturated solution of calcium iodate(V).

State and explain how, if at all, the titre values and calculated K_{sp} would be expected to differ from that obtained in **(a)**.

[Assume that both the experiments were carried out under the same conditions.]

$Ca(IO_3)_2\,(s) \;=\; Ca^{2+}\,(aq) \;+\; 2IO_3^-\,(aq)$---(1)

Presence of common ion Ca^{2+} from $Ca(NO_3)_2$ causes the position of equilibrium (1) to shift left (or the solubility of $Ca(NO_3)_2$ in 0.10 mol dm^{-3} $Ca(NO_3)_2$ is lower) and hence the titre values will be smaller due to lower $[IO_3^-]$ in saturated solution. [1]

However, since the temperature is kept constant, the calculated K_{sp} value would remain the same/unchanged. [1]

Award [1] for correct conclusions: smaller titre and constant K_{sp} value

[2]

[Total: 12]

4 Qualitative Analysis

(a) You are provided with solid **FA 6** which contains $S_2O_8^{2-}$ anion and one cation from the ions listed in the *Qualitative Analysis Notes*.

You are to perform the tests described in Table 4.1 to deduce the nature of **FA 6** and to identify the cation present in **FA 6**.

Record your observations in Table 4.1. Your answers should include
- details of colour changes and precipitates formed,
- the identity of any gases evolved, and details of the test used to identify each one.

You should indicate clearly at what stage in a test a change occurs.
Marks are not given for chemical equations.
No additional or confirmatory tests for ions present should be attempted.

Table 4.1

Tests	Observations
(i) To a spatula measure of **FA 6** in a boiling tube, add 1-2 cm depth of dilute hydrochloric acid and heat cautiously. Retain the solution for **test (ii)**.	• Pungent, yellowish green Cl_2 gas (✓) • bleaches a damp blue litmus paper (✓) • pale yellow solution obtained. {FA 8 oxidises Cl^- to Cl_2}
(ii) To the resulting solution from **test (i)**, add barium nitrate(V) solution.	• White ppt. (✓) insoluble in H^+ {$BaSO_4$ ppt.⇒ SO_4^{2-} formed}
(iii) To a spatula measure of **FA 6** in a test tube, add 1-2 cm depth of freshly prepared solution of iron(II) sulfate solution and warm.	• Pale green Fe^{2+} solution turns yellow • Upon warming, solution turns brown/red-brown/orange-brown/orange. (✓) {FA 8 oxidises Fe^{2+} to Fe^{3+}}
(iv) Place a spatula measure of **FA 6** in a boiling tube and add dilute nitric acid to dissolve the solid. Then add 1 cm depth of manganese(II) sulfate solution and 4 drops of silver nitrate(V) solution to act as a catalyst. Heat cautiously to bring the mixture to boiling.	• Upon heating, pale pink Mn^{2+} solution turns brown (✓) then to a black ppt./purple solution/black suspension. (✓) {FA 8 oxidises Mn^{2+} to Mn^{3+} then to MnO_2/MnO_4^-}
(v) To a spatula measure of **FA 6** in a boiling tube, add 1 cm depth of aqueous sodium hydroxide. Heat cautiously.	• No ppt. (✓) • Upon heating, colourless, pungent NH_3 gas (✓) • turns damp red litmus paper blue (✓) {NH_4^+ present}

[5]

8-9(✓) [5], 6-7(✓) [4], 4-5(✓) [3], 2-3(✓) [2], 1(✓) [1]

(b) **(i)** State, with supporting evidence, the nature of **FA 6**.

nature of **FA 6**: oxidising agent [1]

evidence: FA 6 oxidises Fe^{2+} in test (iii) to Fe^{3+} (or Cl^- in test (i) to Cl_2 or Mn^{2+} in test (iv) to $Mn^{3+}/MnO_2/MnO_4^-$) [1]

(ii) Identify the cation in **FA 6**.

cation: NH_4^+ [1]

(iii) Write the ionic equation, including state symbols, for the reaction that occurs in **test (i)**.

$S_2O_8^{2-}$ (aq) or (s) + $2Cl^-$(aq) → Cl_2(g) + $2SO_4^{2-}$(aq) [1]

[4]

(c) You are provided with an organic solution **FA 7** which contains one functional group.

Care: FA 7 is flammable. Do not use Bunsen burner for heating.
Use the hot water provided.

FA 7 gives a positive test with 2,4–dinitrophenylhydrazine.

Devise **two** other confirmatory tests using the **bench reagents provided** to identify the functional group present in **FA 7**.

Carry out the tests and record details of the tests performed and observations made in Table 4.2.

Table 4.2

Confirmatory Tests	*Observations*
To 1 cm depth of FA 7 in a test-tube, add 1-2 cm depth of dilute H_2SO_4(aq) and 1-2 drop of $KMnO_4$(aq). Heat in hot water-bath. [1]	Purple $KMnO_4$ decolourised. [1]
To 1 cm depth of FA 7 in a test-tube, add 1 cm depth of Fehling's solution. Heat in hot water-bath. [1]	Red-brown / brick-red ppt. formed. [1]

Functional group present in **FA 7**: aliphatic aldehyde [1]

[5]

[Total: 14]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no. ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in excess dilute strong acids)

(c) Tests for gases

gas	*test and test results*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 Prelim Exam Paper 4 Chemical list:

Label	Identity	Preparation	per candidate
FA 1	0.1 mol dm^{-3} hydrochloric acid	Dilute 50 cm^3 of 2.0 mol dm^{-3} HC*l* to 1 dm^3 with deionised water.	200 cm^3
FA 2	0.1 mol dm^{-3} sodium hydroxide	Dissolve 4.00g of NaOH **[C]** in each dm^3 of solution.	200 cm^3
FA 3	Mg ribbon	0.11 – 0.13 g of Mg ribbon supplied in a stoppered weighing bottle (*cannot exceed 0.135 g) Note: sand Mg ribbons and cut into ≈ 1.5 - 2 cm length before weighing	1 bottle
FA 5	2 mol dm^{-3} hydrochloric acid	Dilute 170 cm^3 of concentrated (35-37%; ≈ 11 mol dm^{-3}) hydrochloric acid **[C]** to 1 dm^3 with deionised water	150 cm^3
FA 6	solid ammonium persulfate, $(NH_4)_2S_2O_8$	About 3 g of solid $(NH_4)_2S_2O_8$ supplied in a stoppered weighing bottle	1 bottle
FA 7	Ethanal	10% (v/v) aqueous solution of ethanal (acetaldehyde) To reduce the possibility of the presence of acid, a fresh batch of ethanal should be used.	1 bottle (8-10 cm^3)
Methyl orange indicator			1 bottle

Central Supplies:

aqueous iron(II) sulfate, $FeSO_4$ (freshly prepared)	0.5 mol dm^{-3} $FeSO_4$(aq) Dissolve 140 g of $FeSO_4.7H_2O$ in 1 dm^3 of water containing 7 cm^3 of concentrated H_2SO_4.	2 bottles per lab (about 5 cm^3 per student)
aqueous manganese(II) sulfate, $MnSO_4$	0.1 mol dm^{-3} $MnSO_4$(aq) Dissolve 16.9 g of $MnSO_4.H_2O$ in 1 dm^3 of water	2 bottles per lab (about 5 cm^3 per student)
Fehling's solution		2 bottles per lab (about 5 cm^3 per student)
Hot water		200 cm^3 per student
Small white labels (Teacher's bench)		
Electronic Weighing balance		**4 per lab**

Student's QA reagents:

aq. potassium manganate(VII), $KMnO_4$	Standard QA reagents concentrations	1 bottle
aq. silver nitrate(V), $AgNO_3$		1 bottle
aq. barium nitrate(V), $Ba(NO_3)_2$		1 bottle
aq. sodium hydroxide, NaOH		1 bottle
dilute hydrochloric acid, HC*l*		1 bottle
dilute sulfuric acid, H_2SO_4		1 bottle
dilute nitric acid, HNO_3		1 bottle
aqueous ammonia, NH_3		1 bottle
limewater (freshly prepared)		1 bottle
Red litmus paper		4 pieces
Blue litmus paper		4 pieces
Filter paper strip		2 pieces
Wooden splint		2 pieces

Student's apparatus:		**per candidate**
1	50.00 cm^3 burette	1
2	Burette stand and clamp	1
3	25.0 cm^3 pipette	1
4	Pipette filler	1
5	250 cm^3 conical flask	2
6	Filter funnel	1
7	White tile	1
8	50 cm^3 measuring cylinder	1
9	Styrofoam cup	2 (supported in a big beaker)
10	Thermometer (–5 °C to +50 °C) 0.2 °C interval	1
11	Stop-watch	1
12	Plastic dropper	2
13	100 cm^3 beaker	1 (for burette waste)
14	200 cm^3 beaker	1 (for hot water bath)
15	Wash bottle with deionised water	1
16	Test-tube rack	1
17	Test-tube	6 } inside a Ziploc bag
18	Boiling tube	2
19	Bunsen Burner	1
20	Test-tube holder	1
21	Glass rod	1
22	Test-tube brush	1
23	Delivery tube (for test-tube)	1
24	Delivery tube (for boiling tube)	1
25	Plastic spatula (small measure)	1
26	Paper Towel	2 pieces

Class	Adm No

Candidate Name: ____________________

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **21 Sept 2018**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **thirty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this question paper.
The use of an approved scientific calculator is expected, where appropriate.

FOR EXAMINER'S USE	
TOTAL (30 marks)	

This question paper consists of **11** printed pages and **1** blank page.

1 *Use of the Data Booklet is relevant to this question*.

Which sample of gas below contains the same number of particles as 19.0 g of fluorine gas?

1 2.0 g of helium gas
2 10.1 g of neon gas
3 17.0 g of ammonia gas

A	1 only	**B**	3 only
C	1 and 2 only	**D**	1, 2 and 3

2 Arsenic in the form of arsenic trioxide, As_2O_3, was used in the past as rat poison. To test for the presence of As_2O_3, 1.0 g sample containing some As_2O_3 is dissolved and excess H_2S is then added to the solution. 0.492 g of As_2S_3 is precipitated as a result. The equation for the reaction is given below:

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

What is the percentage by mass of arsenic in the original sample?

A 15.9%
B 29.0%
C 39.5%
D 86.5%

3 *Use of the Data Booklet is relevant to this question*.

Tin(II) ions can be used as a reducing agent. What volume of 0.025 mol dm^{-3} of tin(II) ions is needed to completely reduce 5 × 10^{-4} mol of potassium manganate(VII)?

A	8.00 cm^3	**B**	16.0 cm^3
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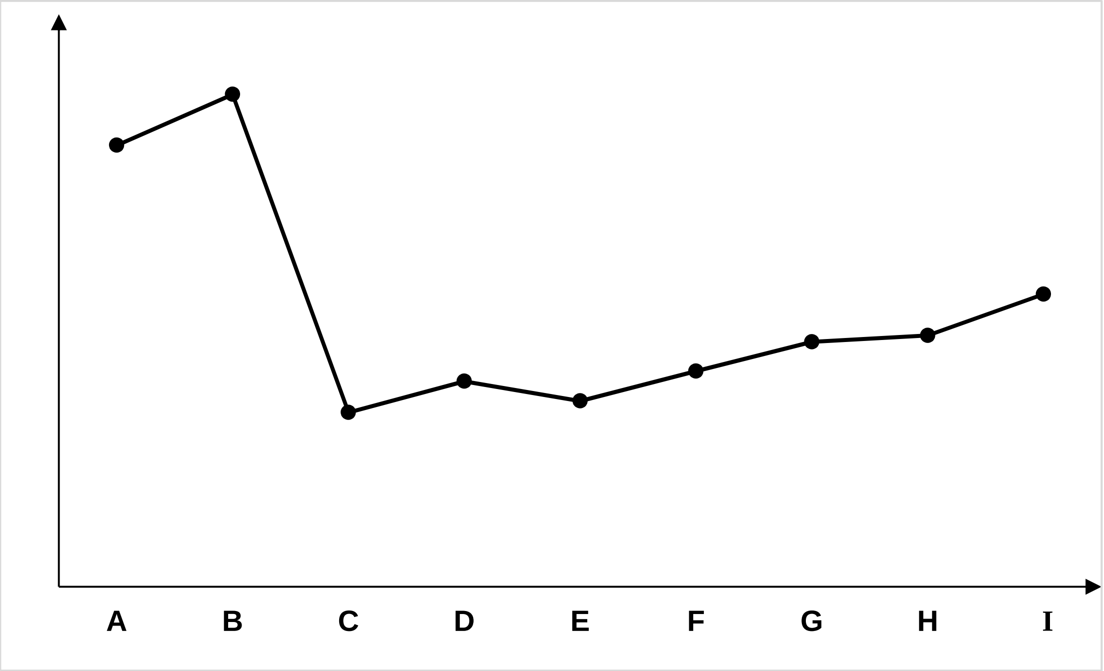
Third ionisation energy



elements

Which of the following statements is correct?

A The 3rd ionisation energy of **B** is the highest as it is the removal of an inner shell electron.

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7 In which set of species do all three compounds have the same shape?

A CO_2, NO_2, SO_2

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$$\mathbf{X} + \mathbf{Y} + \mathbf{Z} \longrightarrow \text{products}$$

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Which of the following graphs is correct of the reaction above?

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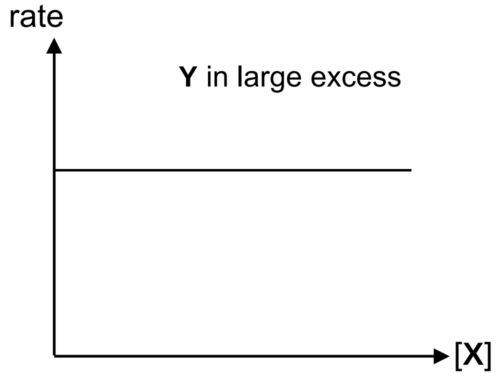
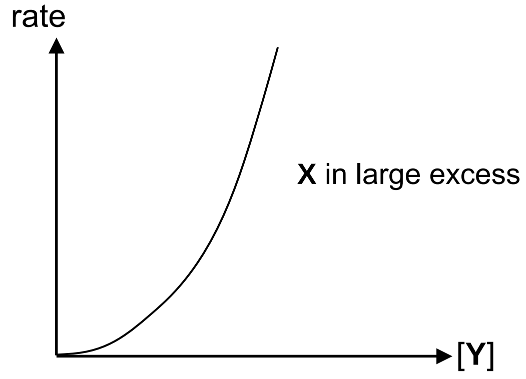


B



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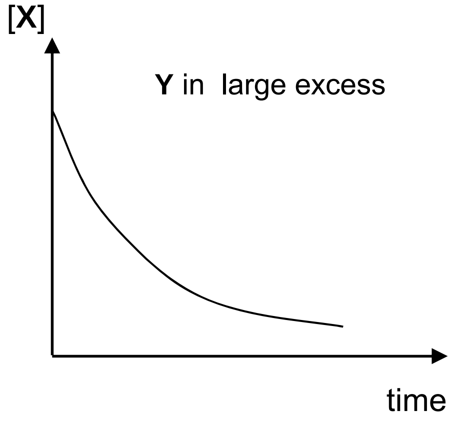
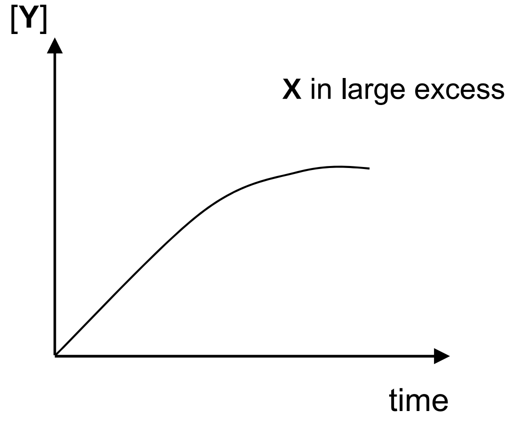


D



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C ionic radii of group 2 metal ions
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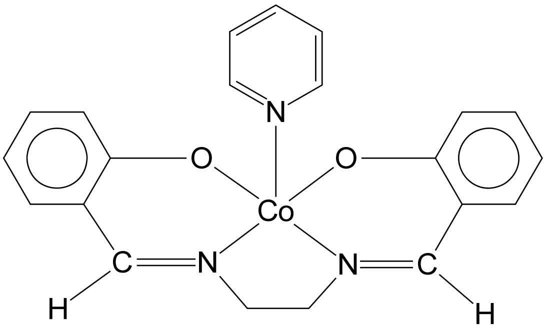

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B $\bullet CHBrCH_3 + HBr \longrightarrow \bullet CBr_2CH_3 + H_2$

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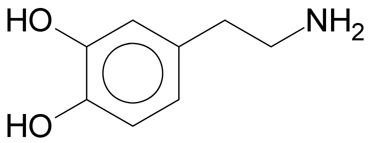

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Which of the following statements is true about dopamine?

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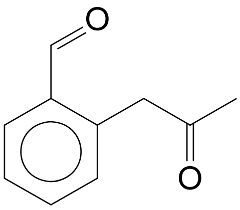

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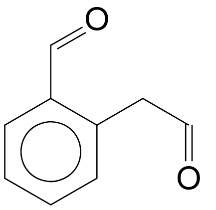

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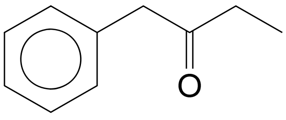
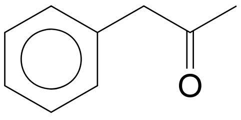


D



29 Phenol is weakly acidic and has a pK_a of 9.95. Which of the following substances, in the presence of water, has a higher pK_a than phenol?

A	chloroethanoic acid	**B**	ethanoyl chloride
C	4-chlorophenol	**D**	ethanol

30 The following fragments were obtained when a polypeptide is hydrolysed.

phe-ser
ala-ala
ser-phe-gly
lys-asp
ala-lys
gly-ala

Given that the polypeptide chain is known to have 8 amino acids residues, which of the following could be the polypeptide?

A ser-phe-ala-ala-gly-ser-lys-asp
B phe-ser-phe-gly-ala-ala-lys-asp
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END OF PAPER

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Class	Adm No

Candidate Name: ____________________

H

millennia institute

2018 Preliminary Examinations
Pre-University 3

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **21 Sept 2018**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

There are **thirty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the Multiple Choice Answer Sheet provided.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this question paper.

The use of an approved scientific calculator is expected, where appropriate.

FOR EXAMINER'S USE	
TOTAL (30 marks)	

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Which sample of gas below contains the same number of particles as 19.0 g of fluorine gas?

1 2.0 g of helium gas
2 10.1 g of neon gas
3 17.0 g of ammonia gas

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2 Arsenic in the form of arsenic trioxide, As_2O_3, was used in the past as rat poison. To test for the presence of As_2O_3, 1.0 g sample containing some As_2O_3 is dissolved and excess H_2S is then added to the solution. 0.492 g of As_2S_3 is precipitated as a result. The equation for the reaction is given below:

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

What is the percentage by mass of arsenic in the original sample?

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C 39.5%
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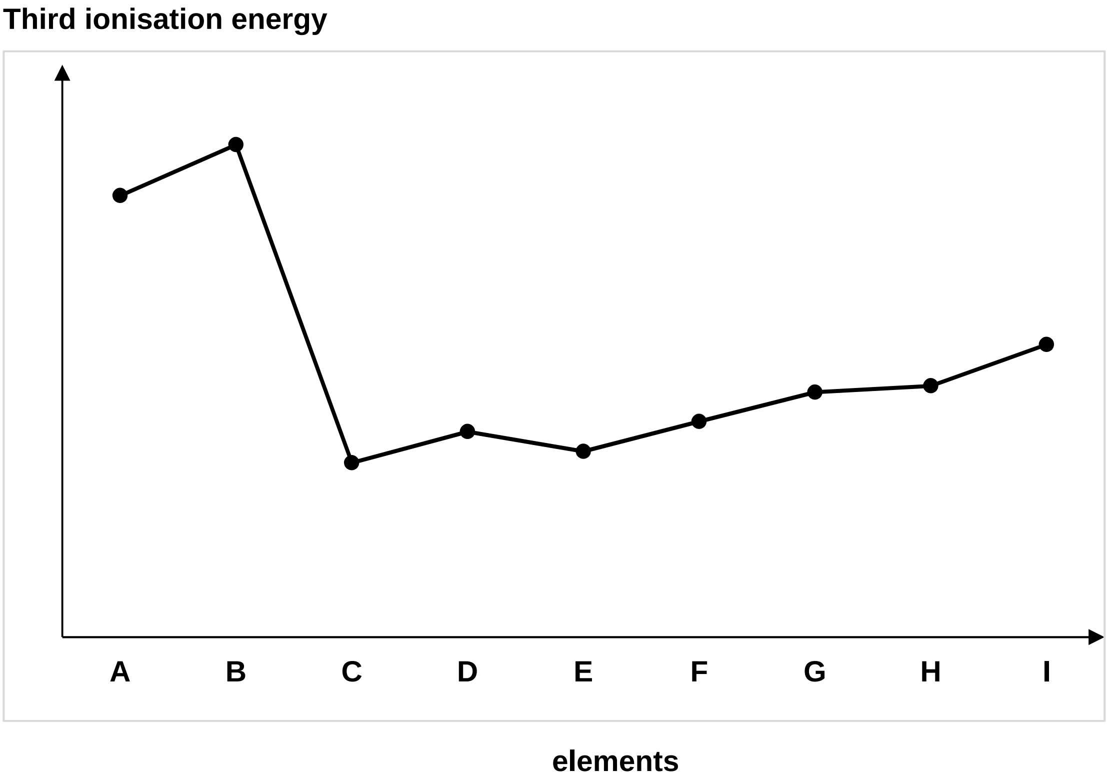

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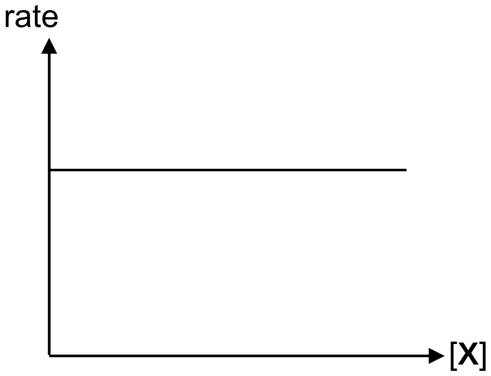

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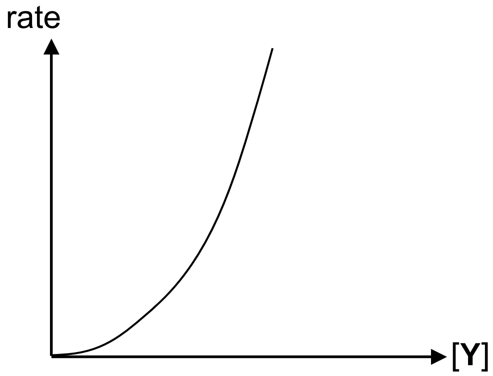

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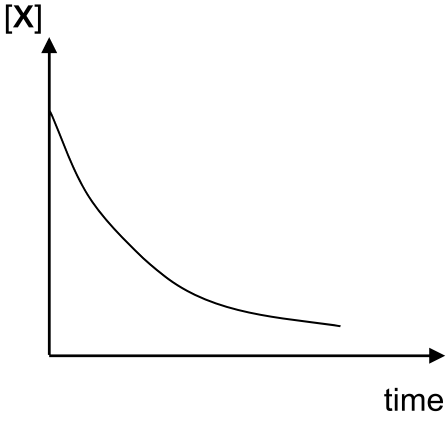

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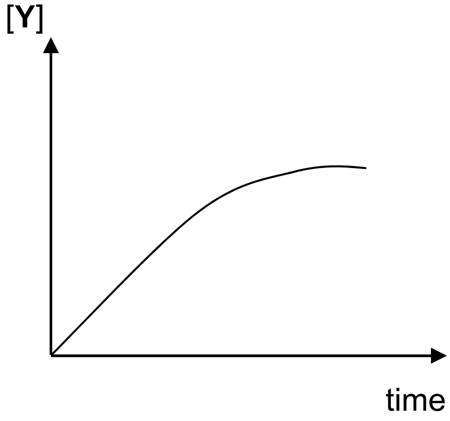

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3 It can dimerise through dative bonding.

A **3** only **B** **1** and **2** only

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18 Group 2 nitrates decompose in this manner: $\mathbf{M}(NO_3)_2 \longrightarrow \mathbf{M}O(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$ and require more energy for decomposition down the group. Which factor best explains this trend?

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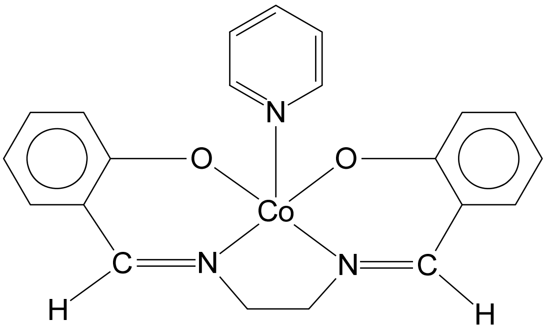

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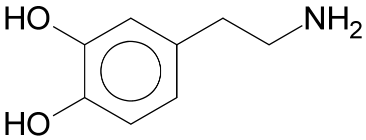

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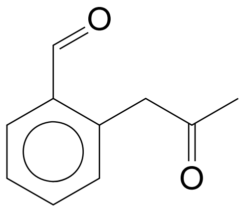
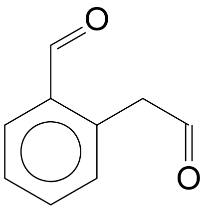


B



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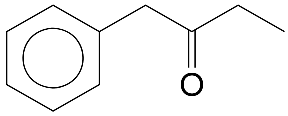

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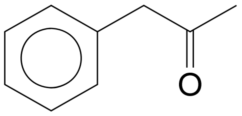

29 Phenol is weakly acidic and has a pK_a of 9.95. Which of the following substances, in the presence of water, has a higher pK_a than phenol?

A	chloroethanoic acid	**B**	ethanoyl chloride
C	4-chlorophenol	**D**	ethanol

30 The following fragments were obtained when a polypeptide is hydrolysed.

phe-ser
ala-ala
ser-phe-gly
lys-asp
ala-lys
gly-ala

Given that the polypeptide chain is known to have 8 amino acids residues, which of the following could be the polypeptide?

A ser-phe-ala-ala-gly-ser-lys-asp
B phe-ser-phe-gly-ala-ala-lys-asp
C phe-ser-ala-gly-ala-ala-lys-asp
D ser-phe-phe-gly-ala-ala-lys-asp

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Class	Adm No

Candidate Name: ____________________

H

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **12th Sept 2018**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Question	1	2	3	4	5	Total
Marks	20	15	12	12	16	75

This question paper consists of **20** printed pages and **2** blank pages.

Answer **all** the questions in the spaces provided.

1 Ruthenium, Ru, is a Period 5 d-block element. Its ions have the ability to form complexes with both organic and inorganic ligands.
One such organic ligand is 2,2-bipyridine which can be represented by bpy.

(a) Define the term *ligand* and suggest why bpy can act as a bidentate ligand.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………[2]

(b) In an experiment, varying volumes of solutions of 0.1 mol dm^{-3} Ru^{2+} and 0.1 mol dm^{-3} bpy are mixed to produce a coloured complex.

$$x\text{Ru}^{2+} + y\text{bpy} \rightarrow [\text{Ru}_x(\text{bpy})_y]^{2+}$$

The concentration of the coloured complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. **Fig 1.1** shows the results experiment.

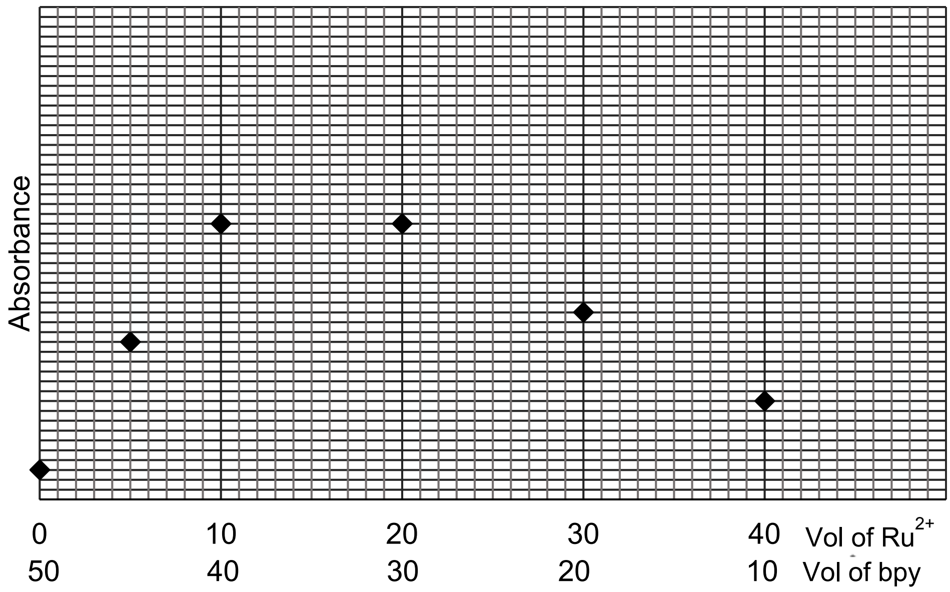


Fig 1.1

For Examiners' Use

By drawing two best-fit lines in **Fig 1.1**, deduce the formula of the complex ion formed between Ru^{2+} and bpy and hence draw the structure of the complex ion.

Formula of complex ion: …………………………..

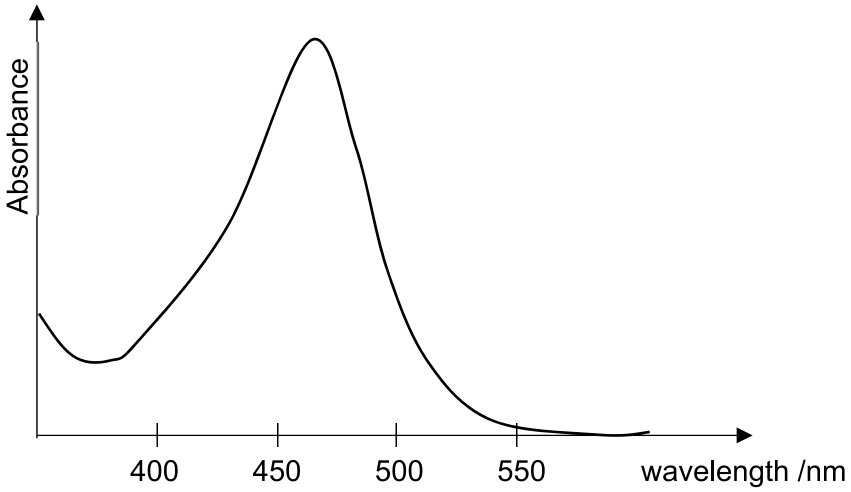
Structure of complex ion:

[3]

(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

Wavelength range (nm)	**Colour**	**Complementary colour**
400 – 450	violet	yellow
450 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue
650 – 700	red	green

The diagram below shows the UV-Visible spectrum of the complex formed between Ru^{2+} and bpy.



Using the data provided, suggest the colour of the complex formed between Ru^{2+} and bpy.

……………………………………………………………………………………….. [1]

(d) Ru^{2+} also forms an octahedral aqua complex with the formula $[Ru(H_2O)_6]^{2+}$. Typically, the colour of the complex changes when the ligands are different. This is due to different ligands causing the five d-orbitals to be split to different extent. **Fig 1.2** shows how the five d-orbitals are split in an octahedral environment.

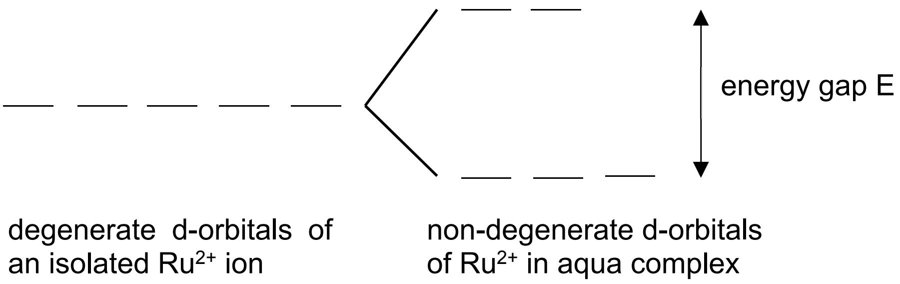


Fig 1.2

(i) With reference **Fig 1.2**, outline why $[Ru(H_2O)_6]^{2+}$ is coloured.

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

The electrons of transition metal ions in complexes can fill the non-degenerate d-orbitals in two different ways, namely the 'high spin' state and the 'low spin' state. This is dependent on the magnitude of the energy gap, E, and the pairing energy, P. Electrons usually prefer to occupy orbitals singly, rather than in pairs. Pairing energy, P, is the energy needed for an electron to fill an orbital that is already occupied by another electron.

In the 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals. This occurs because the magnitude of the energy gap, E, is smaller than the pairing energy, P.

In the 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used. This occurs because the pairing energy, P, is smaller than the magnitude of the energy gap, E.

For Period 4 d-block elements, the electronic configuration of the 3d electrons can be either 'high spin' or 'low spin'. However, for Period 5 d-block elements, the 4d electrons are always in the 'low spin' state.

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.

…………………………………………………………………………………………

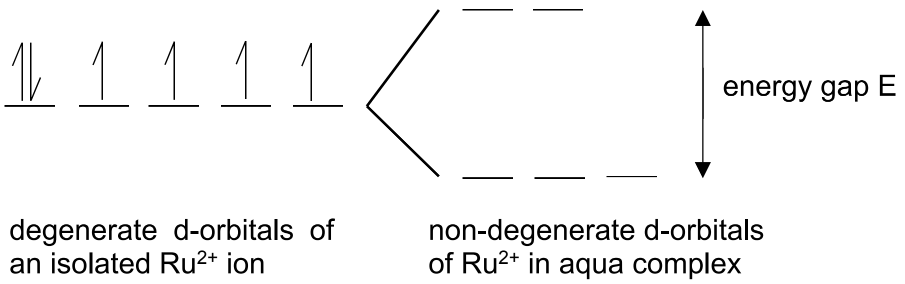
………………………………………………………………………………………[1]

(iii) With reference to the relative sizes of 3d and 4d orbitals, suggest a reason why 4d electrons prefer to pair up in the lower energy d-orbital before filling the higher energy d-orbitals.

…………………………………………………………………………………………

……………………………………………………………………………………… [1]

(iv) In the diagram below, show the electronic distribution of a Ru^{2+} ion in the 'low spin' state, given that the electronic configuration of Ru^{2+} is [Kr] $4d^6$.



[1]

(e) Two galvanic cells were set up under standard conditions to determine the standard electrode potential of Ru^{3+}/Ru^{2+}.

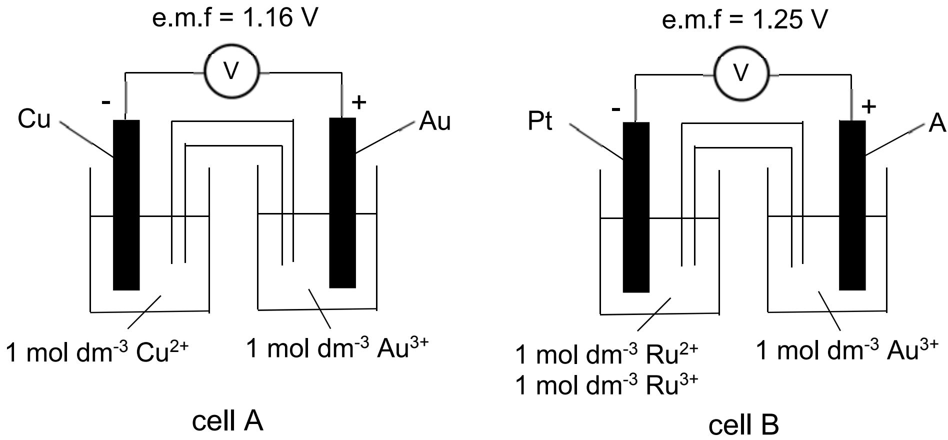


Fig 1.3

(i) Define the term *standard electrode potential*.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………[1]

(ii) Using the data given in **Fig 1.3** and relevant data from the Data Booklet, determine the standard electrode potentials of Au^{3+}/Au and that of Ru^{3+}/Ru^{2+} respectively.

$E^{\ominus}(Au^{3+}/Au)$ = …………………………………

$E^{\ominus}(Ru^{3+}/Ru^{2+})$ = ………………………………… [3]

For Examiners' Use

(iii) Hence using your answer in **(e)(ii)** and relevant data from the Data Booklet, state and explain whether Ru^{3+} is able to act as a homogenous catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

……………………………………………………………………………………………

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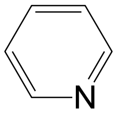
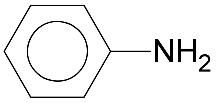
……………………………………………………………………………………………

…………………………………………………………………………………………… [3]

(f) Pyridine and phenylamine are two nitrogen-containing compounds.



pyridine
pK_b = 8.75



phenylamine
pK_b = 9.33

Pyridine has a resonance structure with six p electrons delocalised over the ring. The molecule is planar, with all atoms forming the ring being sp^2 hybridised. The lone pair of electrons on nitrogen occupies one of its sp^2 hybrid orbitals.

With reference to the shape and orientation of the orbitals about the nitrogen atom in both compounds, suggest why pyridine has a lower pK_b value.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [2]

[Total: 20]

2 **(a)** Upon heating at 160 °C, magnesium ethanoate decomposes to give magnesium carbonate and propanone as the products.

$$(CH_3COO)_2Mg \rightarrow MgCO_3 + CH_3COCH_3$$

Upon further heating, $MgCO_3$ undergoes further decomposition.

(i) Write an equation for the decomposition of $MgCO_3$.

……………………………………………………………………………………..[1]

When barium propanoate, $(CH_3CH_2COO)_2Ba$ was heated until constant mass, it was found that $BaCO_3$ and an organic compound **X**, $C_5H_{10}O$, were obtained. Despite further heating, $BaCO_3$ did not undergo decomposition.

When 2,4-dinitrophenylhydrazine was added to compound **X**, an orange precipitate was observed. Compound **X** did not give yellow precipitate with warm aqueous alkaline iodine.

(ii) Explain why $MgCO_3$ undergoes thermal decomposition more readily than $BaCO_3$.

……………………………………………………………………………………...

……………………………………………………………………………………...

……………………………………………………………………………………...

…………………………………………………………………………………….. [2]

(iii) Suggest the structure of **X**.

[1]

(iv) Write a balanced chemical equation for the decomposition of barium propanoate.

……………………………………………………………………………………..[1]

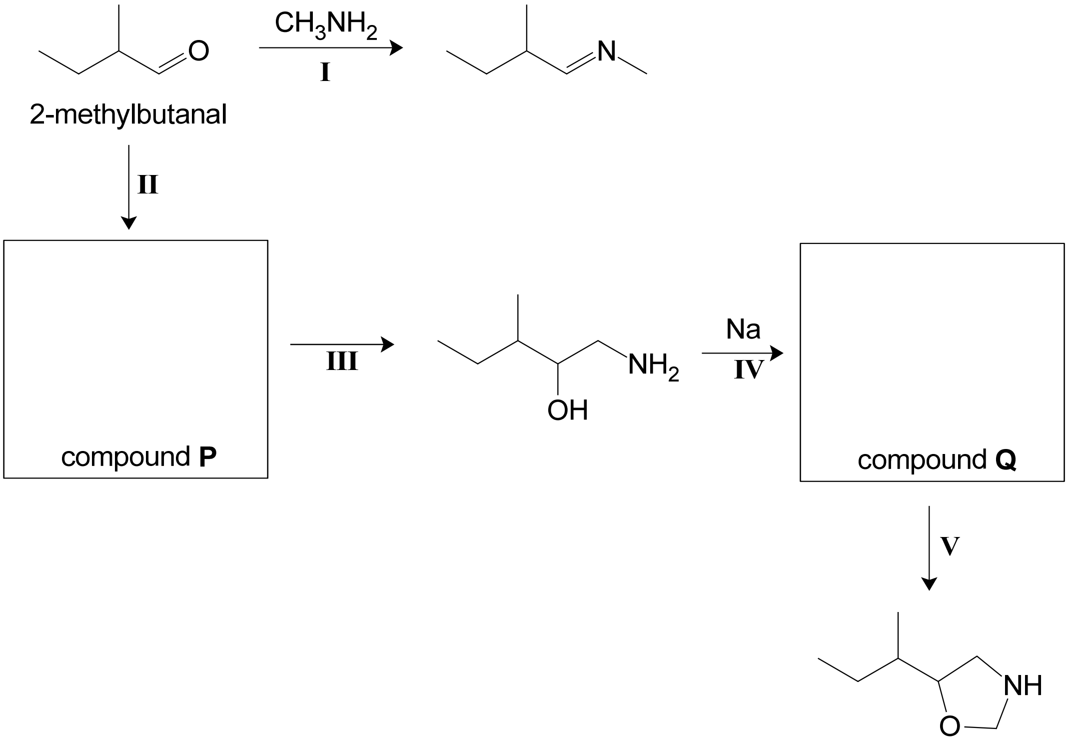
(v) Suggest why barium propanoate undergoes thermal decomposition more readily than barium carbonate.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) The scheme below shows the reactions of 2-methylbutanal.



(i) **R** is a constitutional isomer of 2-methylbutanal. **R** gives yellow precipitate when warmed with aqueous iodine in an alkaline medium. **R** does not decolourise aqueous bromine.

Draw the skeletal formulae of **two** possible structures of **R**.

[2]

(ii) Draw the structure of compounds **P** and **Q** in the boxes provided in the reaction scheme and state the reagents and conditions for steps **II**, **III** and **V**.

Step	**Reagents and Conditions**
II	
III	
V	

[5]

(iii) Suggest the type of reaction undergone by 2-methylbutanal in step **I**.

……………………………………………………………………………………….[1]

[Total: 15]

3 **(a)** Cyanogen is a colourless yet extremely poisonous gas that is used in fumigation. Cyanogen is made up of carbon and nitrogen only, of which 46.2% is composed of carbon by mass.

At 30°C and 1 bar, 1.03 g of cyanogen occupies 0.500 dm^3. It dissolves readily in water.

Calculate the molecular formula of cyanogen.

[3]

(b) Draw the 'dot-and-cross' diagram of the cyanogen molecule and suggest the shape of the molecule with respect to the central atom.

Shape: ………………………………………. [2]

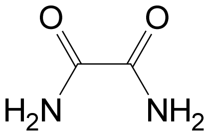
(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

……………………………………………………………………………………………......

……………………………………………………………………………………………….

………………………………………………………………………………………….[2]

(d) Oxamide is manufactured from cyanogen by hydrolysis that only involves water.



Oxamide

(i) Write the balanced equation for the production of oxamide from cyanogen and water. You may use the molecular formula of oxamide in your equation.

……………………………………………………………………………………….[1]

(ii) With the use of Data Booklet, calculate the enthalpy change of the reaction in **(d)(i)**.

[2]

(iii) The entropy change for the reaction in **(d)(i)** is +64.1 J mol^{-1} K^{-1}. Use your answer in **(d)(ii)** to calculate ΔG at 298 K. Hence predict if the reaction is spontaneous at 298 K.

[2]

[Total: 12]

4 **(a)** A bottle of supplement has the following nutritional information.

The serving size is 42.5g and each bottle contains 20 servings.

	Each serving contains	% of Recommended Daily Allowance
Total fat	3 g	5
Dietary Fibre	6 g	24
Protein	15 g	30
Calcium	546 mg	47
Iron	9 mg	43
Iodine	80 μg	48
Vitamin C	30 mg	52
Vitamin K	40 μg	51

Table 4.1

A student weighed out 75 g portion of this supplement and crushed it in a pestle and mortar to form a powder. She then added it to 100 cm^3, an excess, of 1.5 mol dm^{-3} sulfuric acid, stirred it and then filtered it.

She made the volume up to 250 cm^3 forming solution **A**. Finally, she titrated a 25.0 cm^3 portion of solution **A** with 1.8 x 10^{-4} mol dm^{-3} potassium dichromate(VI).

(i) Use the *Data Booklet* to construct an ionic equation for the reaction between Fe^{2+} in solution **A** and dichromate(VI) ions.

…………………………………………………………………………………..……[1]

(ii) Calculate the volume of potassium dichromate(VI) solution that would be required to react with Fe^{2+} in 25.0 cm^3 of solution **A**.

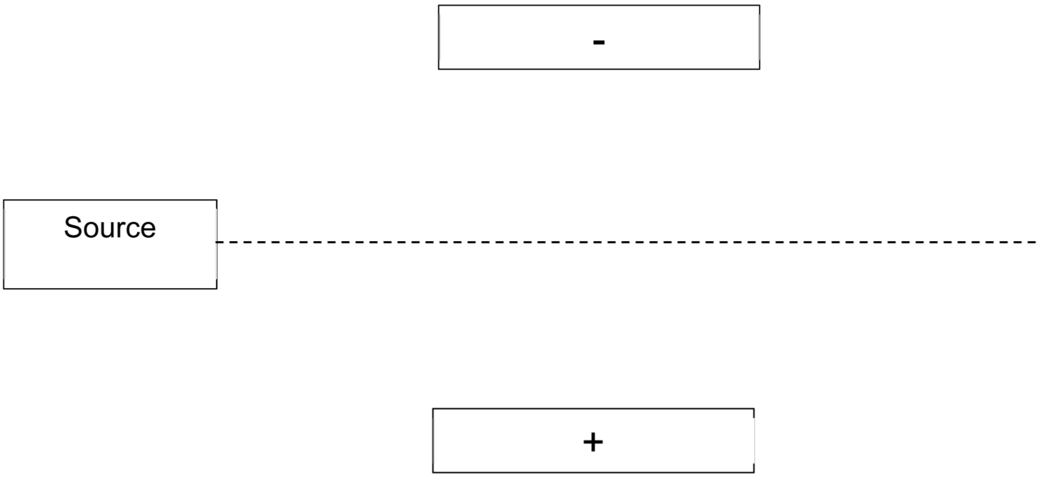
[3]

(b) Overdosage of iodine has many side-effects, including abdominal pain, delirium, fever, vomiting, and shortness of breath.

Assuming that a person does not consume any other food that contains iodine other than the supplement and a serving refers to 5 tablets, deduce if it is within the % daily recommended allowance for him to consume as many as 11 tablets in a single day. Justify with calculations.

[3]

(c) The iodine, calcium and iron content in the supplement is dissolved in water, forming ions. The ions are then isolated. Indicate on the diagram below how a beam of particles containing the three species, travelling at the same speed, behave in the same electric field. State your reasoning.



…………………………………………………………………………………………………..

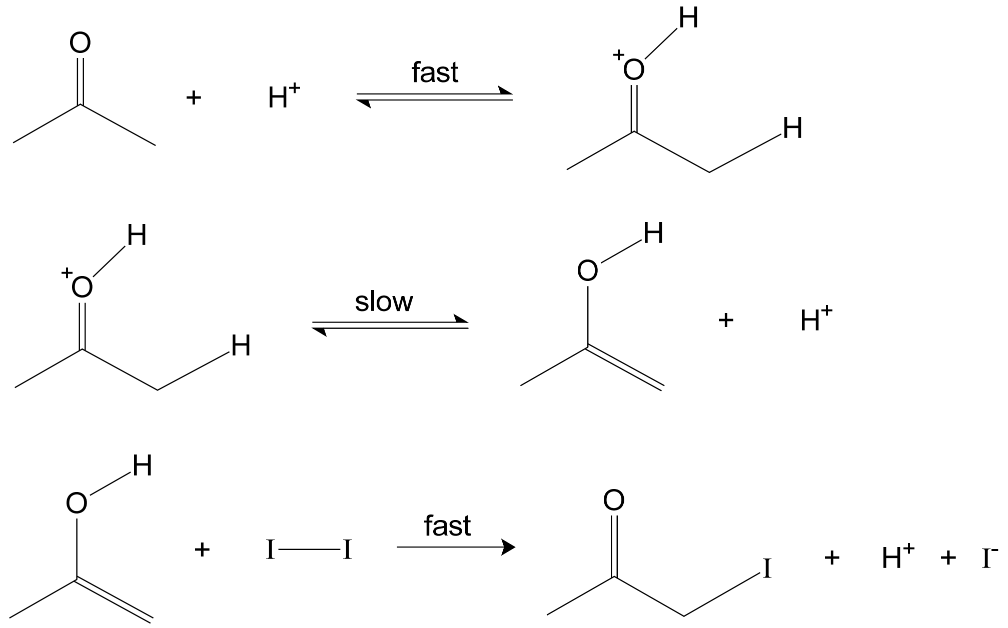
…………………………………………………………………………………………… [5]

[Total: 12]

5 **(a)** Propanone reacts with iodine in the presence of an acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The mechanism of this reaction is thought to be as follows:



(i) On the mechanism shown, draw curly arrows and lone pair of electrons to show the movement of electrons in each of the step. [3]

(ii) Based on the mechanism above, write the rate equation for this reaction.

....[1]

(iii) Hence, sketch the graph of rate against $[I_2]$.

[1]

(b) 5.0 cm^3 of the reaction mixture was taken out when the reaction has proceeded for 30 seconds. The resultant solution was then made up to 100 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium thiosulfate, $K_2S_2O_3$, with the addition of starch solution. The results are shown in **Table 5.1**.

	1	2	3
Initial burette reading / cm^3	0.00	19.95	2.05
Final burette reading / cm^3	19.90	40.05	22.15
Volume of titre / cm^3	19.90	20.10	20.10

Table 5.1

(i) Write the ionic equation for the reaction between potassium thiosulfate and iodine in the solution.

…………………………………………………………………………………..…..[1]

(ii) Use the above results to determine the concentration of iodine in the original 5.0 cm^3 of the aliquot taken out at 30 seconds after the reaction has started.

[3]

(c) The iodine solution was then isolated and boiled to produce I_2(g).

A sketch of $\frac{pV}{RT}$ against p for 1 mole of H_2(g) at 473 K is shown in **Fig 5.1**. On the same axes, sketch the graph of $\frac{pV}{RT}$ against p for 1 mole of I_2(g) at 473 K and for 1 mole of H_2(g) at 500 K. Label your sketch clearly.

Justify the difference in behaviour.

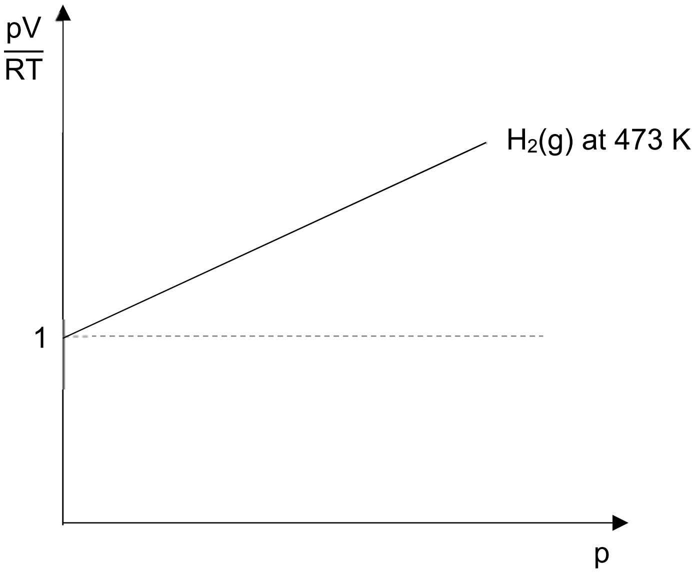


Fig 5.1

………………………………………………………………………………………………......

………………………………………………………………………………………………

…………………………………………………………………………………………….. [4]

(d) Describe all types of interactions found within the lattice structure of solid iodine fully.

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………..[3]

[Total: 16]

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H

millennia institute

2018 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **12th Sept 2018**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

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The number of marks is given in brackets [ ] at the end of each question or part question.

Question	1	2	3	4	5	Total
Marks	20	15	12	12	16	75

1 Ruthenium, Ru, is a Period 5 d-block element. Its ions have the ability to form complexes with both organic and inorganic ligands.

One such organic ligand is 2,2'-bipyridine which can be represented by bpy.

(a) Define the term *ligand* and suggest why bpy can act as a bidentate ligand.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

………………………………………………………………………………………………[2]

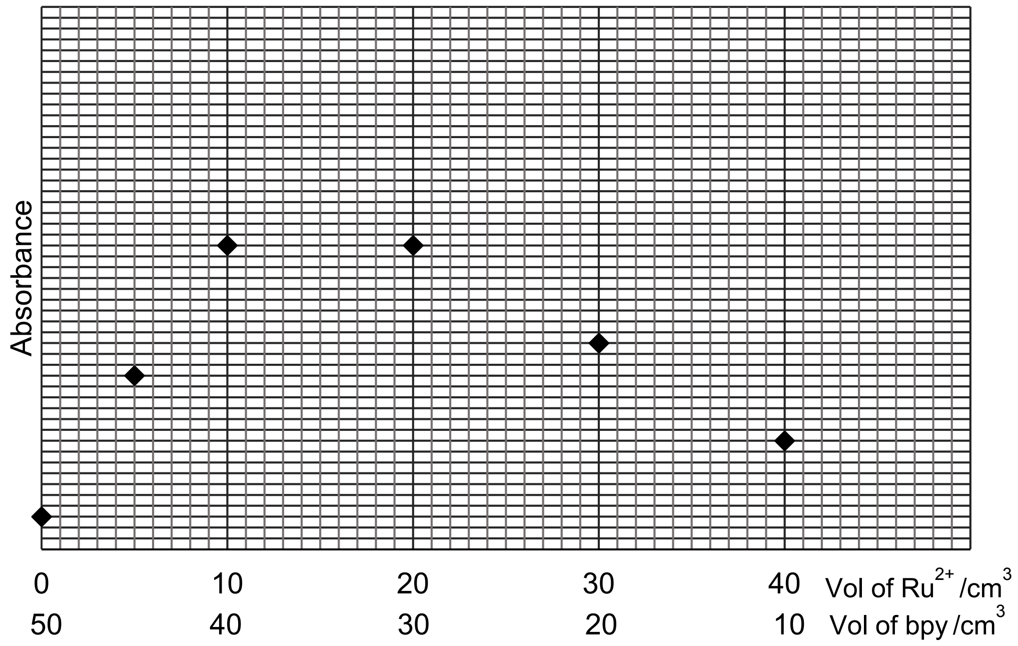
Ligand is a neutral molecule or anion which contain at least one atom bearing a lone pair of electrons which can form a dative bond to a central atom/ion, resulting in the formation of a complex.

Bpy has 2 nitrogen atoms with a lone pair of electrons each, so it can form two dative bonds with the central atom/ion.

(b) In an experiment, varying volumes of solutions of 0.1 mol dm^{-3} Ru^{2+} and 0.1 mol dm^{-3} bpy are mixed to produce a coloured complex.

$$x\text{Ru}^{2+} + y\text{bpy} \rightarrow [\text{Ru}_x(\text{bpy})_y]^{2+}$$

The concentration of the coloured complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. The following graph is plotted using the results of the experiment.



By drawing two best-fit lines on the graph, deduce the formula of the complex ion formed between Ru^{2+} and bpy and hence draw the structure of the complex ion.

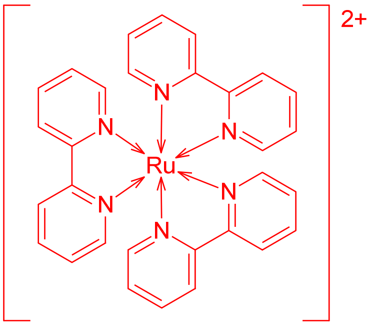
Formula of complex: …………………………..

Structure of complex ion:

[3]

Draw two straight lines that intersect one another.
Point of intersection shows $V_{Ru}{}^{2+} = 12.5\ cm^3$ and $V_{bpy} = 37.5\ cm^3$
Ratio of Ru^{2+} to bpy = 1:3 ;

formula = $[Ru(bpy)_3]^{2+}$

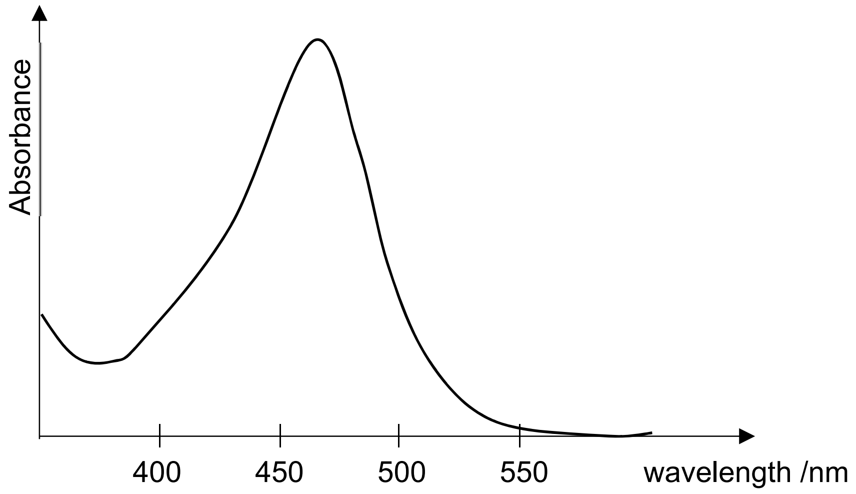


(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

Wavelength range (nm)	Colour	Complementary colour
400 – 450	violet	yellow
450 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue

650 – 700	red	green

The diagram below shows the UV-Visible spectrum of the complex formed between Ru^{2+} and bpy.



Use the data given to suggest the colour of the complex formed between Ru^{2+} and bpy.

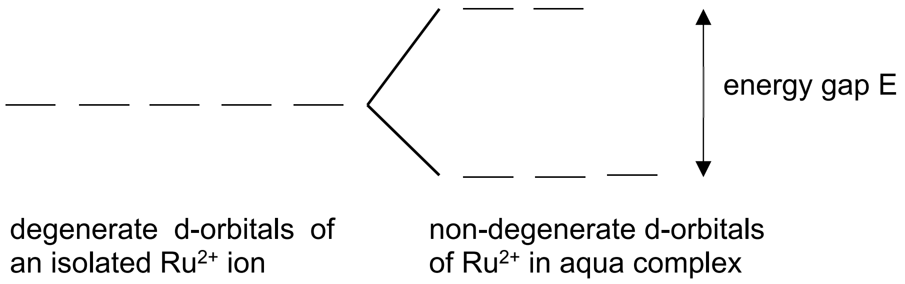
.... [1]

Blue is absorbed hence the complex is orange ;

(d) Ru^{2+} also forms an octahedral aqua complex with the formula $[Ru(H_2O)_6]^{2+}$.

Typically, the colour of the complex changes when the ligands are different. This is due to different ligands causing the five d-orbitals to be split to different extent.

The following diagram shows how the five d-orbitals are split in an octahedral environment.



(i) With reference to this diagram, outline why $[Ru(H_2O)_6]^{2+}$ is coloured.

....

....

.... [2]

The electrons in the lower energy d-orbital absorbs radiation from the visible region of the electromagnetic spectrum and get promoted to the higher energy d-orbital.
The complementary colour of the light absorbed is shown as the colour of $[Ru(H_2O)_6]^{2+}$.

The electrons of transition metal ions in complexes can fill the non-degenerate d-orbitals in two different ways, namely the ‘high spin’ state and the ‘low spin’ state. This is dependent on the magnitude of the energy gap, E, and the pairing energy, P. Electrons usually prefer to occupy orbitals singly, rather than in pairs. Pairing energy, P, is the energy needed for an electron to fill an orbital that is already occupied by another electron.

In the ‘high spin’ state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals. This occurs because the magnitude of the energy gap, E, is smaller than the pairing energy, P.

In the ‘low spin’ state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used. This occurs because the pairing energy, P, is smaller than the magnitude of the energy gap, E.

For Period 4 d-block elements, the electronic configuration of the 3d electrons can be either ‘high spin’ or ‘low spin’. However, for Period 5 d-block elements, the 4d electrons are always in the ‘low spin’ state.

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.

………………………………………………………………………………………

………………………………………………………………………………………[1]

Electrons are negatively charged and will exert repulsive force against each other.

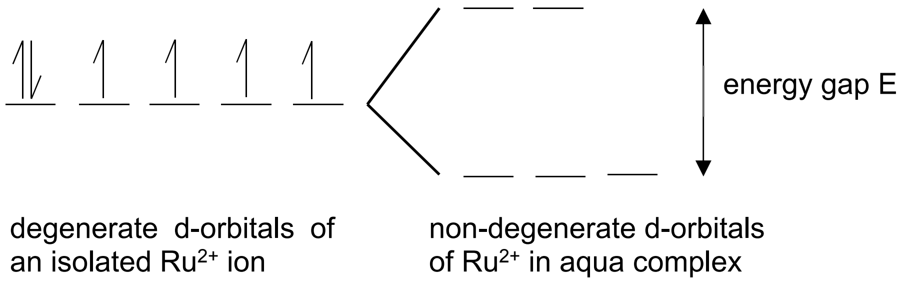
(iii) With reference to the relative sizes of 3d and 4d orbitals, suggest a reason why 4d electrons prefer to pair up in the lower energy d-orbital before filling the higher energy d-orbitals.

………………………………………………………………………………………

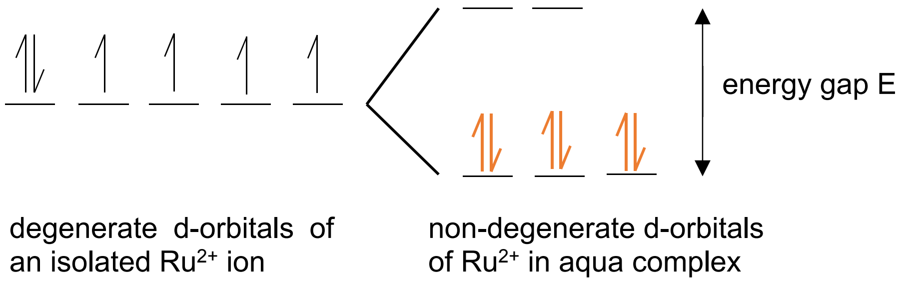
……………………………………………………………………………………… [1]

4d is bigger in size compared to 3d orbitals. The bigger space causes the repulsion between electrons to be smaller hence the pairing energy becomes smaller than the magnitude of the energy gap.

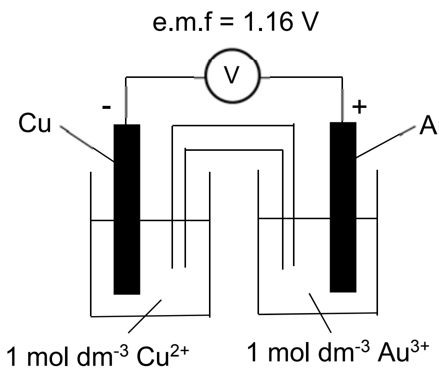
(iv) In the diagram below, show the electronic distribution of a Ru^{2+} ion in the ‘low spin’ state, given that the electronic configuration of Ru^{2+} is [Kr] $4d^6$.



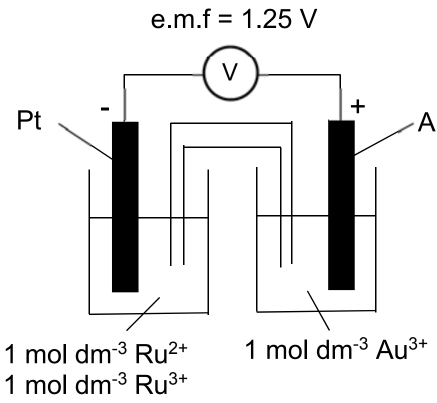
[1]



(e) Two galvanic cells were set up under standard conditions to determine the standard electrode potential of Ru^{3+}/Ru^{2+}.



cell A



cell B

(i) Define the term *standard electrode potential*.

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

Standard electrode potential is the relative potential of the electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.

(ii) Using the data given and relevant data from the Data Booklet, determine the standard electrode potentials of Au^{3+}/Au and that of Ru^{3+}/Ru^{2+} respectively.

$E^{\ominus}(Au^{3+}/Au)$ = ……………………………………

$E^{\ominus}(Ru^{3+}/Ru^{2+})$ = …………………………………… [3]

$1.16 = E^{\ominus}(Au^{3+}/Au) – (+0.34)$

$E^{\ominus}(Au^{3+}/Au) = +1.50$ V ;

$1.25 = +1.50 - E^{\ominus}(Ru^{3+}/Ru^{2+})$

$E^{\ominus}(Ru^{3+}/Ru^{2+}) = +0.25$ V ;

working ;

(iii) Hence using your answer in **(e)(ii)** and relevant data from the Data Booklet, state and explain whether Ru^{3+} is able to act as a homogenous catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [3]

$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$ +0.25 V

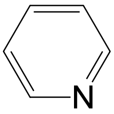
$I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V ;

$2Ru^{3+} + 2I^- \rightarrow 2Ru^{2+} + I_2$

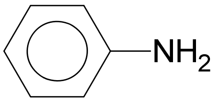
$E^{\ominus}_{cell} = +0.25 – 0.54 = - 0.29$ V ;

$E^{\ominus}_{cell} < 0$ hence reaction is not feasible and Ru^{3+} cannot be a catalyst;

(f) Pyridine and phenylamine are two nitrogen-containing compounds.



pyridine
pK_b = 8.75



phenylamine
pK_b = 9.33

Pyridine has a resonance structure with six p electrons delocalised over the ring. The molecule is planar, with all atoms forming the ring being sp^2 hybridised. The lone pair of electrons on nitrogen occupies one of its sp^2 hybrid orbitals.

With reference to the shape and orientation of the orbitals about the nitrogen atom in both compounds, suggest why pyridine has a lower pK_b value.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

………………………………………………………………………………………… [2]

The lone pair on N atom of phenylamine is in the p-orbital which lies perpendicular to the benzene plane hence able to delocalise into the ring.

The lone pair on N atom of pyridine is in the sp^2 hybrid orbital which lies on the same plane as the benzene ring hence unable to delocalise into the ring.

The lone pair on N atom of pyridine is more available for protonation hence it is a stronger base and therefore has a lower pK_b value.

2 **(a)** Upon heating at 160 °C, magnesium ethanoate decomposes to give magnesium carbonate and propanone as the products.

$$(CH_3COO)_2Mg \rightarrow MgCO_3 + CH_3COCH_3$$

Upon further heating, $MgCO_3$ undergoes further decomposition.

(i) Write an equation for the decomposition of $MgCO_3$.

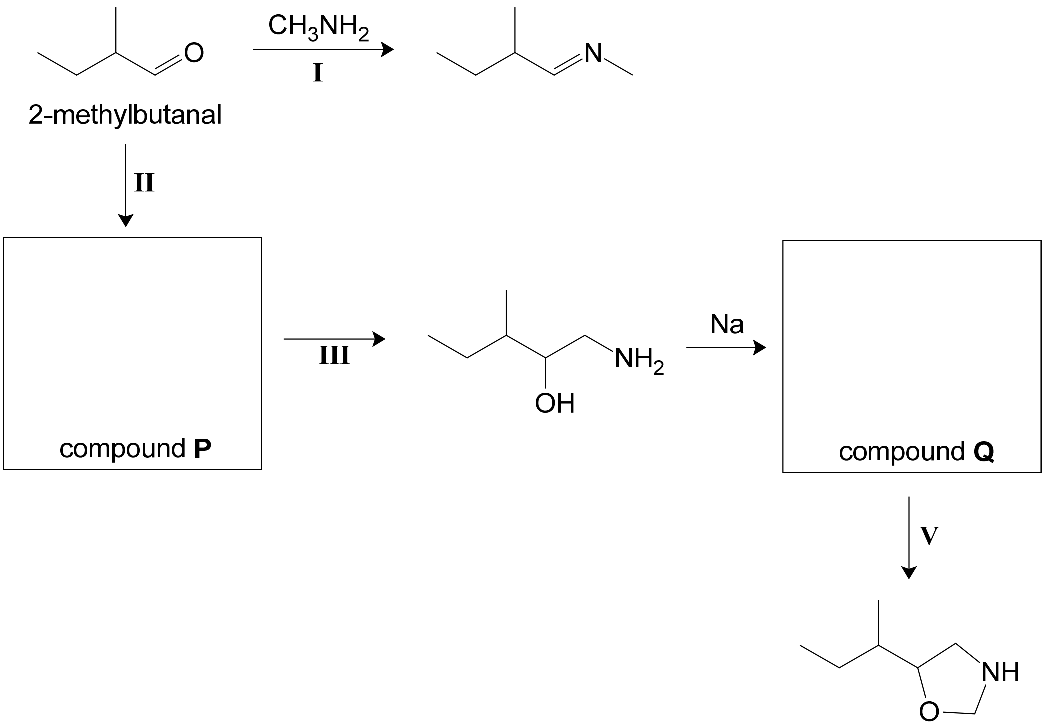
…………………………………………………………………………………….[1]

$MgCO_3 \rightarrow MgO + CO_2$

When barium propanoate, $(CH_3CH_2COO)_2Ba$ was heated until constant mass, it was found that $BaCO_3$ and an organic compound **X**, $C_5H_{10}O$, were obtained. Despite further heating, $BaCO_3$ did not undergo decomposition.

When 2,4-dinitrophenylhydrazine was added to compound **X**, an orange precipitate was observed. Compound **X** did not give yellow precipitate with warm aqueous alkaline iodine.

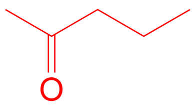
		(ii)	Explain why $MgCO_3$ undergoes thermal decomposition more readily than $BaCO_3$. …………………………………………………………………………………………... …………………………………………………………………………………………... ………………………………………………………………………………………… [2]	
			Mg^{2+} has a smaller ionic radius hence a higher charge density, its higher polarising power allows it to distort the electron cloud of carbonate to a greater extent. The C-O bond in $MgCO_3$ is weakened to a greater extent hence more easily decomposed.	
		(iii)	Suggest the structure of **X**. [1]	
			$CH_3CH_2COCH_2CH_3$	
		(iv)	Write a balanced chemical equation for the decomposition of barium propanoate. …………………………………………………………………………………………..[1]	
			$(CH_3CH_2COO)_2Ba \rightarrow BaCO_3 + CH_3CH_2COCH_2CH_3$	
		(v)	Suggest why barium propanoate undergoes thermal decomposition more readily than barium carbonate. …………………………………………………………………………………………… …………………………………………………………………………………………... …………………………………………………………………………………………[2]	
			Propanoate ion has a larger electron cloud size ; hence it is more easily polarised ;	
	(b)	The scheme below shows the reactions of 2-methylbutanal.		

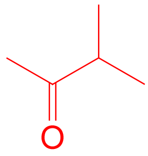


(i) **R** is a constitutional isomer of 2-methylbutanal. **R** gives yellow precipitate when warmed with aqueous iodine in an alkaline medium. **R** does not decolourise aqueous bromine.

Draw the skeletal formulae of **two** possible structures of **R**.

[2]





;;

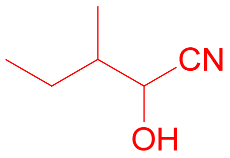
(ii) Draw the structure of compounds **P** and **Q** in the boxes provided in the reaction scheme and state the reagents and conditions for steps **II**, **III** and **V**.

Step	Reagents and Conditions
II	
III	

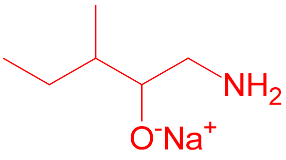
V	

[5]

Step	Reagents and Conditions
II	cold HCN, trace NaCN or NaOH
III	$LiAlH_4$ in dry ether
V	CH_2Cl_2



P



Q

(iii) Suggest the type of reaction undergone by 2-methylbutanal in step **I**.

…………………………………………………………………………………………[1]

condensation

3 **(a)** Cyanogen is a colourless yet extremely poisonous gas that is used in fumigation. Cyanogen is made up of carbon and nitrogen only, of which 46.2% is composed of carbon by mass.

At 30°C and 1 bar, 1.03 g of cyanogen occupies 0.500 dm^3. It dissolves readily in water.

Calculate the molecular formula of cyanogen.

[3]

	C	N
% by mass	46.2	53.8
A_r	12.0	14.0
Amount	3.85	3.84
Ratio	1	1

EF: CN (;)

$pV=nRT$

$10^5 \times 0.5 \times 10^{-3} = n(8.31)(303)$

$n = 0.01986$ mol

$n = \frac{mass}{Mr} = \frac{1.03}{Mr} = 0.01986$

$M_r = 51.87$ (;)

MF = $(CN)_y$

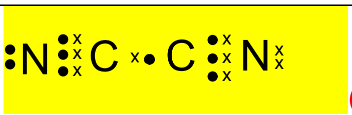
$y = \frac{51.87}{12+14} = 2$

MF: $(CN)_2$ (;)

(b) Draw the ‘dot-and-cross’ diagram of the cyanogen molecule and suggest the shape of the molecule with respect to the central atom.

Shape: ....

[2]



(;)

Shape: linear(;)

(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

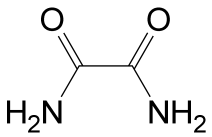
……………………………………………………………………………………………….....

………………………………………………………………………………………………..

……………………………………………………………………………………………[2]

Energy given out from the formation of hydrogen bonding between cyanogen and water (;) is sufficient to overcome the instantaneous dipole-induced dipole between cyanogen molecules(;) and hydrogen bonding between water molecules.

(d) Oxamide is manufactured from cyanogen by hydrolysis that only involves water.



Oxamide

(i) Write the balanced equation for the reaction of manufacturing oxamide from cyanogen and water. You may use the molecular formula of oxamide in your equation.

…………………………………………………………………………………….[1]

$(CN)_2 + 2\ H_2O \rightarrow H_2NC(O)C(O)NH_2$

(ii) With the use of Data Booklet, calculate the enthalpy change of the reaction in **(d)(i)**.

[2]

ΔH_{rxn} = 890x2+ 350 + 4(460) – [4(390) + 2(305) +2(740) +350](;)

= -30.0 kJ mol^{-1}(;)

(iii) The entropy change for the reaction in **(d)(i)** is +64.1 J mol^{-1} K^{-1}. Use your answer in **(d)(ii)** to calculate ΔG at 298 K. Hence predict if the reaction is spontaneous at 298 K.

[2]

ΔG_{rxn} = -30 – 298(+64.1x10^{-3}) = -49.1 kJ mol^{-1} (;)

ΔG_{rxn} < 0 The reaction is spontaneous at 298 K (;)

4 **(a)** A bottle of supplement has the following nutritional information.

The serving size is 42.5g and each bottle contains 20 servings.

	Each serving contains	% of Recommended Daily Allowance
Total fat	3 g	5
Dietary Fibre	6 g	24
Protein	15 g	30
Calcium	546 mg	47
Iron	9 mg	43
Iodine	80 µg	48
Vitamin C	30 mg	52
Vitamin K	40 µg	51

A student weighed out 75 g portion of this supplement and crushed it in a pestle and mortar to form a powder. She then added it to 100 cm^3, an excess, of 1.5 mol dm^{-3} sulfuric acid, stirred it and then filtered it.

She made the volume up to 250 cm^3 forming solution **A**. Finally, she titrated a 25.0 cm^3 portion of solution **A** with 1.8 x 10^{-4} mol dm^{-3} potassium dichromate(VI).

(i) Use the *Data Booklet* to construct an ionic equation for the reaction between Fe^{2+} in solution **A** and dichromate(VI) ions.

....[1]

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(ii) Calculate the volume of potassium dichromate(VI) solution that would be required to react with Fe^{2+} in 25.0 cm^3 of solution **A**.

[3]

Mass of Fe^{2+} in 75 g serving = $\frac{75}{42.5}$ × 9 = 15.88 mg

Amount of Fe^{2+} in 75 g serving = $\frac{15.88\times10^{-3}}{55.8}$ = 0.0002846 mol (;)

[Fe^{2+}] in solution **A** = $\frac{0.0002846}{\frac{250}{1000}}$ = 0.001138 mol dm^{-3}

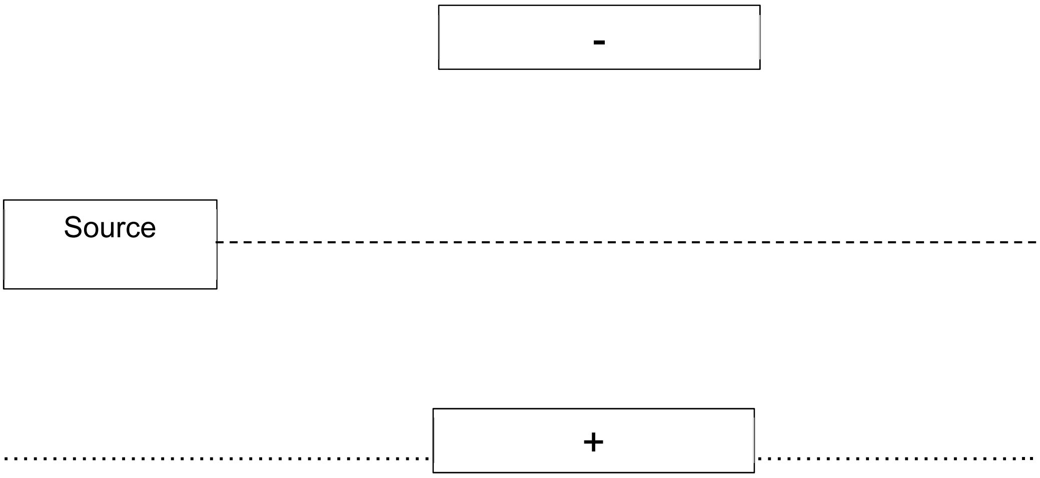
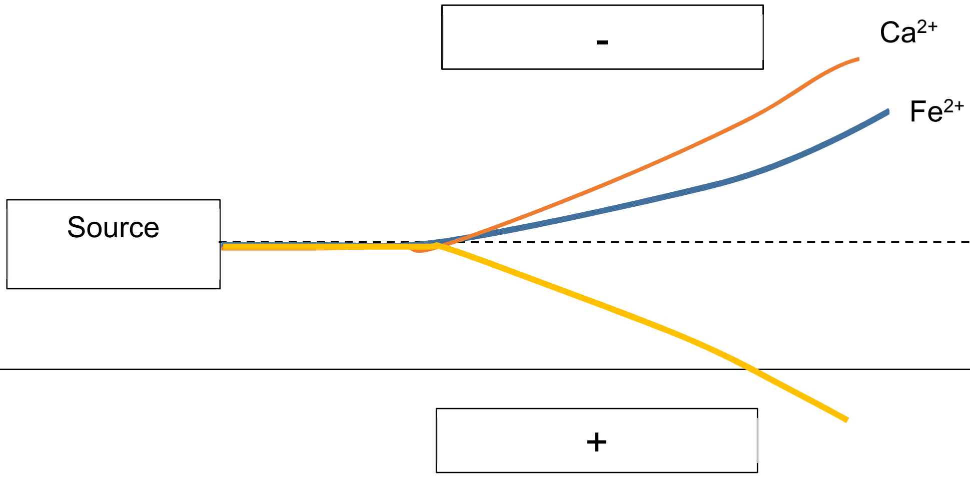
Amount of Fe^{2+} in 25 cm^3 of solution **A** = $\frac{25}{1000}$ × 0.001138 = 0.00002846 mol (;)

Amount of $Cr_2O_7^{2-}$ to titrate with 25 cm^3 of solution **A** = $\frac{0.00002846}{6}$ = 0.000004744 mol

Volume of $Cr_2O_7^{2}$ = $\frac{0.000004744}{1.8\times10^{-4}}$ = 26.4 cm^3

(b) Overdosage of iodine has many side-effects, including abdominal pain, delirium, fever, vomiting, and shortness of breath.

Assuming that a person does not consume any other food that contains iodine other than the supplement and a serving refers to 5 tablets, deduce if it is within the % daily recommended allowance for him to consume as many as 11 tablets in a single day. Justify with calculations.

		[3]	
		Daily recommended allowance of iodine= $80 \div \frac{48}{100}$ = 166.7 µg (;) No of tablets within daily recommended allowance = $\frac{166.7}{80} \times 5$ = 10.4 (;) It is not within the % daily recommended allowance. (;)	
	(c)	The iodine, calcium and iron content in the supplement is dissolved in water, forming ions. The ions are then isolated. Indicate on the diagram below how a beam of particles containing the three species, travelling at the same speed, behave in the same electric field. State your reasoning.  ……………………………………………………………………………………… [5] [Total: 12 marks]	
			

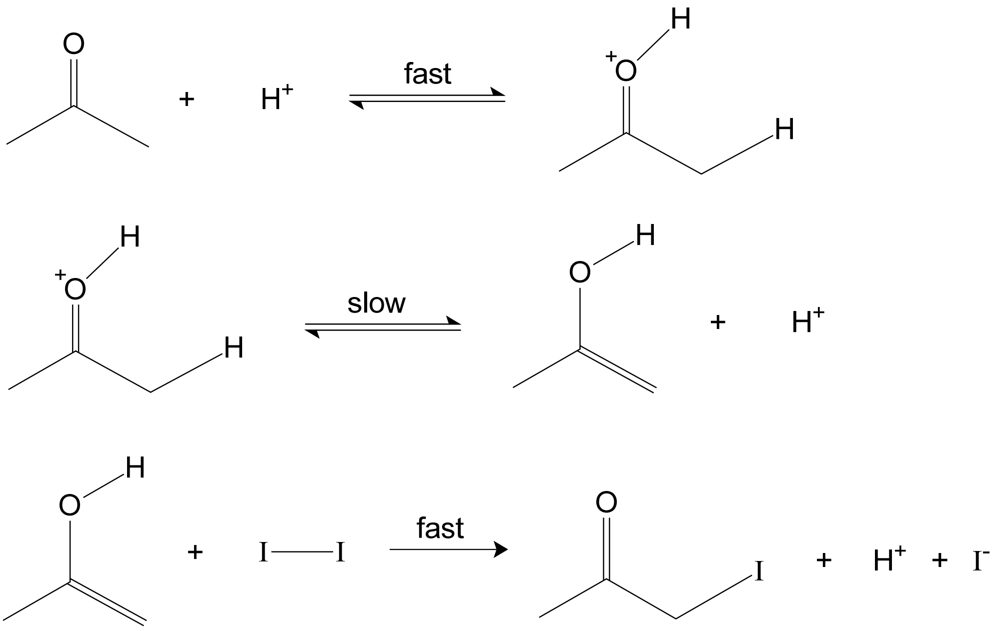
I^-

Iodide is an anion while Ca^{2+} and Fe^{2+} are cations. Thus anion will be deflected towards the positively charged plate while the cations will be deflected towards the negatively charged plate(;) Based on charge/mass ratio, Fe^{2+} will have a smaller magnitude as it has a larger A_r, thus the angle of deflection will be smaller.(;)

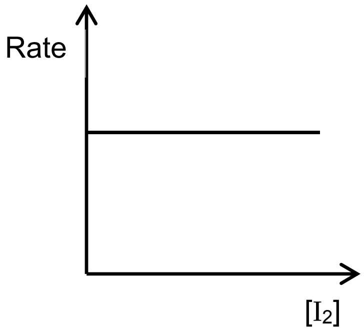
5 **(a)** Propanone reacts with iodine in the presence of an acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The mechanism of this reaction is thought to be as follows:



(i) On the mechanism shown, draw curly arrows and lone pair of electrons to show the movement of electrons in each of the step. [3]

			+ H I + H^+ + I^- [1] per step ;;;	
		(ii)	Based on the mechanism above, write the rate equation for this reaction. …………………………………………………………………………………….[1]	
			Rate = k[CH_3COCH_3][H^+]	
		(iii)	Hence, sketch the graph of rate against [I_2] [1]	
				

(b) 5.0 cm^3 of the reaction mixture was taken out when the reaction has proceeded for 30 seconds. The resultant solution was then made up to 100 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium thiosulfate, $K_2S_2O_3$, with the addition of starch solution. The results are shown below.

	1	2	3
Initial burette reading / cm^3	0.00	19.95	2.05
Final burette reading / cm^3	19.90	40.05	22.15
Volume of titre / cm^3	19.90	20.10	20.10

(i) Write the ionic equation for the reaction between potassium thiosulfate and iodine in the solution.

……………………………………………………………………………………………[1]

$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$

(ii) Use the above results to determine the concentration of iodine in the original 5.0 cm^3 of the aliquot taken out at 30 seconds after the reaction has started.

[3]

Average titre volume = $\frac{20.10 + 20.10}{2}$ = 20.10 cm^3 (;)

Amount of $S_2O_3^{2-}$ = $\frac{20.10}{1000} \times 0.100$ = 0.00201 mol

Amount of I_2 in the 25.0 cm^3 solution= 0.00201 / 2 = 0.001005 mol(;)

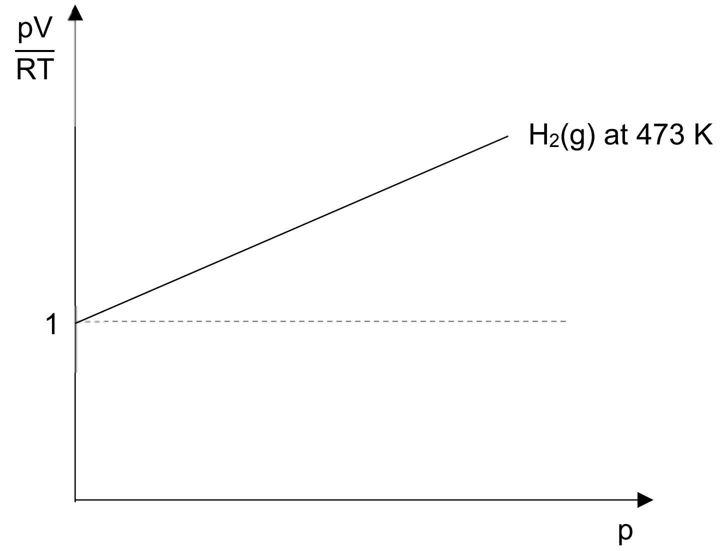
Amount of I_2 in the 100 cm^3 solution= 0.001005 x 4 = 0.00402 mol

$[I_2] = \frac{0.00402}{\frac{5}{1000}} = 0.804 \text{ mol dm}^{-3}$ (;)

(c) The iodine solution was then isolated and boiled to produce $I_2(g)$.

A sketch of $\frac{pV}{RT}$ against p for 1 mole of $H_2(g)$ at 473 K is shown below. On the same axes, sketch the graph of $\frac{pV}{RT}$ against p for 1 mole of $I_2(g)$ at 473 K and for 1 mole of $H_2(g)$ at 500 K. Label your sketch clearly.

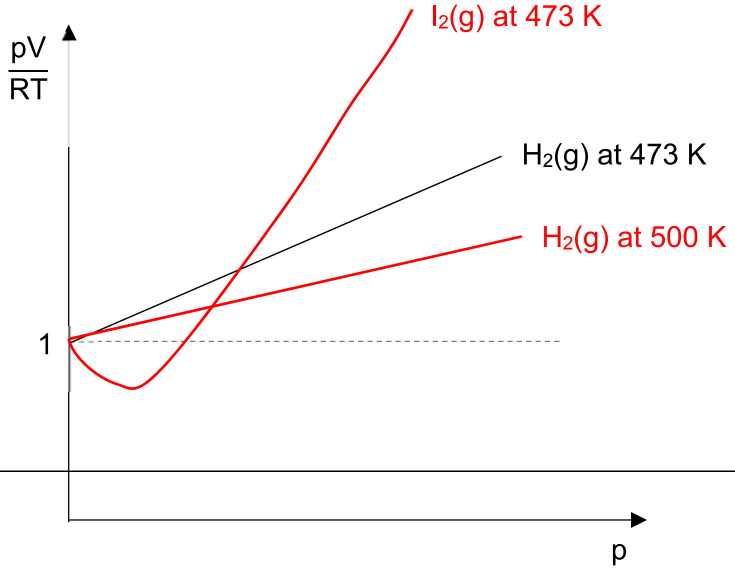
Justify the difference in behaviour.



………………………………………………………………………………………………………

………………………………………………………………………………………………………

……………………………………………………………………………………………… [4]



		$H_2(g)$ behaves more ideally than $I_2(g)$ as it has a weaker instantaneous dipole-induced dipole forces of attraction between molecules due to smaller size of electron cloud. (;) At higher temperature, $H_2(g)$ has higher kinetic energy and moves more quickly. Thus, the molecules are further away and there will be weaker forces of attraction between them. (;)	
	(d)	Describe all types of interactions found within the lattice structure of solid iodine fully. ……………………………………………………………………………………………… ……………………………………………………………………………………………… ……………………………………………………………………………………………….. [3] [Total: 16 marks]	
		Iodine molecules are held by instantaneous dipole-induced dipole forces of attraction between molecules(;) and strong covalent bonds between iodine atoms within the molecule(;). The covalent bond is the electrostatic forces of attraction between the bond pair and the nuclei of the iodine atoms.(;)	

Class | Adm No

Candidate Name: ____________________

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sept 2018**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

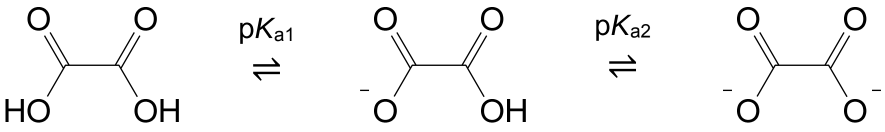
The number of marks is given in brackets [ ] at the end of each question or part question.

Question	Section A			Section B		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

Section A

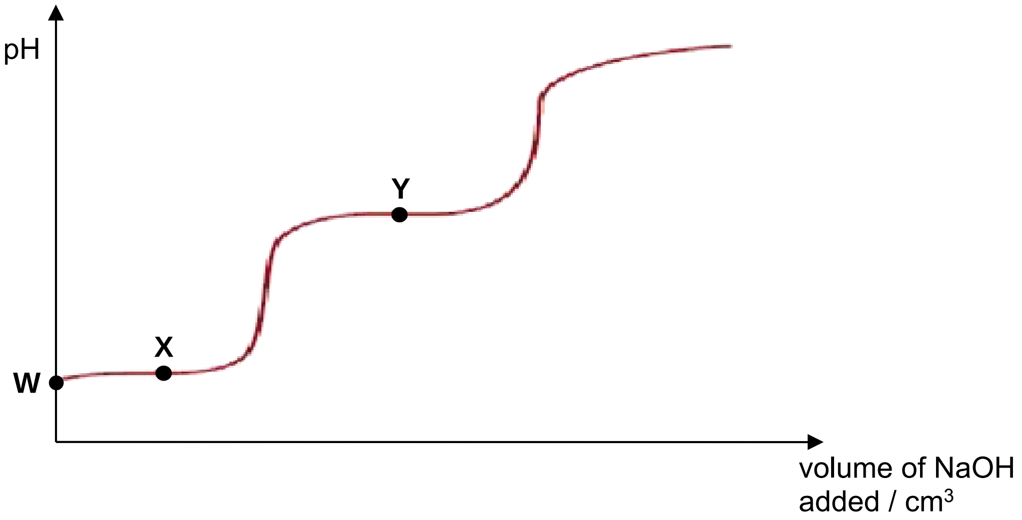
Answer **all** questions from this section.

1 Oxalic acid is a weak diprotic Brønsted acid with pK_{a1} and pK_{a2} values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(a) Suggest why the value of pK_{a2} is larger than pK_{a1}. [2]

(b) **(i)** Calculate the value of pH at point **W**. [1]

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

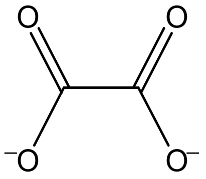
(c) **(i)** Define the term *buffer*. [1]

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of OH$^-$(aq) is added. [1]

(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

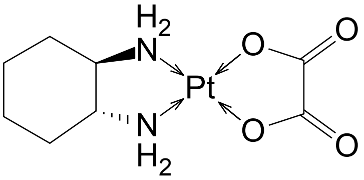
The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

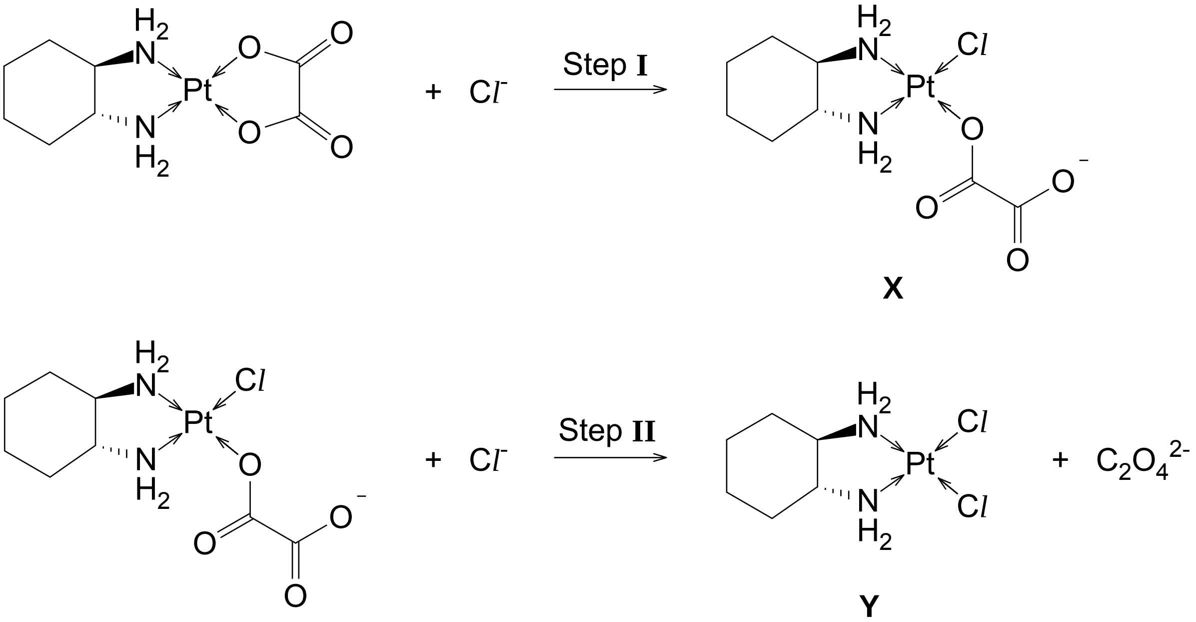
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step **I** is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]

[Total: 23]

2 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*. [1]

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]

A fixed current was passed through the cell for a duration of time to determine the experimental values of *F* and *L*. The following are the results obtained.

current passed through the cell = 0.500 A
duration of time = 30.0 min
change in mass of cathode = 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of *L*. [3]

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

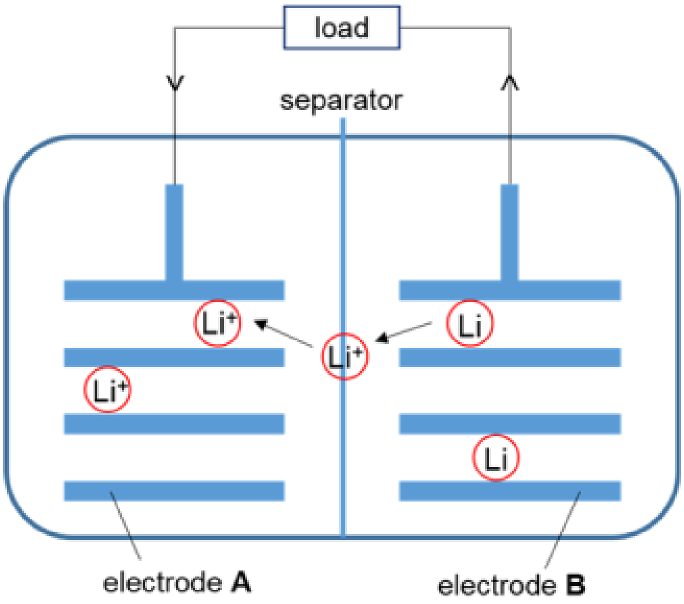
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

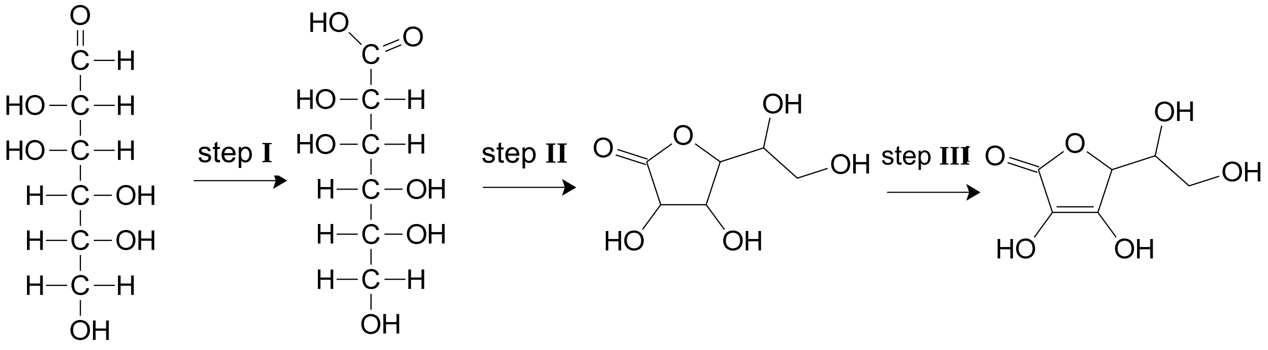
1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

[Total: 20]

3 Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



Glucose **Intermediate A** **Intermediate B** **Ascorbic Acid**

(a) State the functional groups present in intermediate **B**. [2]

(b) State the reagent and conditions required for step **II**. [1]

(c) State the type of reaction for steps **I** and **II**. [2]

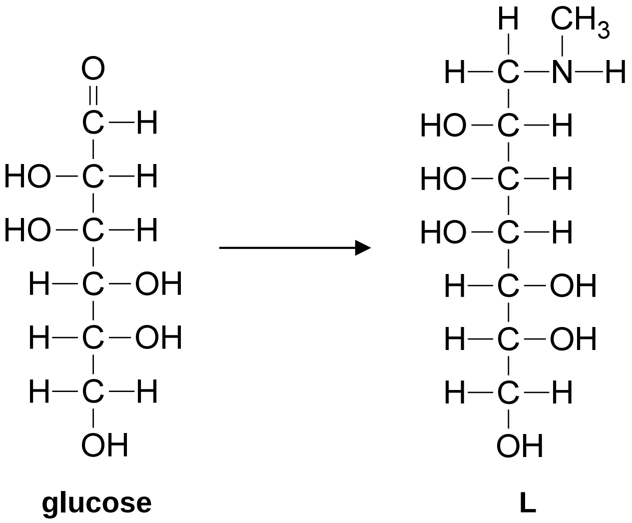
(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

(e) Explain why ascorbic acid is water soluble. [2]

(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

- **(i)** PCl_5
- **(ii)** excess hot acidified $K_2Cr_2O_7$
- **(iii)** Na(s)

(g) Compound **L** can be formed from glucose.



Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

[Total: 17]

Section B

Answer **one** question from this section.

4 In the chlor-alkali industry, 19.8 g impure sample of NaCl(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas.[1]

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

[Total: 20]

5 **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

(v) State and explain the role of acid in this overall reaction. [2]

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

[Total: 20]

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Class	Adm No

Candidate Name: ____________________

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sept 2018**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

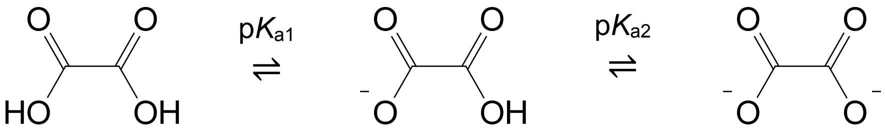
Question	Section A			Section B		Total
	1	2	3	4	5	
Marks	23	20	17	20	20	80

This question paper consists of **11** printed pages and **1** blank page.

Section A

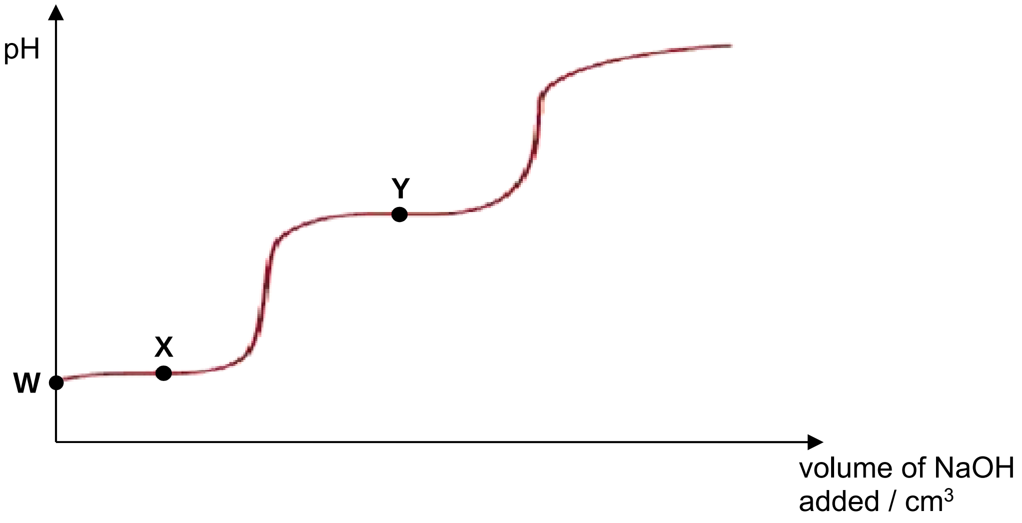
Answer **all** questions from this section.

1 Oxalic acid is a weak diprotic Brønsted acid with $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(a) Suggest why the value of $\mathrm{p}K_{a2}$ is larger than $\mathrm{p}K_{a1}$. [2]

Removal of H^+ for $\mathrm{p}K_{a2}$ is from a negatively charged species while that for $\mathrm{p}K_{a1}$ is from a neutral species, hence dissociation for $\mathrm{p}K_{a2}$ is more difficult / $(COOH)COO^-$ is less acidic than $(COOH)_2$ and the value of $\mathrm{p}K_{a1}$ is larger.

or

The first conjugate base of oxalic acid is stabilised by an intramolecular ion-dipole interaction with the OH group of $(COOH)COO^-$, hence dispersing the negative charge to a greater degree and increasing the acid strength. Thus the first $\mathrm{p}K_a$ value is smaller than the second $\mathrm{p}K_a$ as the second conjugate base formed does not have this extra stability.

(b) **(i)** Calculate the value of pH at point **W**. [1]

$[H^+] = \sqrt{(10^{-1.25})(0.50)}$

$= 0.1677$ mol dm^{-3}

pH = 0.776

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

Amount of oxalic acid = 0.50 x $\frac{25}{1000}$
= 0.0125 mol

pH = pK_{a1} + log $\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$

Let x be the amount of salt $(COOH)COO^{-}$, which is also the amount of NaOH added.

1.25 = 1.25 + $\log\left(\frac{x/V}{(0.0125-x)/V}\right)$

$\frac{x}{0.0125-x}$ = 1

x = 0.00625 mol

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Amount of oxalic acid reacted = 0.0125/2 = 0.00625 mol

= Amount of NaOH added

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

Since pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Since EP(1) vol. of NaOH = $\left(\frac{0.0125}{1}\right)$ = 0.0125 dm^3 = 12.5 cm^3

vol. of NaOH added at HEP(1) = 12.5/2 = 6.25 cm^3

(c) **(i)** Define the term *buffer*. [1]

A buffer is a solution which is able to resist pH changes when small quantities of acid or base are added.

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of $OH^{-}(aq)$ is added. [1]

$(COOH)COO^{-} + OH^{-} \rightarrow (COO^{-})COO^{-} + H_2O$

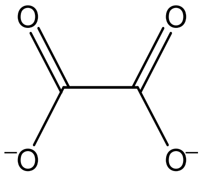
(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

Colourless solution turns pale pink.

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

Indicators are weak acids/bases. Addition of more indicator could cause a significant change in the pH of the solution, affecting the accuracy of the titration.

The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

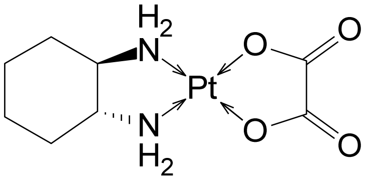
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

In water, Pt^{2+} exists as the tetraaqua complex $[Pt(H_2O)_4]^{2+}$

$[Pt(H_2O)_4]^{2+} \rightarrow [Pt(H_2O)_3(OH)]^+ + H^+$

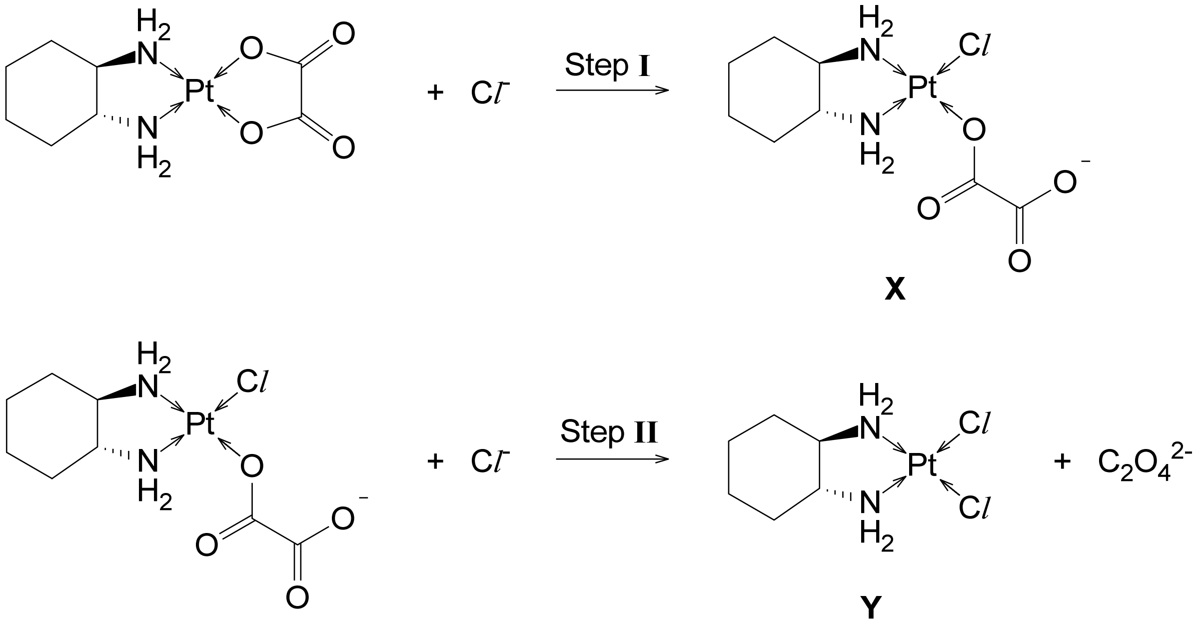
Transition metal ions such as Pt have a high charge density and can polarise the H_2O ligands to release H^+, making the solution acidic.

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step **I** is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

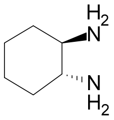
Not feasible, as entropy change of the ligand exchange reaction is negative / reaction is entropically disfavoured due to a decrease in the number of particles.

Enthalpy change of the ligand exchange reaction.

accept ΔG; BE(Pt-Cl) and BE(Pt-O)

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

None of the three complexes can exhibit cis-trans isomerism.

The bidentate  ligand cannot be forced into a trans conformation. *OWTTE*

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

Amount of AgCl = 1.35 / (107.9+35.5) = 0.009414 mol
= Amount of free Cl^-

∴ 1 mol of isomer contains 1 mol of free Cl^-.

$[Pt(C_6H_{14}N_2)(Cl)(H_2O)]^+Cl^-.H_2O$

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

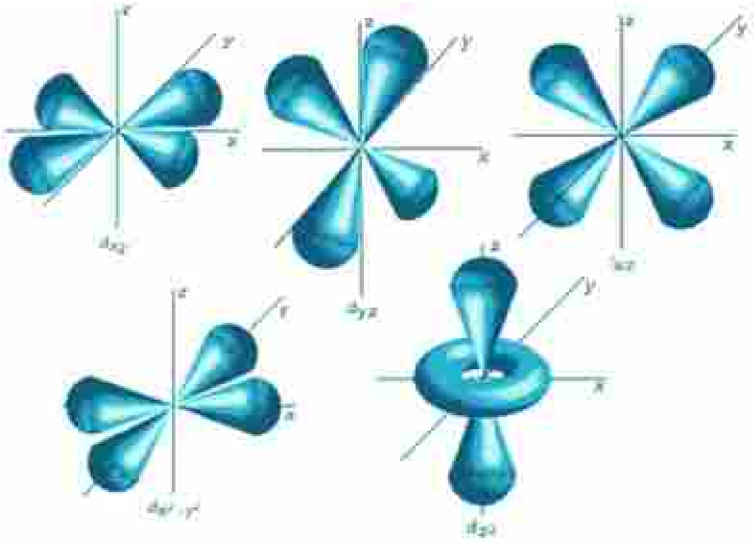
24 protons, 28 neutrons, 21 electrons

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]



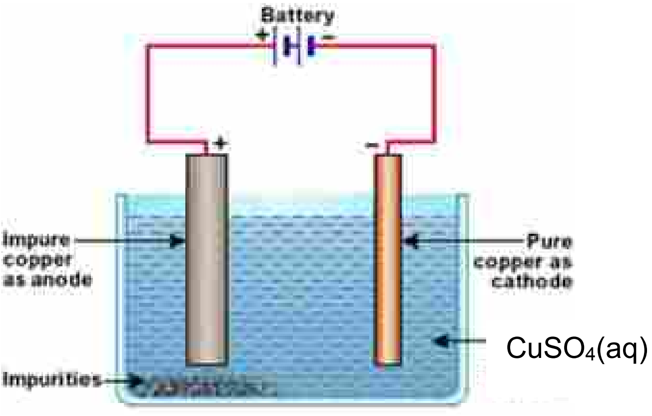
[Total: 23]

2 **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*. [1]

F = Le

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]



Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

A fixed current was passed through the cell for a duration of time to determine the experimental values of *F* and *L*. The following are the results obtained.

current passed through the cell = 0.500 A
duration of time = 30.0 min
change in mass of cathode = 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of *L*. [3]

Q= It = 0.500 x 30.0 x 60 = 900C

Amount of copper deposited = 0.299 / 63.5 = 0.004709 mol
$Cu^{2+} + 2e^- \rightarrow Cu$
Amount of e^- = 0.004709 x 2 = 0.00942 mol
Q = nF
F = 900 / 0.00942 = 95568.5

F= Le
$L = 95568.5 / 1.602 \times 10^{-19} = 5.97 \times 10^{23}$ (3 sf)

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

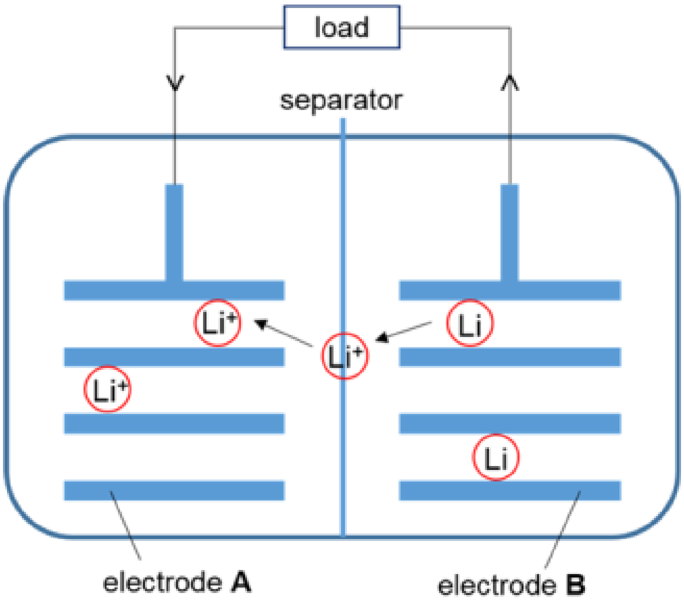
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

$CoO_2 + Li \rightarrow LiCoO_2$ *or* $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$ [no marks awarded]

$\Delta G = -nFE = -1 \times 96500 \text{ C mol}^{-1} \times 3.70\text{V} = -357 \text{ kJ mol}^{-1}$

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

Electrode **A** is CoO_2 / $LiCoO_2$.

Amount of CoO_2 (charged) = 10.0 / [58.9 + 2(16.0)]
= 0.1100 mol

Amount of LiC_6 (charged) = 10.0 / [6.9 + 6(12.0)]
= 0.1267 mol
= Amount of Li^+ available

CoO_2 is the limiting reagent / Li^+ is in excess.

Amount of $LiCoO_2$ (discharged) = 0.1100 mol
Mass of $LiCoO_2$ (discharged) = 0.1100 x [6.9 + 58.9 + 2(16.0)] = 10.8 g (3 sf)

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

Electrode **B** is C_6 / LiC_6.
Mass of LiC_6 = 10.0 g ;

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

1. Water will undergo electrolysis to produce H_2 and O_2
2. Lithium reacts violently with water

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

Rate of reaction / discharge / flow of ions is lowered when temperature decreases.

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

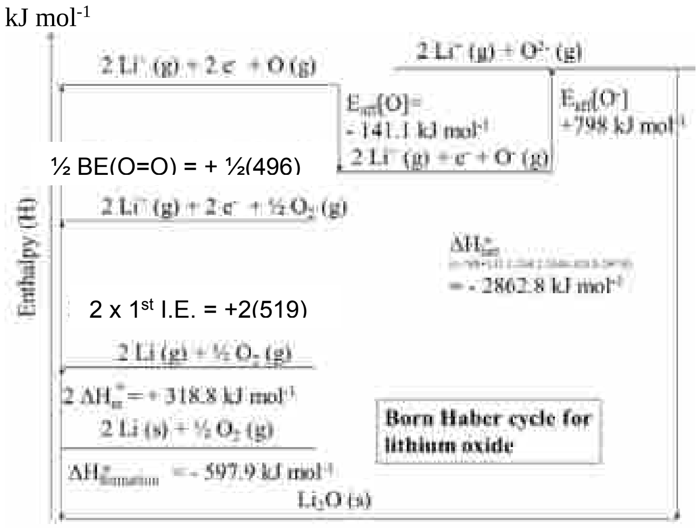
(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

$2Li^+(g) + O^{2-}(g) \rightarrow Li_2O(s)$

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

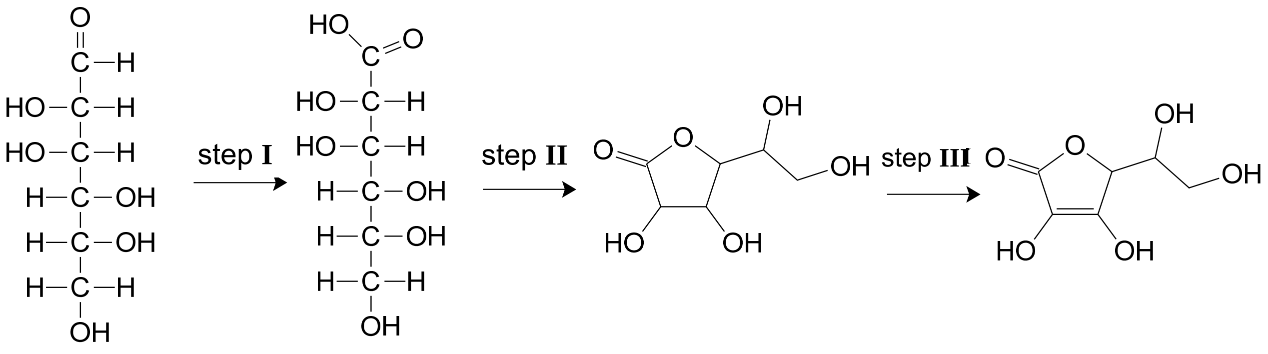


L.E. = -798 – (-141.1) – ½(496) – 2(519) – 2(159.4) + (-597.9)
= -2859.6 kJ mol^{-1}
= -2860 kJ mol^{-1} (3 sf)

[Total: 20]

3 Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



Glucose **Intermediate A** **Intermediate B** **Ascorbic Acid**

(a) State the functional groups present in intermediate **B**. [2]

Ester, 2^0 alcohol, 1^0alcohol

(b) State the reagent and conditions required for step **II**. [1]

Conc. H_2SO_4, heat

(c) State the type of reaction for steps **I** and **II**. [2]

Step I: oxidation

Step II: condensation / nucleophilic (acyl) substitution

(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

Enantiomerism.

total number of possible stereoisomers = $2^2 = 4$

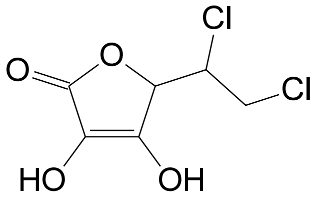
(e) Explain why ascorbic acid is water soluble. [2]

Energy released from the hydrogen bonding between ascorbic acid and water

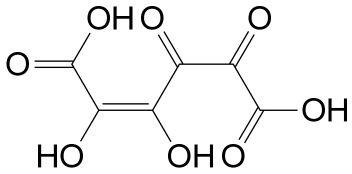
is sufficient to overcome the hydrogen bonding between ascorbic acid molecules and hydrogen bonding between water molecules. Hence, ascorbic acid is water soluble.

(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

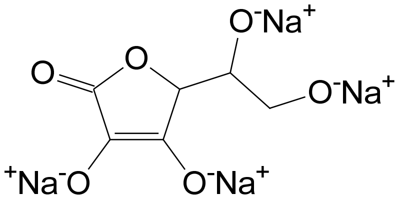
(i) PCl_5



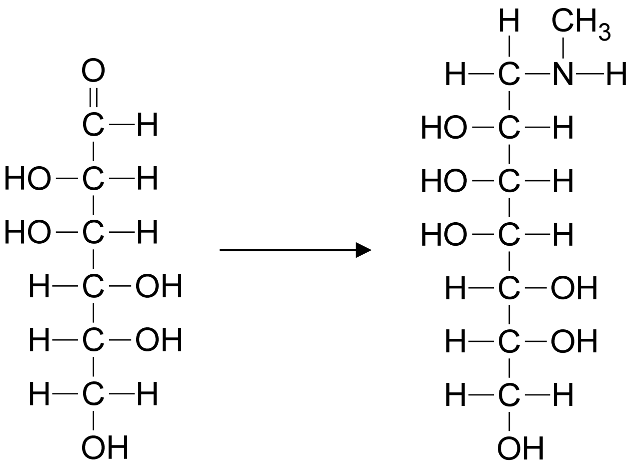
(ii) excess hot acidified $K_2Cr_2O_7$



(iii) Na(s)



(g) Compound **L** can be formed from glucose.



glucose **L**

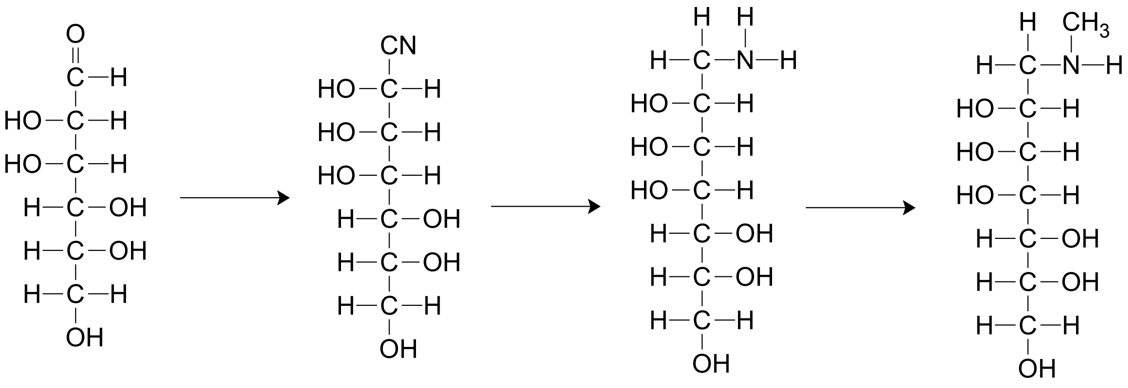
Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

Step1: HCN, trace amount of NaOH, cold

Step 2: $LiAlH_4$ in dry ether

Step 3: Limited CH_3Cl, heat



[Total: 17]

Section B

Answer **one** question from this section.

4 In the chlor-alkali industry, 19.8 g impure sample of NaC*l*(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

$Cl_2 + H_2 \rightarrow 2HCl$

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

Ultraviolet light provides sufficient energy to break the C*l*-C*l* bond to form the chlorine radicals for the reaction to start.

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas.[1]

Free radical substitution

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

Amount of hydrogen chloride = 1.8/36.5 = 0.0493 mol

Number of hydrogen chloride = 0.0493 x 6.02 x 10^{23} = 2.97 x 10^{22}

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

$HCl : Cl_2 : H_2 : NaCl$

2 : 1 : 1 : 2

Amount of sodium chloride in 50 cm^3 = 0.04931 mol

Amount of sodium chloride in 150 cm^3 = 0.04931 x 3 = 0.1479 mol

Mass of NaC*l* = 0.1479 x (23.0 + 35.5) = 8.654 g

% purity of NaC*l* = 8.654/19.8 x 100% = 43.7% (3 sf)

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

Dehydrating agent.

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

Both HC*l* and HBr have simple molecular structures. HBr has a larger and more polarisable electron cloud / larger number of electrons compared to HC*l*,

thus more energy is needed to overcome the stronger instantaneous dipole-induced dipole forces of attraction between HBr molecules. Hence, HC*l* has a lower boiling point than HBr.

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the rates of the forward and backward reactions have become equal and there is no net change in the concentrations of the products and reactants.

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

100-84 = 16% of each gas remained at equilibrium.

Since V and T are constant, $P \propto n$.

Equilibrium pressure of HC*l* = $NH_3 = \frac{0.16 \times 2.5}{2} = 0.2$ atm

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

$$= \frac{1}{(0.2)^2}$$

$$= 25 \text{ atm}^{-2}$$

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

I. By Le Chatelier's Principle, when temperature decreases, the system increases the temperature of the system by favouring the exothermic backward reaction. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases and the value of K_p decreases.

or

When temperature decreases at constant volume, total pressure decreases and partial pressure of the gases decrease. Hence K_p increases.

II. When the volume of the chamber increases, the pressure of the chamber decreases. By Le Chatelier's Principle, the system increases the pressure of the system by favouring the backward reaction to produce more gaseous particles. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases. Value of K_p does not change as temperature is constant.

or

When volume increases at constant temperature, total pressure decreases and partial pressure of the gases decrease. K_p does not change as temperature is constant.

III. When 2 atm of neon gas is inserted, the partial pressure of the gases and K_p remains unchanged
since neon is an inert noble gas and does not react with the other gases in the chamber.

[Total: 20]

5 **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(1) Rate = k $[CH_3COCH_3][H^+]$
(2) Rate = k $[CH_3COCH_3]^2$
(3) Rate = k $[H^+]^2$

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

Ecf from rate equation

(1) $[CH_3COCH_3]$ doubles, rate doubles **and** $[H^+]$ doubles, rate doubles
$[Br_2]$ doubles, no effect on rate

(2) $[CH_3COCH_3]$ doubles, rate quadruples
$[Br_2]$ or $[H^+]$ doubles, no effect on rate

(3) $[H^+]$ doubles, rate quadruples
$[CH_3COCH_3]$ or $[Br_2]$ doubles, no effect on rate

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

Constant half life

At least two sets of data to justify statement
e.g. [ ] from 1.6 to 0.8 mol dm^{-3} 10 min, 0.8 to 0.4 10min , 0.4 to 0.2 10min

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

Colour intensity / absorbance of aq bromine

(v) State and explain the role of acid in this overall reaction. [2]

Catalyst.

Increases rate of reaction by lowering activation energy.

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

Atomic radius increases down Group 17.

Down the group, the number of principal quantum shells increases and the distance between the valence electron and the nucleus increases / effective nuclear charge decreases as the increase in screening effect outweighs the effect of increasing nuclear charge.

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

	E^o / V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07

at least 3 values cited

Reactivity (oxidising power) increases in the order $Br_2 < Cl_2 < F_2$

The larger the E^o value, the more likely the halogen is reduced, and the stronger its oxidising power.

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

Displacement reaction. Add aqueous chlorine to a solution of bromide ions. The colourless bromide solution turns orange as chlorine has oxidised bromide to bromine.

$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$ $E^\theta_{cell} = +0.29V$ [equation not required]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

In comparison to other substances, the halogens have relatively large positive E^o values. This makes them more reactive as oxidising agents.

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

Order of Thermal Stability: HF(g) > HCl(g) > HBr(g)
at least 3 stated, or trend down the group

Down Group 17, bond energy of the H–X bond decreases. The weaker the H–X bond, the lower the amount of energy required to break it, and the less thermally stable the HX.

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

$O^{2-} + H_2O \rightarrow 2OH^-$

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

It is a simple covalent oxide and does not dissociate in water to give the oxide ion.

or

It is a non-metal oxide.

[Total: 20]

Apparatus

For each candidate

1	1 x 50 cm^3 burette 1 x stand and burette clamp 1 x small funnel for filling the burette 1 x 25 cm^3 pipette 1 x pipette filler 1 x 250 cm^3 beaker 2 x Styrofoam cup 1 x thermometer (–10 °C to 50 °C) methyl orange indicator indicator [place with bench reagents] 2 x 250 cm^3 conical flask
2	1 x test-tube holder (wooden instead of plastic) 1 x boiling-tube 1 x spatula 1 x Bunsen burner and lighter 1 x wooden tongs access to a balance weighing to 0.1 g or better
3	2 x test-tube 1 x boiling-tube 2 x dropping pipette 2 x spatula 1 x 50 cm^3 beaker 1 x glass rod wooden splints distilled water additional test-tubes and dropping pipettes should be available typical inorganic QA bench reagents: NaOH(aq), $BaNO_3$(aq), red litmus paper

Chemicals Required

	label	per candidate	identity	notes (hazards given in this column are for the raw materials)	reference
1	**FA 1**	230 cm^3	1.8 mol dm^{-3} potassium hydrogen carbonate, $KHCO_3$		2016 PU1 H2 Expt 7
	FA 2	130 cm^3	1.0 mol dm^{-3} of potassium hydroxide, KOH		
	FA 3	100 cm^3	1.6 mol dm^{-3} of hydrochloric acid, HC*l*		
2	**FA 4**	5 g	a mixture of $NaHCO_3$ and Na_2CO_3	Prepare a mixture containing 3 parts by mass $NaHCO_3$ and 1 part by mass anhydrous Na_2CO_3. The anhydrous Na_2CO_3 should be dried before use by heating in an oven at 110 °C and cooled in a desiccator. **Do not heat the $NaHCO_3$.** **Ensure the mixture is as uniform as possible.** Each candidate should be provided with 5 g of the mixture in a labelled, capped container.	2010 Nov 9701/34
3	**FA 5**	1 g	ammonium ferric sulfate, $NH_4Fe(SO_4)_2 \cdot 12H_2O$ / $NH_4[Fe(H_2O)_6](SO_4)_2 \cdot 6H_2O$	Pure solid, keep dry. Solid is chunky and should be broken up to smaller bits. Each candidate should be provided with 1-1.2 g of the mixture in a labelled, capped container.	–
	zinc powder	0.5 g (sufficient for about 2 spatulas)	zinc powder	Pure solid, keep dry.	
	barium nitrate	for QA (about 3 cm^3)	0.1 mol dm^{-3} barium nitrate	Dissolve 26.1g of $Ba(NO_3)_2$ in each dm^3 of solution.	

Class	Adm No

Candidate Name: ____________________

H

Shift
Laboratory

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical

10th Sept 2018

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Question	1	2	3	4	Total
Marks	26	13	6	10	55

1 Investigation of acid-base titrations involving sodium hydrogen carbonate

According to the Arrhenius theory of acids and bases, an acid produces H^+(aq) ions and a base produces OH^-(aq) ions. The reaction of these two ions to form water molecules is known as acid-base neutralisation.

The equation for this neutralisation reaction is given below, and strong acid–strong base reactions are known to have an enthalpy change of neutralisation (ΔH_{neu}) of approximately –57.1 kJ mol^{-1}.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neu} = -57.1 \text{ kJ mol}^{-1}$$

However, the ΔH_{neu} for weak acid–strong base reactions are known to differ. Sodium hydrogen carbonate, $NaHCO_3$, is an example of a weak acid.

FA 1 is 1.8 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$.
FA 2 is sodium hydroxide, NaOH, of concentration between 0.9 – 1.2 mol dm^{-3}.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

As the precise concentration of **FA 2** is unknown, determination of $\Delta H_{neu}'$ can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as $\Delta H_{neu}'$. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform a weak acid–strong base thermometric titration. The data from this titration will be used to determine:

- the titration value at equivalence point, V_{eq},
- the precise concentration of **FA 2**, [NaOH],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of neutralisation, $\Delta H_{neu}'$.

(a) Determination of V_{eq} and ΔH_{neu}' using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 1** have been added.

In an appropriate format in the space provided on the **next page**, prepare a table to record your results. Record all values of temperature, T, to 0.1°C, and each total volume of **FA 1** added.

Note: You should aim to perform each subsequent addition of **FA 1** quickly.

1. Fill a burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 2**. Record this temperature.
4. Add 2.00 cm^3 of **FA 1** from the burette to the **FA 2** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 1** added.
6. Repeat steps **4** and **5** until a total volume of 30.00 cm^3 of **FA 1** has been added.

Results

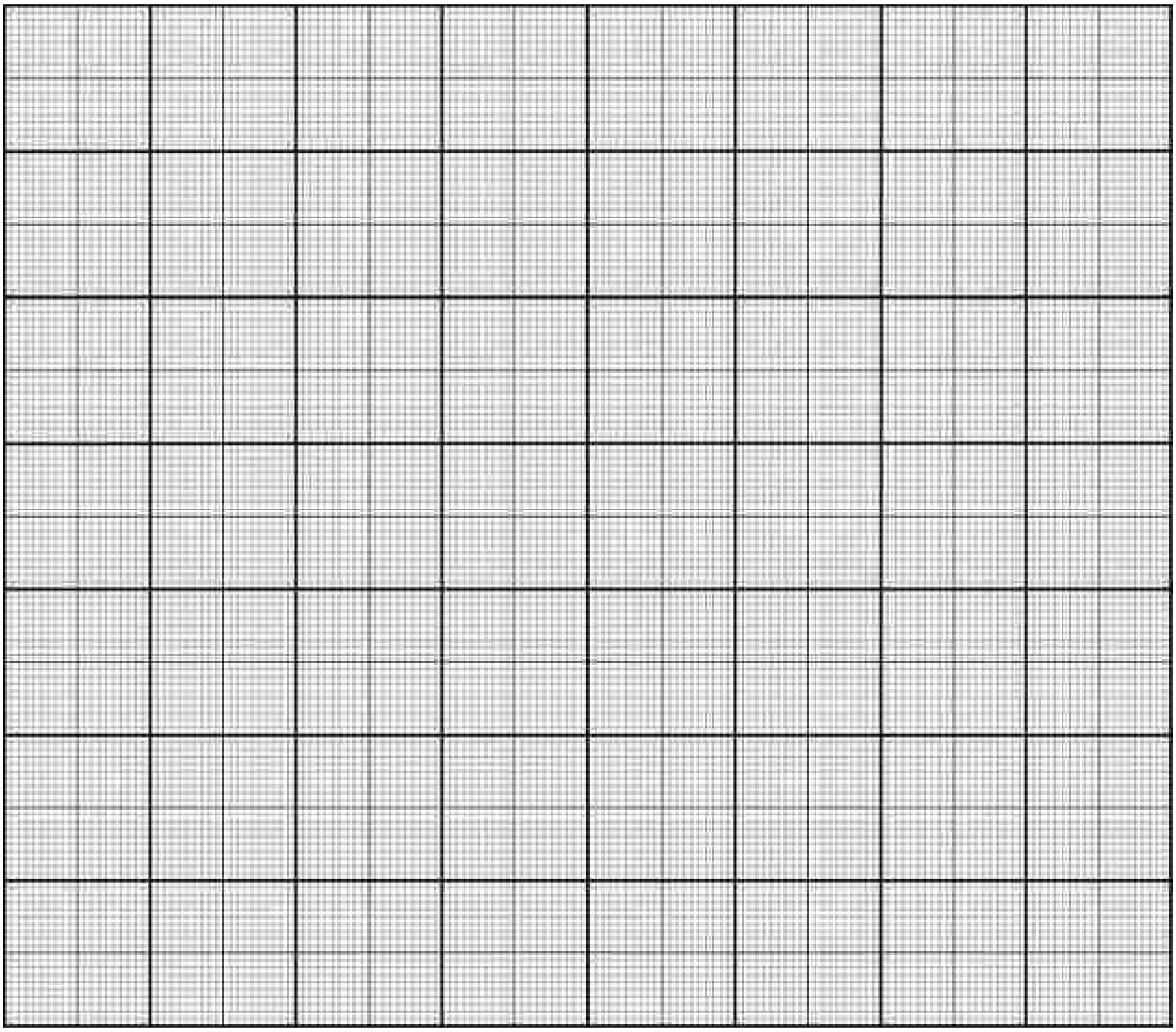
M1

M2

[2]

(i) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 1** added, on the *x*-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.5 °C greater than the maximum temperature recorded.



M3

M4

M5

Fig. 1.1

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points.

Extrapolate (extend) these two best-fit lines until they cross each other. [3]

(ii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

V_{eq} = ……………………… cm^3

M6

T_{max} = ………………………. °C

M7

ΔT_{max} = ………………………. °C

M8

[3]

(iii) Determine the concentration of NaOH, [NaOH], in **FA 2**.

M9

[NaOH] in **FA 2** = ………………………. [1]

(iv) Determine the enthalpy change of neutralisation, ΔH_{neu}'.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, *c*, of 4.18 J g^{-1} K^{-1}.

M10

M11

ΔH_{neu}' = ………………………. [3]

M12

(v) Comment on your value of ΔH_{neu}' obtained compared to ΔH_{neu} = –57.1 kJ mol^{-1}.

…………………………………………………………………………………………………

……………………………………………………………………………………………[1]

M13

(vi) From your graph in **Fig. 1.1**, explain the shape of your best-fit line **before** equivalence point.

…………………………………………………………………………………………………

……………………………………………………………………………………………[1]

M14

(b) **Determination of titration value at equivalence point, V_{eq}', using 'regular' titration**

FA 3 is hydrochloric acid, HC*l*, of unknown concentration.

Sodium hydrogen carbonate, $NaHCO_3$, is also able to act as a weak base. In **1(a)**, $NaHCO_3$ acts as the acid while in **1(b)**, $NaHCO_3$ is acts as the base.

For this experiment, you will titrate **FA 3** against **FA 1** to determine the titration value at equivalence point, V_{eq}', using methyl orange as the indicator.

(i) The use of thermometric titration in **1(a)** eliminated the need for an indicator as the equivalence point was located by observing temperature changes. 'Regular' acid-base titrations however, require the use of an indicator.

Explain why an indicator is required for 'regular' acid-base titrations (such as in **1(b)**).

....

....[1] **M15**

Titration of FA 3 against FA 1

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask.
3. Add 2 – 3 drops of methyl orange indicator into the same conical flask.
4. Run **FA 1** from the burette into this flask until end-point is reached.
5. Record your titration results in the space provided. Make certain that your recorded results show the precision of your working.
6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

M16

M17

M18

[3]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations (titre at equivalence point, V_{eq}'). Show clearly how you obtained this value.

V_{eq}' = ... cm^3 [1] **M19**

(iii) Determine the concentration of HC*l*, [HC*l*], in **FA 3**.

M20

[HC*l*] in **FA 3** = ..……………………… [1]

(iv) Suggest if the use of more drops of methyl orange indicator is appropriate for this titration.

……………………………………………………………………………………………………

M21

…………………………………………………………………………………………….... [1]

(c) Planning

The same 'regular' titration in **1(b)** can also be performed using an alternative method involving a pH meter, which is an instrument that can measure the pH of water-based solutions at any one instance of time.

Usage of a pH meter is simple as a digital pH reading will be displayed upon placing it into the solution of interest. However, it is known that most pH meters have to be calibrated (correlate to a standard) before each experiment to ensure the accuracy of measurements. For this titration, the standard chosen for calibration is usually a buffer solution of pH ≈ 4.0.

Plotting pH against titration volume, *V*, will give a pH curve that enables the determination of titration value at equivalence point, V_{eq}''.

Plan an experiment to determine the titration value at equivalence point, V_{eq}'', for the titration of **FA 3** against **FA 1** using a pH meter.

You may assume that you are provided with

- a pH meter,
- **FA 1** and **FA 3**,
- 1.0 mol dm^{-3} of ethanoic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$),
- 1.0 mol dm^{-3} of sodium ethanoate solution, $CH_3COO^-Na^+$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the preparation of a suitable standard solution for calibration of the pH meter,
- the procedure that you would follow,
- the measurements you would take,
- an outline of how you would use your results to determine V_{eq}''.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

For Examiners' Use

....[5]

M22

M23

M24

M25

M26

[Total: 26]

2 Determination of the major component in a solid mixture

Sodium hydrogen carbonate, $NaHCO_3$, also commonly known as *baking soda*, is a white crystalline solid primarily used in baking as a raising agent.

To increase the strength of *baking soda* as a raising agent, cream of tartar (a dry acid) is mixed with sodium hydrogen carbonate. This mixture is known as *baking powder*.

FA 4 is a sample of *baking powder*.

In this experiment, you will determine if sodium hydrogen carbonate is the major component, by mass, of the mixture **FA 4**.

(a) Thermal decomposition of *baking powder*

You may assume that the cream of tartar in **FA 4** is inert and does not decompose when heated.

1. Weigh and record the mass of an empty boiling-tube.
2. Transfer approximately 2 g of **FA 4** into the weighed boiling-tube. Reweigh and record the mass of the boiling-tube and **FA 4**.
3. Gently heat the **FA 4** in the boiling-tube for 2 minutes, then heat strongly for a further 2 minutes. **Take care not to lose any solid from the tube during heating.**
4. Warm the upper parts of the boiling-tube to evaporate any water that may have condensed while heating the solid.
5. Place the hot tube on the test-tube rack and leave to cool. **You are advised to continue with part 2(c) or to start another question while the tube cools.**
6. When cool, reweigh the boiling-tube and the residual solid.
7. Reheat, cool and reweigh the tube until decomposition is complete.

In an appropriate form in the space below, record all your balance readings, the mass of **FA 4** heated, the mass of residual solid, and the mass lost on heating.

Results

M27

M28

M29

M30

M31

[5]

The thermal decomposition of $NaHCO_3$ produces Na_2CO_3 and two gases at the temperature of decomposition, CO_2 and H_2O.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

(i) By finding the average M_r of the two gases produced, use your results in **(a)** calculate the **total** amount of gases lost upon complete decomposition of **FA 4**.

[A_r: C, 12.0; H, 1.0; Na, 23.0; O,16.0]

total amount of gases lost = …………………… mol [1]

M32

(ii) Taking into account the mole ratio of gases in the decomposition equation given, calculate the amount of CO_2(g) lost upon complete decomposition of **FA 4**.

M33

amount of CO_2(g) lost = …………………… mol [1]

(iii) Hence, calculate the mass of $NaHCO_3$ in the sample of **FA 4** heated.

M34

mass of $NaHCO_3$ = ……………………… g [1]

(iv) By means of calculation or otherwise, justify if $NaHCO_3$ is the major component, by mass, of **FA 4**.

…………………………………………………………………………………………………

…………………………………………………………………………………………….. [1]

M35

(b) **Do not carry out your suggestions.**

Suggest two ways in which you could show that cream of tartar does not decompose on heating.

(i) ....

....

(ii) **M36**

.... [2] **M37**

(c) A student is asked to weigh, with maximum precision, a solid.

Three balances are available.

- Balance A, reading to 1 decimal place,
- Balance B, reading to 2 decimal places,
- Balance C, reading to 3 decimal places.

Balance readings can be treated similarly to burette readings.

For example, the smallest division on a burette is 0.1 cm^3.
The maximum error in a single burette reading is ±0.05 cm^3.

Complete the following table.

balance	maximum error for a single balance reading /g	maximum % error when weighing:
A	±	8.0 g of solid =
B	±	4.00 g of solid =
C	±	0.400 g of solid =

M38

M39

[2]

[Total: 13]

3 Qualitative Analysis of an unknown double salt

Double salts are salts that contain more than one cation or anion, and are synthesised by crystallising a solution containing the different ions.

FA 5 is a double salt which contains **two cations** and **one anion**.

Empty out the **FA 5** provided into a 50 cm^3 beaker. To this beaker, add 10 cm^3 of water and stir to dissolve as much of the solid as possible.

This solution will be referred to as '**FA 5** solution'.

(a) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

tests		observations
1.	Add about 1 cm depth of **FA 5** solution to a boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	
2.	Add about 2 cm depth of **FA 5** solution to a test-tube. To this test-tube, add about half a spatula of zinc powder. Observe the mixture until no further changes are seen.	
3.	Add about 1 cm depth of **FA 5** solution into a test-tube. To this test-tube, add barium nitrate dropwise.	

M40

M41

M42

M43

[4]

(b) Based on your observations in **3(a)**, deduce the identities of the ions present in **FA 5**.

M44

cation 1: ……….. cation 2: ……….. anion: ……….. [1]

(c) Hence, suggest a possible chemical formula of the double salt **FA 5**.

M45

chemical formula of **FA 5**: …………………… [1]

[Total: 6]

4 Planning

The condenser is an apparatus frequently used in organic synthesis. It comprises of concentric glass tubes, an inner one through which hot gases can pass through, and an outer one through which a cool fluid can pass through.

Use of the condenser is required for the organic synthesis of aldehydes and carboxylic acids from alcohols. The product of the reaction between potassium dichromate, $K_2Cr_2O_7$, and primary alcohols can either be an aldehyde or a carboxylic acid depending on how the condenser is orientated.

(a) Some organic synthesis procedures require *heating under reflux*.

Explain the role of the condenser in such procedures.

…… **M46**

………………………………………………………………………………………………………. [2] **M47**

(b) Plan an experiment to synthesise **propanal** (boiling point: 20 °C) from **propan-1-ol** (boiling point: 97 °C).

You may assume that you are provided with

- propan-1-ol, $CH_3CH_2CH_2OH$,
- potassium dichromate, $K_2Cr_2O_7$,
- commonly used organic chemicals
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include

- the reactants and conditions that you would use,
- a well-labelled diagram of the set-up that you would use,
- the procedure that you would follow and the safety precautions taken,
- how you would check the purity of your product.

……

……

……

……

For Examiners' Use

....

....

....

....

.... **M48**

.... **M49**

.... **M50**

.... **M51**

....[4]

(c) Suggest appropriate modifications to your plan to synthesise **propanoic acid** (boiling point: 141 °C) from propan-1-ol instead of propanal.

You may wish to use diagrams to complement your answer.

....

.... **M52**

.... **M53**

....[2]

(d) Give an explanation for any **two** modifications you have made in **(c)**.

....

.... **M54**

.... **M55**

....[2]

[Total: 10]

End of Paper 4

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Class	Adm No

Candidate Name: ____________________

Shift
Laboratory

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical **10th Sept 2018**

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Question	1	2	3	4	Total
Marks	26	13	6	10	55

This question paper consists of **18** printed pages and **0** blank pages.

1 Investigation of acid-base titrations involving sodium hydrogen carbonate

According to the Arrhenius theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions. The reaction of these two ions to form water molecules is known as acid-base neutralisation.

The equation for this neutralisation reaction is given below, and strong acid–strong base reactions are known to have an enthalpy change of neutralisation (ΔH_{neu}) of approximately –57.1 kJ mol^{-1}.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neu} = -57.1 \text{ kJ mol}^{-1}$$

However, the ΔH_{neu} for weak acid–strong base reactions are known to differ. Sodium hydrogen carbonate, $NaHCO_3$, is an example of a weak acid.

FA 1 is 1.8 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$.
FA 2 is sodium hydroxide, NaOH, of concentration between 0.9 – 1.2 mol dm^{-3}.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

As the precise concentration of **FA 2** is unknown, determination of $\Delta H_{neu}'$ can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as $\Delta H_{neu}'$. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform a weak acid–strong base thermometric titration. The data from this titration will be used to determine:

- the titration value at equivalence point, V_{eq},
- the precise concentration of **FA 2**, [NaOH],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of neutralisation, $\Delta H_{neu}'$.

(a) Determination of V_{eq} and ΔH_{neu}' using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 1** have been added.

In an appropriate format in the space provided on the **next page**, prepare a table to record your results. Record all values of temperature, T, to 0.1°C, and each total volume of **FA 1** added.

Note: You should aim to perform each subsequent addition of **FA 1** quickly.

1. Fill a burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 2**. Record this temperature.
4. Add 2.00 cm^3 of **FA 1** from the burette to the **FA 2** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 1** added.
6. Repeat steps **4** and **5** until a total volume of 30.00 cm^3 of **FA 1** has been added.

Results

Vol of FA 1 added / cm^3	T / °C
0.00	29.4
2.00	30.4
4.00	31.5
6.00	32.2
8.00	32.9
10.00	33.4
12.00	34.0
14.00	33.9
16.00	33.6
18.00	33.3
20.00	33.0
22.00	32.8
24.00	32.6
26.00	32.4
28.00	32.3
30.00	32.2

M1
all 16 readings of vol and T tabulated with correct headers and units

M2
T to ±0.1 °C

[2]

(i) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 1** added, on the *x*-axis on the grid in **Fig. 1.1**.

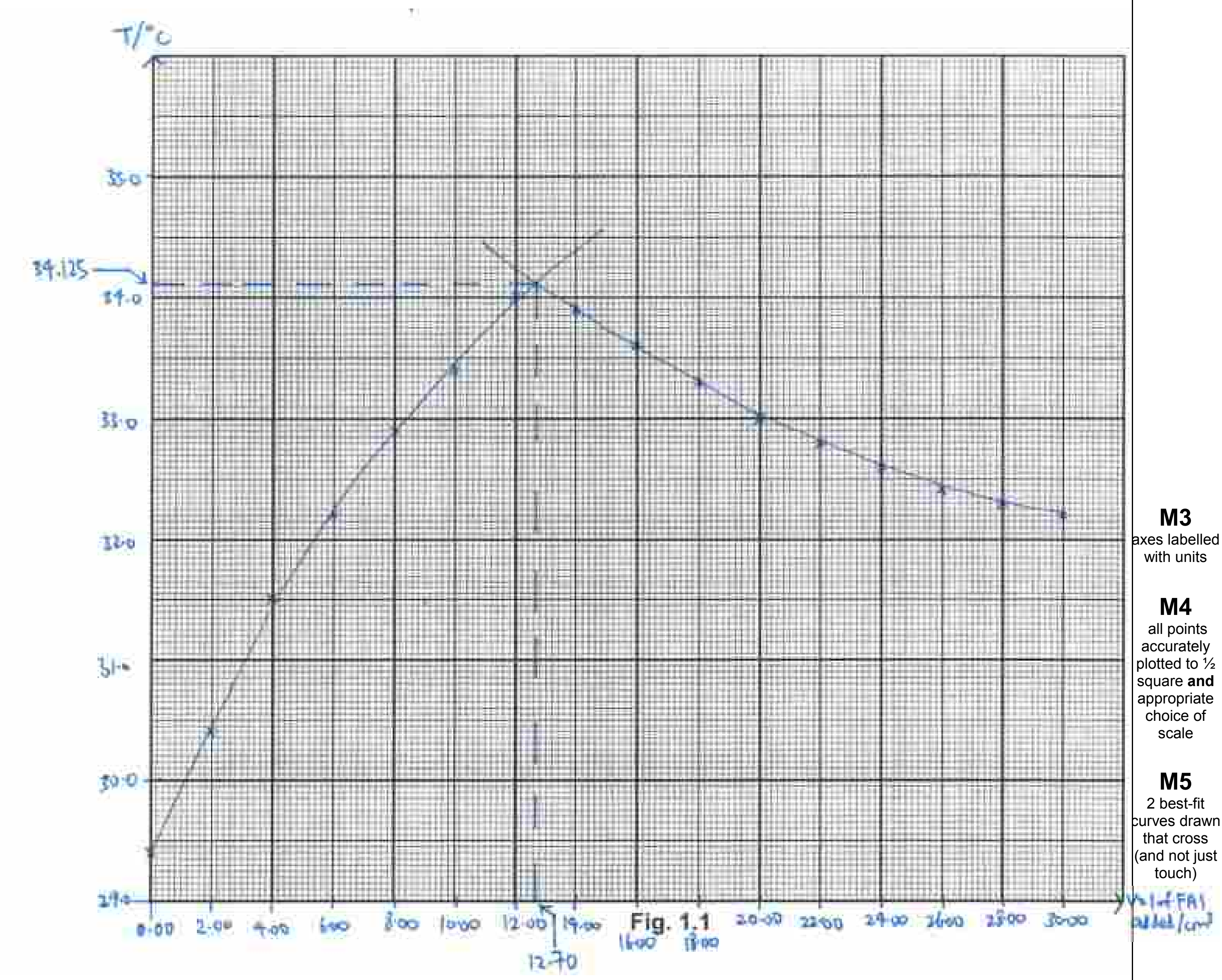


Fig. 1.1

M3
axes labelled with units

M4
all points accurately plotted to ½ square **and** appropriate choice of scale

M5
2 best-fit curves drawn that cross (and not just touch)

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points.

Extrapolate (extend) these two best-fit lines until they cross each other. [3]

For Examiners' Use

(ii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

M6 both construction lines shown on graph

ΔT_{max} = 34.125 – 29.4 = 4.7 °C

V_{eq} = 12.70 cm^3

M7 both readings correct to ½ square

T_{max} = 34.1 °C

M8 accuracy of ΔT_{max}, student value ≤0.6 from supervisor's value

ΔT_{max} = 4.7 °C

[3]

(iii) Determine the concentration of NaOH, [NaOH], in **FA 2**.

Amount of $NaHCO_3$ reacted = 1.8 x 12.70 x 10^{-3} = 0.02286 mol

[NaOH] = $\frac{0.2286}{25.0\times10^{-3}}$ = 0.914 mol dm^{-3}

M9

[NaOH] in **FA 2** = 0.914 mol dm^{-3} [1]

(iv) Determine the enthalpy change of neutralisation, ΔH_{neu}'.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, *c*, of 4.18 J g^{-1} K^{-1}.

m = 25.0 + 12.70 = 37.7 g

M10 correct mass used

q = mcΔT = (37.7)(4.18)(4.7) = 740.6 J

ΔH = $-\frac{q}{n_{LR}} = -\frac{740.6}{0.02286}$ = –32.4 kJ mol^{-1} (3 sf)

M11 correct calculations, do not mark for sign

ΔH_{neu}' = –32.4 kJ mol^{-1} [3]

M12 all calc in (a) to 3 or 4 sf and have correct units and correct sign for ΔH

(v) Comment on your value of ΔH_{neu}' obtained compared to ΔH_{neu} = –57.1 kJ mol^{-1}.

The value of ΔH_{neu}' obtained is less exothermic, as some of the heat energy released was used to completely dissociate the weak acid $NaHCO_3$. [1]

M13 comparison unambiguous (do not accept "value is more/less")

(vi) From your graph in **Fig. 1.1**, explain the shape of your best-fit line **before** equivalence point.

The curve is increasing with a decreasing gradient as the exothermic reaction releases the same amount of heat energy for each addition of FA 1, which causes a smaller temperature rise as the mass of the mixture increases. [1]

M14

For Examiners' Use

(b) **Determination of titration value at equivalence point, V_{eq}', using 'regular' titration**

FA 3 is hydrochloric acid, HC*l*, of unknown concentration.

Sodium hydrogen carbonate, $NaHCO_3$, is also able to act as a weak base. In **1(a)**, $NaHCO_3$ acts as the acid while in **1(b)**, $NaHCO_3$ is acts as the base.

For this experiment, you will titrate **FA 3** against **FA 1** to determine the titration value at equivalence point, V_{eq}', using methyl orange as the indicator.

(i) The use of thermometric titration in **1(a)** eliminated the need for an indicator as the equivalence point was located by observing temperature changes. 'Regular' acid-base titrations however, require the use of an indicator.

Explain why an indicator is required for 'regular' acid-base titrations (such as in **1(b)**).

M15

To give a visible observation that corresponds to completion of reaction. [1]

Titration of FA 3 against FA 1

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask.
3. Add 2 – 3 drops of methyl orange indicator into the same conical flask.
4. Run **FA 1** from the burette into this flask until end-point is reached.
5. Record your titration results in the space provided. Make certain that your recorded results show the precision of your working.
6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

	1	2	3
Initial burette reading / cm^3	0.00	6.70	
Final burette reading / cm^3	21.60	28.20	
Volume of **FA 1** added / cm^3	21.60	21.50	
	✓	✓	

[3]

M16 correct headers and units

M17 volumes to ±0.05 cm^3 and correct subtraction

M18 accuracy, student value ≤0.6 from supervisor's value

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations (titre at equivalence point, V_{eq}'). Show clearly how you obtained this value.

$$V_{eq}' = \frac{21.60+21.50}{2} = 21.55 \text{ cm}^3$$

M19

V_{eq}' = 21.55 cm^3 [1]

(iii) Determine the concentration of HC*l*, [HC*l*], in **FA 3**.

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

Amount of $NaHCO_3$ = 1.8 x 21.55 x 10^{-3} = 0.03879 mol
= Amount of HC*l*

$[HCl] = \frac{0.03879}{25.0\times10^{-3}}$ = 1.55 mol dm^{-3} (3 sf)

[HC*l*] in **FA 3** = 1.55 mol dm^{-3} [1]

M20

(iv) Suggest if the use of more drops of methyl orange indicator is appropriate for this titration.

No, it is not appropriate as indicators are weak acids or bases and will affect the pH of the solution. [1]

M21

(c) Planning

The same 'regular' titration in **1(b)** can also be performed using an alternative method involving a pH meter, which is an instrument that can measure the pH of water-based solutions at any one instance of time.

Usage of a pH meter is simple as a digital pH reading will be displayed upon placing it into the solution of interest. However, it is known that most pH meters have to be calibrated (correlate to a standard) before each experiment to ensure the accuracy of measurements. For this titration, the standard chosen for calibration is usually a buffer solution of pH ≈ 4.0.

Plotting pH against titration volume, V, will give a pH curve that enables the determination of titration value at equivalence point, V_{eq}''.

Plan an experiment to determine the titration value at equivalence point, V_{eq}'', for the titration of **FA 3** against **FA 1** using a pH meter.

You may assume that you are provided with

- a pH meter,
- **FA 1** and **FA 3**,
- 1.0 mol dm^{-3} of ethanoic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$),
- 1.0 mol dm^{-3} of sodium ethanoate solution, $CH_3COO^-Na^+$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the preparation of a suitable standard solution for calibration of the pH meter,
- the procedure that you would follow,
- the measurements you would take,
- an outline of how you would use your results to determine V_{eq}''.

$$\text{pH} = \text{p}K_a + \lg\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$4.0 = -\lg(1.8 \times 10^{-5}) + \lg\frac{n_{CH_3COO^-}/V}{n_{CH_3COOH}/V}$$

$$\frac{n_{CH_3COO^-}}{n_{CH_3COOH}} = 0.18$$

Since concentrations of ethanoic acid and sodium ethanoate are the same, n ∝ V.
∴ for 18 cm^3 of ethanoic acid used, use 100 cm^3 of sodium ethanoate.

M22
correct choice of volumes to obtain pH between 3.9-4.1

Preparation of standard solution and calibration of pH meter

1. Using two separate burettes, add 18.00 cm^3 of 1.0 mol dm^{-3} ethanoic acid and 100.00 cm^3 of 1.0 mol dm^{-3} sodium ethanoate to a 250 cm^3 volumetric flask.
2. Top up the volumetric flask to the mark with distilled water, stopper, invert and shake until homogeneous.
3. Pour out some of the standard solution into a 50 cm^3 beaker and place the pH meter probe into it. Calibrate the pH meter to read 4.0.
4. Wash the pH meter probe with distilled water before usage in experiment.

M23
correct procedures for preparation of std sol

M24
calibration of pH meter, including washing of probe

Procedures for titration and measurements taken

5. Carry out the same 'regular' titration as in **1(b)**, replacing the methyl orange indicator with the pH meter probe.
6. Record the pH measurements at 1 cm^3 intervals until 25.00 cm^3 of **FA 3** has been added.

M25
correct modification and measurements taken

Determining V_{eq}''

7. Plot a graph of pH against volume of **FA 3** added. The vertical region corresponds to the equivalence point.
8. Draw a vertical construction line from this vertical region to the x-axis to determine the value of V_{eq}''.

M26
correct usage of plot / sketch of plot to determine V_{eq}''

[5]

[Total: 26]

2 Determination of the major component in a solid mixture

Sodium hydrogen carbonate, $NaHCO_3$, also commonly known as *baking soda*, is a white crystalline solid primarily used in baking as a raising agent.

To increase the strength of *baking soda* as a raising agent, cream of tartar (a dry acid) is mixed with sodium hydrogen carbonate. This mixture is known as *baking powder*.

FA 4 is a sample of *baking powder*.

In this experiment, you will determine if sodium hydrogen carbonate is the major component, by mass, of the mixture **FA 4**.

(a) Thermal decomposition of *baking powder*

You may assume that the cream of tartar in **FA 4** is inert and does not decompose when heated.

1. Weigh and record the mass of an empty boiling-tube.
2. Transfer approximately 2 g of **FA 4** into the weighed boiling-tube. Reweigh and record the mass of the boiling-tube and **FA 4**.
3. Gently heat the **FA 4** in the boiling-tube for 2 minutes, then heat strongly for a further 2 minutes. **Take care not to lose any solid from the tube during heating.**
4. Warm the upper parts of the boiling-tube to evaporate any water that may have condensed while heating the solid.
5. Place the hot tube on the test-tube rack and leave to cool. **You are advised to continue with part 2(c) or to start another question while the tube cools.**
6. When cool, reweigh the boiling-tube and the residual solid.
7. Reheat, cool and reweigh the tube until decomposition is complete.

In an appropriate form in the space below, record all your balance readings, the mass of **FA 4** heated, the mass of residual solid, and the mass lost on heating.

M27
at least 4 balance readings and 1 calculation (accept tare)

Results

Mass of empty boiling-tube / g	30.03
Mass of boiling-tube + **FA 4** / g	32.14
Mass of **FA 4** heated / g	2.11
Mass of boiling-tube + residual solid (1) / g	31.55
Mass of boiling-tube + residual solid (2) / g	31.53
Mass of residual solid / g	1.50
Mass lost / g	0.61

[5]

M28
correct headers (at most 1 missing) and units and all mass readings to 2dp

M29
correct subtractions (all three)

M30
evidence of constant mass (within 0.05g)

M31
accuracy of ratio (mass heated / mass of residue) ≤0.2 from supervisor's value

-

The thermal decomposition of $NaHCO_3$ produces Na_2CO_3 and two gases at the temperature of decomposition, CO_2 and H_2O.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

(i) By finding the average M_r of the two gases produced, use your results in **(a)** calculate the **total** amount of gases lost upon complete decomposition of **FA 4**.

[A_r: C, 12.0; H, 1.0; Na, 23.0; O,16.0]

average $M_r = \frac{[12.0+2(16.0)]+[2(1.0)+16.0]}{2} = 31.0$

total amount of gases lost $= \frac{0.61}{31.0} = 0.0197$ mol (3 sf)

M32

total amount of gases lost = 0.0197 mol [1]

(ii) Taking into account the mole ratio of gases in the decomposition equation given, calculate the amount of CO_2(g) lost upon complete decomposition of **FA 4**.

amount of CO_2 lost = 0.0197 / 2

= 0.00984 mol (3 sf)

M33

amount of CO_2(g) lost = 0.00984 mol [1]

(iii) Hence, calculate the mass of $NaHCO_3$ in the sample of **FA 4** heated.

amount of $NaHCO_3$ decomposed = 2 x 0.009838

= 0.01967 mol

mass of $NaHCO_3$ = 0.01967 x [23.0 + 1.0 + 12.0 + 3(16.0)]

= 1.65 g (3 sf)

M34

mass of $NaHCO_3$ = 1.65 g [1]

(iv) By means of calculation or otherwise, justify if $NaHCO_3$ is the major component, by mass, of **FA 4**.

% by mass of $NaHCO_3$ = $\frac{1.652}{2.11} \times 100$

= 78.3 % (3 sf)

$NaHCO_3$ is the major component as it makes up more than 50% of the sample.

M35

[1]

(b) **Do not carry out your suggestions.**

For Examiners' Use

Suggest two ways in which you could show that cream of tartar does not decompose on heating.

(i) There is no change in mass when cream of tartar is heated. **M36**

(ii) There is no change in the volume of a gas syringe connected to the boiling-tube when cream of tartar is heated. [2]

M37
award 1m if both mass and volume stated but no mention of absence of change

(c) A student is asked to weigh, with maximum precision, a solid.

Three balances are available.

- Balance A, reading to 1 decimal place,
- Balance B, reading to 2 decimal places,
- Balance C, reading to 3 decimal places.

> Balance readings can be treated similarly to burette readings.
>
> For example, the smallest division on a burette is 0.1 cm^3.
> The maximum error in a single burette reading is ±0.05 cm^3.

Complete the following table.

balance	maximum error for a single balance reading / g	maximum % error when weighing:
A	± 0.05	8.0 g of solid = $\frac{2\times0.05}{8.0}\times 100$ = 1.25%
B	± 0.005	4.00 g of solid = $\frac{2\times0.005}{4.00}\times 100$ = 0.250%
C	± 0.0005	0.400 g of solid = $\frac{2\times0.0005}{0.400}\times 100$ = 0.250%

M38 correct max error

M39 ecf only if (i) max error given is x2 (ii) max errors are incorrect by factor 10

[2]

[Total: 13]

For Examiners' Use

3 Qualitative Analysis of an unknown double salt

Double salts are salts that contain more than one cation or anion, and are synthesised by crystallising a solution containing the different ions.

FA 5 is a double salt which contains **two cations** and **one anion**.

Empty out the **FA 5** provided into a 50 cm^3 beaker. To this beaker, add 10 cm^3 of water and stir to dissolve as much of the solid as possible.

This solution will be referred to as '**FA 5** solution'.

(a) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

tests		observations	
1.	Add about 1 cm depth of **FA 5** solution to a boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	Red-brown ppt forms, insoluble in excess NaOH(aq). Gas produced turns red litmus paper blue.	**M40** **M41**
2.	Add about 2 cm depth of **FA 5** solution to a test-tube. To this test-tube, add about half a spatula of zinc powder. Observe the mixture until no further changes are seen.	Yellow solution decolourises / turns pale green. *accept: gas produced extinguishes lighted splint with a 'pop' sound*	**M42**
3.	Add about 1 cm depth of **FA 5** solution into a test-tube. To this test-tube, add barium nitrate dropwise.	White ppt forms, insoluble in excess HNO_3(aq). *allow omission of solubility in strong acid, but do not award M44 if sulfite is proposed as anion*	**M43**

[4]

(b) Based on your observations in **3(a)**, deduce the identities of the ions present in **FA 5**.

cation 1: Fe^{3+} cation 2: NH_4^+ anion: SO_4^{2-} [1]

M44
do not accept H+ as it was not in original salt

(c) Hence, suggest a possible chemical formula of the double salt **FA 5**.

chemical formula of **FA 5**: $\underline{Fe(NH_4)(SO_4)_2}$ [1]

M45
ecf only if H^+ instead of NH_4^+ and others correct

[Total: 6]

4 Planning

The condenser is an apparatus frequently used in organic synthesis. It comprises of concentric glass tubes, an inner one through which hot gases can pass through, and an outer one through which a cool fluid can pass through.

Use of the condenser is required for the organic synthesis of aldehydes and carboxylic acids from alcohols. The product of the reaction between potassium dichromate, $K_2Cr_2O_7$, and primary alcohols can either be an aldehyde or a carboxylic acid depending on how the condenser is orientated.

(a) Some organic synthesis procedures require *heating under reflux*.

Explain the role of the condenser in such procedures. **M46**

To prevent the loss of volatile / low boiling point organic reagents **M47**
by condensing hot vapour back into the reaction flask. [2]

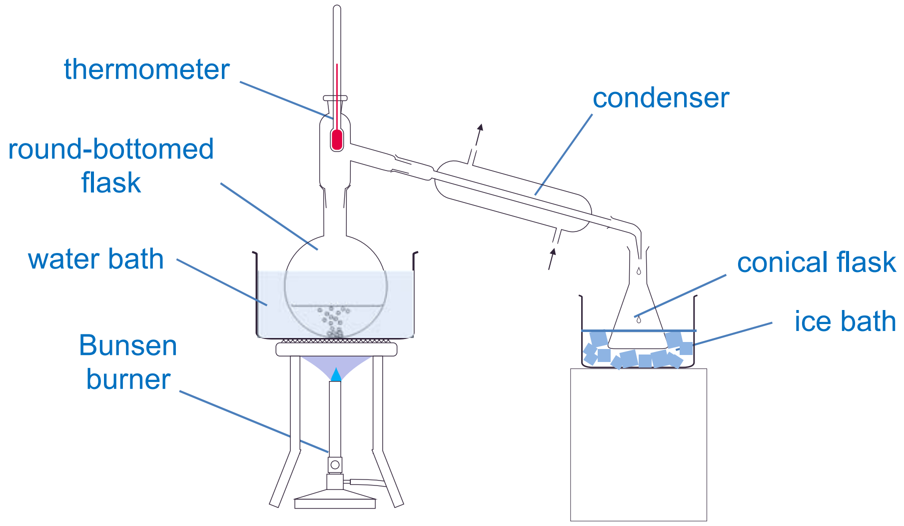
(b) Plan an experiment to synthesise **propanal** (boiling point: 20 °C) from **propan-1-ol** (boiling point: 97 °C).

You may assume that you are provided with

- propan-1-ol, $CH_3CH_2CH_2OH$,
- potassium dichromate, $K_2Cr_2O_7$,
- commonly used organic chemicals
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include

- the reactants and conditions that you would use,
- a well-labelled diagram of the set-up that you would use,
- the procedure that you would follow and the safety precautions taken,
- how you would check the purity of your product.



M48 correct distillation setup with labels (accept hot plate, do **not** mark for ice bath)

Reactants: $CH_3CH_2CH_2OH$, $K_2Cr_2O_7$, dilute H_2SO_4
Conditions: heat with distillation

M49 correct R&C (must have dilute acid added), do **not** mark for precalc of quantities

Procedure

1. To the 100 cm^3 round-bottomed flask, add $CH_3CH_2CH_2OH$, $K_2Cr_2O_7$, and dilute H_2SO_4.
2. Set up the apparatus as shown in the diagram above in the fume cupboard / while wearing gloves / safety goggles.
3. Start the flow of water through the condenser and turn on the Bunsen burner to start the reaction. Maintain the water bath at approximately 40 °C. The temperature reading should remain constant at approximately 20 °C until all the propanal synthesised has boiled off.
4. When the temperature starts to increase further / no further distillate is collected in the conical flask, turn off the Bunsen burner to stop the reaction.
5. Test the purity of the propanal distillate by means of thin layer chromatography. A pure sample would only contain one spot after chromatography.

[4]

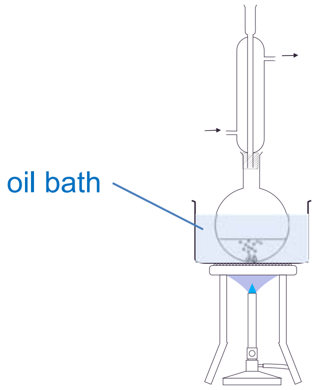
For Examiners' Use

M50
any 1 safety procedure written

M51
use of TLC to test for purity of product

(c) Suggest appropriate modifications to your plan to synthesise **propanoic acid** (boiling point: 141 °C) from propan-1-ol instead of propanal.

You may wish to use diagrams to complement your answer.



Use a reflux setup instead of a distillation setup by orientating the condenser vertically.

Use a separatory funnel to extract out the propanoic acid product from the reaction mixture before testing its purity.

[2]

M52 diagram *or* mention of orientating condenser vertically. do not accept simply changing to $KMnO_4$

M53 mentions method to extract product from reaction mixture

(d) Give an explanation for any **two** modifications you have made in **(c)**.

Reflux: To ensure that the volatile propanal does not escape the reaction flask and can continue to further be oxidised by $K_2Cr_2O_7$ into propanoic acid.

Separatory funnel: Unlike distillation, the propanoic acid product is mixed with residual reagents (such as propan-1-ol, $K_2Cr_2O_7$ and water) and has to be purified.

M54

M55

$KMnO_4$: Stronger oxidising agent used to ensure that all the propan-1-ol is fully oxidised into propanoic acid.

Heat longer: To ensure that all the propan-1-ol is fully oxidised into propanoic acid.

Oil bath: To allow for heating at higher temperatures close to boiling point of propan-1-ol as water will boil.

[2]

[Total: 10]

End of Paper 4

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt. insoluble in excess	green ppt. insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Test for gases

ions	*reaction*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Class	Reg Number
17	

Name ______________________________

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9729/01

Paper 1 **21 September 2018**
1 hour

Additional Material: *Data Booklet*
OMS

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces provided at the top of this page.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the use of OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **16** printed pages (including this cover page)

Answer all questions.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 Zinc ethanoate, $(CH_3CO_2)_2Zn$ (M_r = 183.4) may be taken as a dietary supplement to prevent zinc deficiency.

What is the total number of ions present in a 5 cm^3 solution of aqueous zinc ethanoate given that the solution has a concentration of 10.64 g dm^{-3}?

A 1.7×10^{19} **B** 5.2×10^{20} **C** 3.5×10^{22} **D** 1.0×10^{23}

2 Gases given off during volcanic eruptions include H_2S and CS_2.

A 40 cm^3 gaseous sample of H_2S and CS_2, present in a 3 : 1 ratio respectively, was analysed by combustion using 100 cm^3 of oxygen. After measuring the volume of gas remaining, the product was treated with an excess of aqueous sodium hydroxide and the volume of gas measured again.

Any sulfur present is converted to SO_2 after combustion.

Given that all volume measurements were made under room conditions, what were the measured volumes?

	volume of gaseous mixture after burning / cm^3	volume of gaseous mixture after adding NaOH (aq) / cm^3
A	60	0
B	60	50
C	85	25
D	85	75

3 Consider the following reactions:

Reaction 1 $3\,F_2 + 4\,NH_3 \longrightarrow 3\,NH_4F + NF_3$

Reaction 2 $3\,Cl_2 + 8\,NH_3 \longrightarrow 6\,NH_4Cl + N_2$

Which of the following correctly shows the increasing order of reducing strength of the three species, Cl_2, F_2 and NH_3?

A $F_2 < Cl_2 < NH_3$

B $Cl_2 < F_2 < NH_3$

C $NH_3 < F_2 < Cl_2$

D $NH_3 < Cl_2 < F_2$

4 The successive ionization energies (I.E.) of two elements, **L** and **M**, are shown below:

IE / kJ mol^{-1}	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**	**8th**
L	1000	2252	3357	4556	7004	8496	27107	31719
M	578	1817	2745	11577	14842	18379	23326	27465

What is the likely formula of the compound formed when **L** and **M** reacts together?

A L_3M_2

B L_2M_3

C LM_3

D L_3M

5 Gaseous particle **X** has a charge of +1 and a proton number, n.

Gaseous particle **Y** has a proton number of (n+1) and is isoelectronic with **X**.

Which of the following statements correctly describes **X** and **Y**?

A **X** and **Y** are isotopes.

B **X** and **Y** atoms have same full electronic configurations.

C **Y** has a charge of +1 and same charge density as that of **X**.

D **Y** has a charge of +2 and smaller ionic radius than **X**.

6 Which of the following pairs of molecules satisfies both of the following conditions?

- Only one molecule is polar.
- The second molecule has a larger bond angle than the first molecule.

	First molecule	**Second molecule**
A	CO_2	F_2O
B	NF_3	SO_3
C	SF_6	XeF_4
D	SO_2	NO_2

7 Which of the following statements about A*l* is correct?

1 It has high melting point due to strong attraction between the delocalised electrons and residual cations.

2 It has stronger metallic bonding than Na.

3 It has high electrical conductivity due to the ability of its ions to carry the current.

A **1**, **2** and **3**

B **1** and **2** only

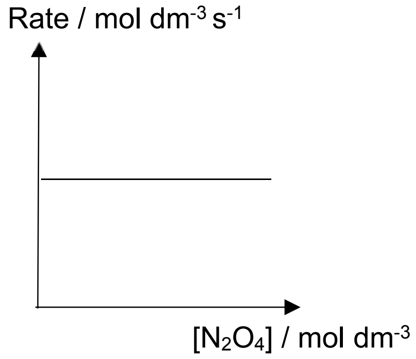
C **1** only

D **2** and **3** only

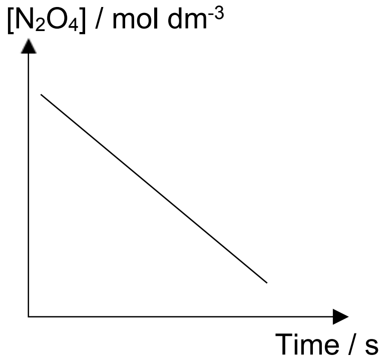
8 The decomposition of dinitrogen tetroxide, N_2O_4 is found to be first order with respect to the concentration of N_2O_4.

Which of the following graphs confirms the above finding?

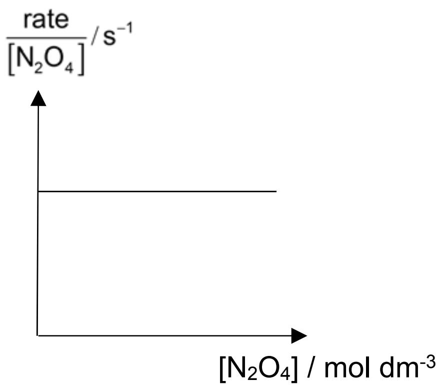
A



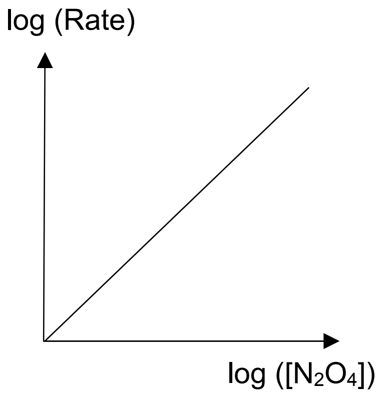
B



C



D



9 The hydrolysis of the anticancer drug *cis–platin* in water follows a first–order kinetics with a rate constant of 0.09 h^{-1} at 25 °C.

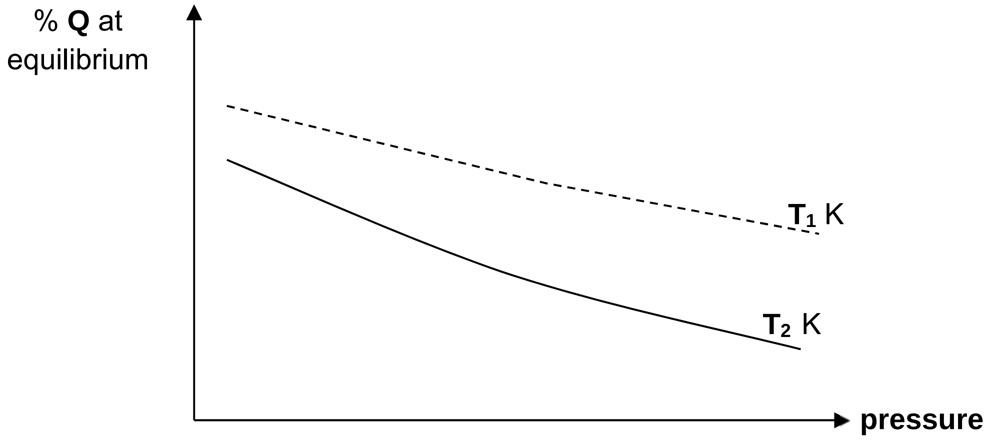
How long will it take for the concentration of a freshly prepared aqueous solution of *cis–platin* to decrease to 18% of its original concentration?

A 7.7 h **B** 15.4 h

C 19.0 h **D** 42.8 h

10 The graph below shows the variation of the percentage of **Q** present at equilibrium, with temperature and pressure.

$$3O_2(g) + 4NH_3(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1248 \text{ kJ mol}^{-1}$$



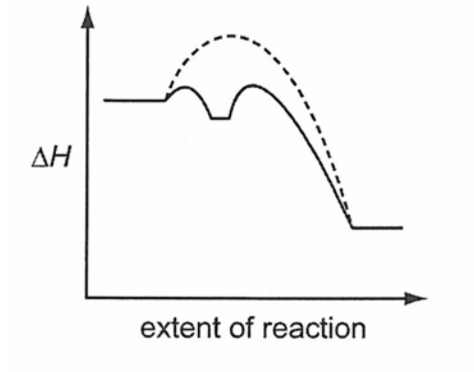
Which of the following systems could **Q** represent?

	Q	Temperature
A	O_2	$\mathbf{T_1 > T_2}$
B	NH_3	$\mathbf{T_2 > T_1}$
C	N_2	$\mathbf{T_1 > T_2}$
D	H_2O	$\mathbf{T_2 > T_1}$

11 The uncatalysed reaction between SO_2 and O_2 is slow.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

This reaction is speeded up in the presence of a suitable catalyst. The reaction profile diagram shows the energy changes involved during the catalyzed and uncatalysed reaction.



The uncatalysed reaction is shown as a dashed line.

Which of the following statements is true?

1 It involves a homogenous catalyst.

2 It involves a stable intermediate.

3 Both the activation energies of the forward and backward reaction are lowered in the presence of the catalyst.

A	**1** only	**B**	**3** only
C	**2** and **3** only	**D**	**1**, **2** and **3**

12 Water dissociates into ions according to the following equilibrium.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H^\ominus = +57 \text{ kJ mol}^{-1} \text{ at } 25°C$$

Which of the following is **incorrect** as temperature is increased to 50°C?

A The dissociation constant of water, K_w, increases

B pH of water remains at 7

C $[H^+]$ increases.

D $[H^+] = [OH^-]$

13 Which of the following pair of solutions will form an alkaline buffer solution that **best** resists pH changes when a small amount of acid or base is added.

A 10 cm^3 of 0.1 mol dm^{-3} NaOH and 20 cm^3 of 0.2 mol dm^{-3} $NH_4^+Cl^-$

B 25 cm^3 of 0.10 mol dm^{-3} NaOH added to 50 cm^3 0.10 mol dm^{-3} $CH_3CO_2^-Na^+$

C 10 cm^3 of 1 mol dm^{-3} H_2SO_4 and 20 cm^3 of 1 mol dm^{-3} $CH_3CH_2NH_2$

D 50 cm^3 of 0.05 mol dm^{-3} NaOH added to 50 cm^3 0.10 mol dm^{-3} $CH_3NH_3^+Cl^-$

14 The table shows some data of two acid–base indicators.

indicator	**approximate pH range of colour change**	**colour change**	
		acid	**alkali**
bromophenol–blue	3.0 – 4.6	yellow	purple
phenol–red	6.8 – 8.5	yellow	red

Which conclusion can be drawn about a solution when it turns bromophenol–blue purple and phenol–red yellow?

A The solution is weakly acidic.

B The solution is strongly acidic.

C The solution is weakly alkaline.

D The solution is strongly alkaline.

15 Below is one of the propagation steps in the reaction between CH_4 and Cl_2.

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl \qquad \Delta H^\ominus_r = ?\ \text{kJ mol}^{-1}$$

Given the standard enthalpy changes of formation for CH_4, CH_3 radical and HC*l* are provided, which other enthalpy value is required to calculate $\Delta H^\ominus_r$?

A Standard enthalpy change of atomisation of chlorine

B Standard enthalpy change of formation of HC*l* (aq)

C Standard enthalpy change of formation of Cl_2 gas

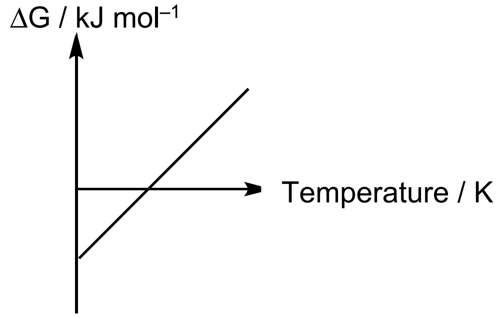
D Bond dissociation value for C–H bond

16 The combustion of gaseous hydrogen is a strongly exothermic process with equation as follows:

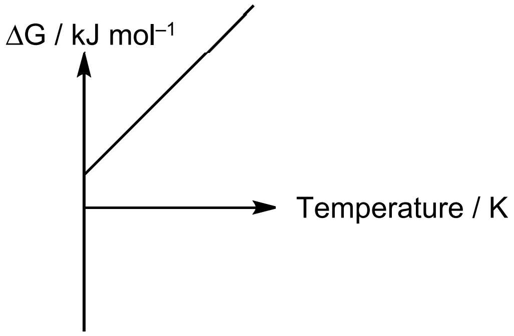
$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g)$$

Which of the following graphs best illustrates how ΔG varies with temperature?

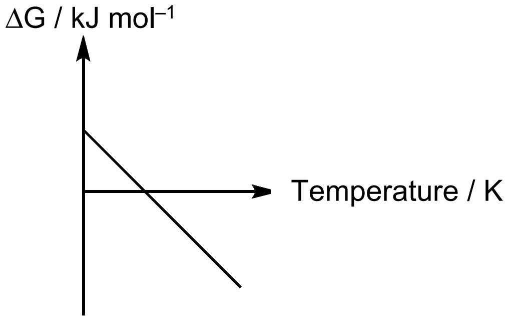
A



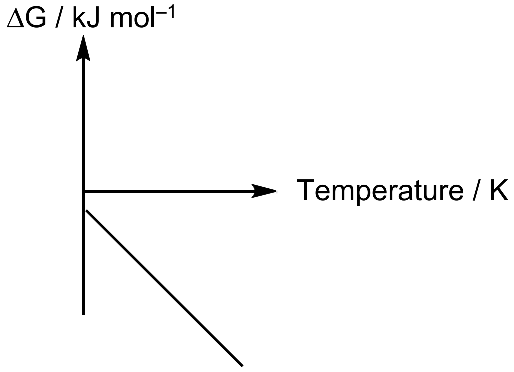
B



C



D



17 A student wanted to predict the solubility of barium chloride using calculation based on the following values.

Enthalpy change	**Numerical value / kJ mol^{-1}**
Lattice energy of barium chloride	2053
$\Delta H^{\ominus}_{hydration}$ for Ba^{2+}	1309
$\Delta H^{\ominus}_{hydration}$ for Cl^{-}	378

The student wrongly concluded that "barium chloride has $\Delta H^{\ominus}_{solution}$ of 366 kJ mol^{-1}, hence it is insoluble."

Which of the following should be the correct conclusion?

A Barium chloride is insoluble. However, $\Delta H^{\ominus}_{solution}$ should be +366 kJ mol^{-1}, the positive sign needs to be shown.

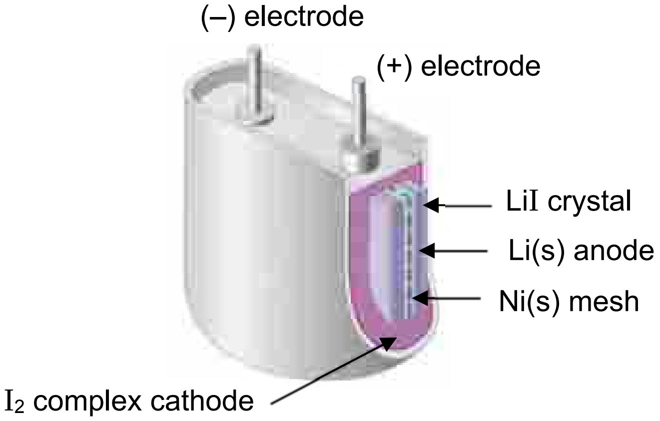
B Barium chloride is insoluble. However, $\Delta H^{\ominus}_{solution}$ should be +12 kJ mol^{-1}.

C $\Delta H^{\ominus}_{solution}$ should be –366 kJ mol^{-1}, hence barium chloride is soluble

D $\Delta H^{\ominus}_{solution}$ should be –12 kJ mol^{-1}, hence barium chloride is soluble

18 *Use of the Data Booklet is relevant for this question.*

Artificial pace makers are used to regulate the heartbeat of cardiac patients. The device is powered by a water–free lithium iodide battery as shown below.



Which of the following statements about the lithium iodide battery is correct?

A The I_2 complex cathode carries a negative charge.

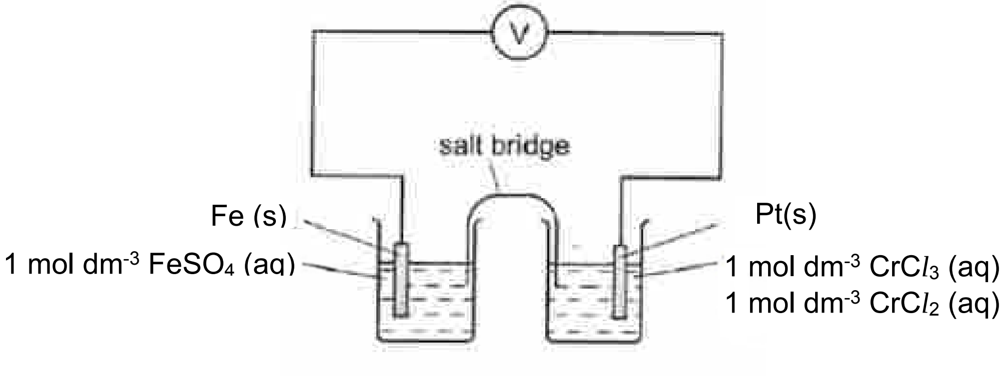
B The cell potential of the lithium iodide battery has a value of +2.50 V.

C The Ni mesh provides a medium for Li^+ ions to flow from Li (s) to I_2 complex.

D The pacemaker will last for less than 3 years if it contains 5 g of reactive Li(s) and operates at 0.8 mA.

19 *Use of the Data Booklet is relevant for this question.*

The following electrochemical cell was set up.



Which change to the half–cells could result in a cell potential of 0.00 V?

1 increase [$FeSO_4$]

2 decrease [$CrCl_2$]

3 decrease [$CrCl_3$]

4 increase the surface area of the Fe electrode

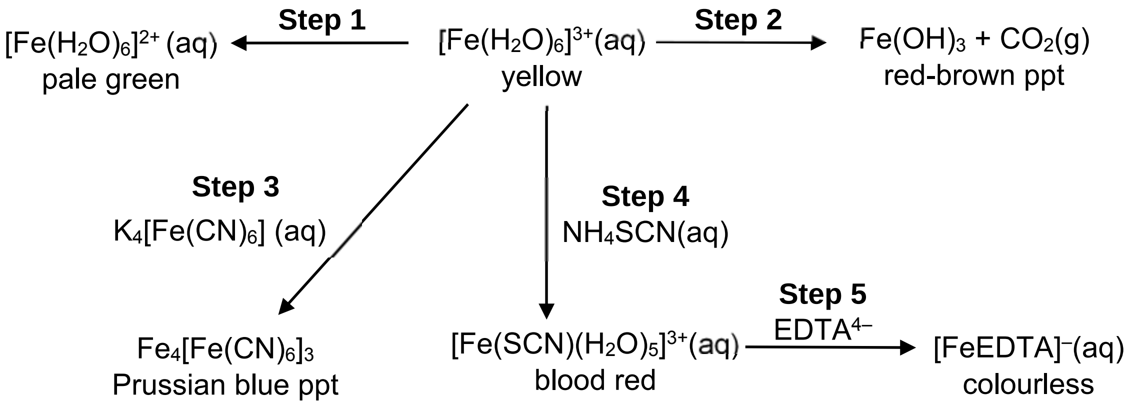
A **1** and **2** only

B **1** and **3** only

C **1**, **2** and **3** only

D **3** and **4** only

20 The following shows a reaction scheme involving aqueous Fe(III) ions.



Which of the following statements regarding the reaction scheme shown above is correct?

A Step **1** and Step **4** are ligand exchange reactions.

B The increasing order of ligand strength is $H_2O < CN^- < SCN^- < EDTA^{4-}$.

C NaOH (aq) can be used as a reagent in Step **2**.

D Both Fe(II) and Fe(III) ions exist in the $Fe_4[Fe(CN)_6]_3$.

21 *Use of the Data Booklet is relevant for this question.*

Vanadyl (IV) sulfate, $VOSO_4(H_2O)_5$, is a hygroscopic blue solid and is a common source of vanadium in the laboratory.

Which of the following statements is true for an aqueous solution of $VOSO_4$?

1 VO^{2+}(aq) can serve as a homogeneous catalyst in the reaction between iodide ions and peroxodisulfate ions.

2 The solution appears blue as the d–orbitals are split by the presence of the sulfate ions.

3 Zn metal can reduce VO^{2+}(aq) to V^{2+}(aq).

A **1** and **2** only

B **1** and **3** only

C **2** and **3** only

D **1**, **2** and **3**

22 The properties of the oxides of four elements in Period 3, **E, F, G** and **H** are given below.

1 The oxide of **E** is amphoteric.

2 The oxide of **F** dissolves in water to form a strongly alkaline solution.

3 The oxide of **G** reacts with dilute sodium hydroxide at room temperature.

4 The oxide of **H** is insoluble in water but is soluble in concentrated sodium hydroxide.

Which of the following shows the correct sequence of the four elements in order of increasing proton number?

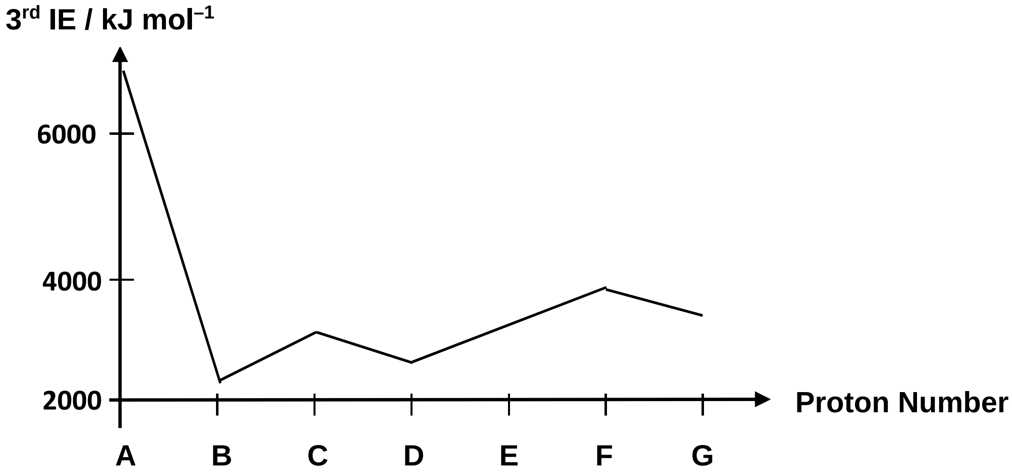
A **F, E, G, H**

B **F, E, H, G**

C **G, F, E, H**

D **G, F, H, E**

23 The diagram shows the third ionisation energy of seven consecutive elements, **A** to **G** in the Periodic Table. Their atomic numbers lie between 3 and 20.



Which of the following statements is correct?

1 Element **A** is strongly oxidising.

2 Oxide of **B** is soluble in water.

3 Oxide of **C** is acidic.

4 Element **E** forms a hydride of general formula H_2**E**.

A **1** and **4** only

B **1, 3** and **4** only

C **2, 3** and **4** only

D **3** and **4** only

24 A student conducted the following experiment using the setup below and recorded his observations.

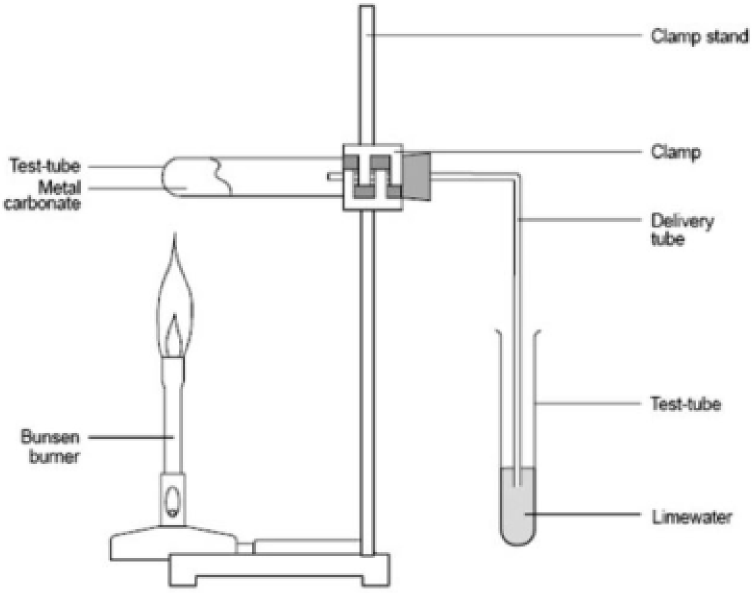


Fig 1: Setup of experiment

Carbonate	***Colour before heating***	***Colour after heating***	***Observations***
$CaCO_3$	white	white	white ppt formed with limewater
$BaCO_3$	white	white	white ppt formed with limewater
$CuCO_3$	green	black	white ppt formed with limewater

Using the above data and relevant data from the *Data Booklet*, which of the following statements concerning the metal carbonates is correct?

1 Lattice energy of calcium carbonate is more exothermic than that of barium carbonate.

2 Carbon dioxide is produced at a lower temperature from calcium carbonate than from barium carbonate.

3 The oxide from the copper carbonate is formed more readily than that from calcium carbonate.

A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** only

25 3–ethylpentane can react with bromine in the presence of sunlight to give a mixture of three possible monosubstituted halogenoalkanes, 1–bromo–3–ethylpentane, 2–bromo–3–ethylpentane and 3–bromo–3–ethylpentane.

Given the relative rates of abstracting H atoms are:

Type of H atom	Primary	Secondary	Tertiary
Relative rate of abstraction	1	4	6

What is the expected ratio of 1–bromo–3–ethylpentane, 2–bromo–3–ethylpentane and 3–bromo–3–ethylpentane formed?

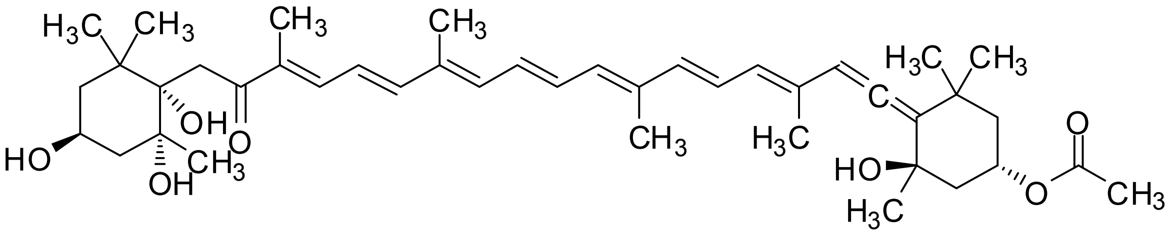
A 1 : 1 : 1

B 1 : 4 : 6

C 3 : 8 : 2

D 9 : 6 : 1

26 *Fucoxanthin* is a carotenoid which is found as an accessory pigment in the chloroplasts of brown algae and most other heterokonts, giving them a brown or olive–green colour.



Fucoxanthin

How many organic compounds will be formed when *Fucoxanthin* reacts with hot acidified $KMnO_4$?

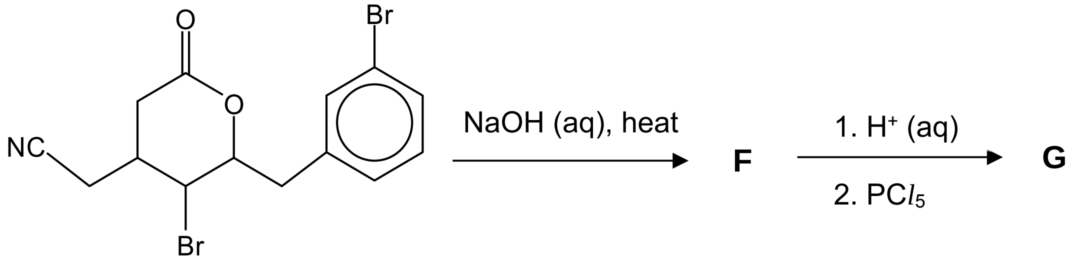
A 3

B 4

C 5

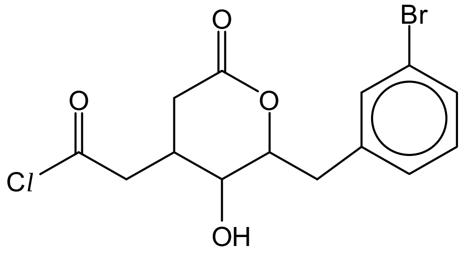
D 6

27 The reaction scheme below shows the formation of compound **G:**

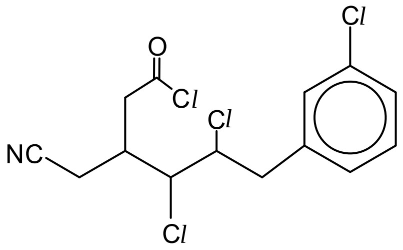


What is the structure of compound **G**?

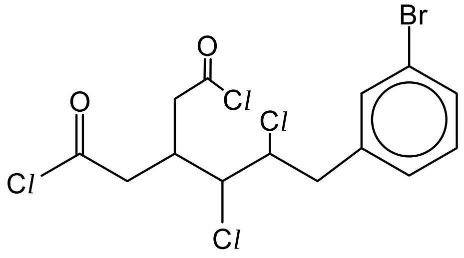
A



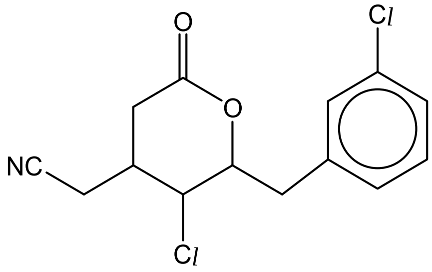
B



C

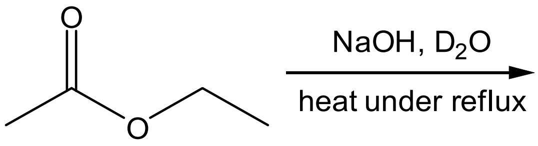


D

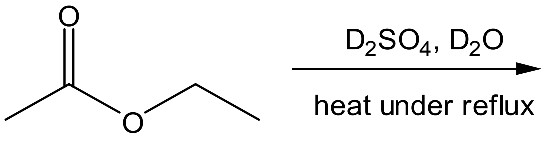


28 Which of the following reactions will **not** incorporate deuterium (D) into any of the organic products formed? (D= $^{2}_{1}$H, an isotope of hydrogen)

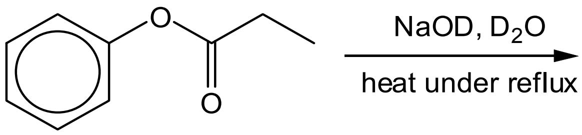
A

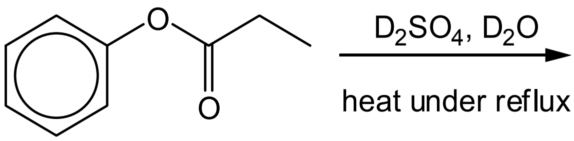


B



C



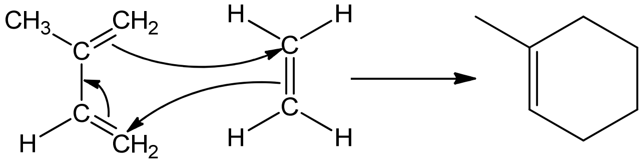
D 

D_2SO_4, D_2O

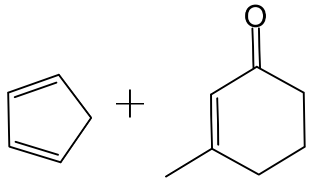
heat under reflux

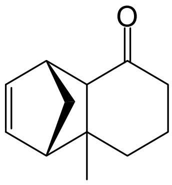
29 *Limonene* can be obtained via a series of organic reactions involving the *Diels–Alder* reaction.

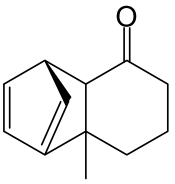
The *Diels–Alder* reaction involves a concerted cycloaddition mechanism.

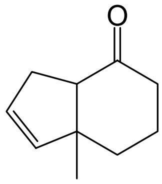


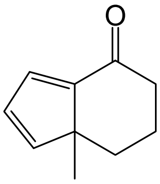
What would be the product form when the following diene and alkene reacts in a 1:1 ratio?



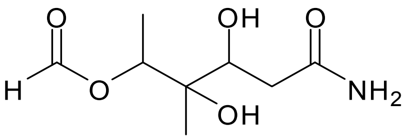
A 

B 

C 

D 

30 Which of the following statements is true of compound **A**, shown below?



Compound **A**

1 Upon reaction with hot acidified $KMnO_4$, an organic compound containing 5 oxygen atoms is formed.

2 Compound **A** has a total of 6 stereoisomers.

3 On reacting with $LiAlH_4$, one molecule with one –OH group is formed together with another molecule that has 4 –OH groups.

A	**1** and **2** only	**B**	**2** and **3** only
C	**1** only	**D**	**3** only

END OF PAPER

Class	Reg Number
17	

Name Suggested Solutions

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry 9729/01

Paper 1 **21 September 2018**
1 hour

Additional Material: *Data Booklet*
OMS

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces provided at the top of this page.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the use of OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **13** printed pages (including this cover page)

Qn	Ans	Qn	Ans	Qn	Ans
1	B	11	D	21	B
2	C	12	B	22	B
3	A	13	D	23	D
4	A	14	A	24	A
5	D	15	A	25	C
6	B	16	A	26	B
7	B	17	D	27	C
8	C	18	D	28	C
9	C	19	B	29	A
10	D	20	D	30	C

1 **Answer: B**

$[(CH_3CO_2)_2Zn] = \frac{10.64}{183.4} = 0.0580$ mol dm^{-3}

Amount of $(CH_3CO_2)_2Zn = \frac{5}{1000} \times 0.0580 = 2.90 \times 10^{-4}$ mol

$(CH_3CO_2)_2Zn \equiv 2CH_3CO_2^- \equiv Zn^{2+}$

Total amount of ions = $3 \times 2.90 \times 10^{-4} = 8.70 \times 10^{-4}$ mol

Total number of ions = $8.70 \times 10^{-4} \times 6.02 \times 10^{23}$ = 5.2×10^{20} ions

2 **Answer: C**

Explanation:

volume of H_2S = $\frac{3}{4} \times 40$ = 30 cm^3 and volume of CS_2 = $\frac{1}{4} \times 40$ = 10 cm^3

Combustion equations:

$H_2S\ (g) + \frac{3}{2}O_2\ (g) \rightarrow SO_2\ (g) + H_2O\ (l)$ and
30 cm^3 45 cm^3 30 cm^3

$CS_2\ (g) + 3O_2\ (g) \rightarrow CO_2\ (g) + 2SO_2$
10 cm^3 30 cm^3 10 cm^3 20 cm^3
Total volume of SO_2 formed = 30 + 20 = **50 cm^3**
Volume of CO_2 formed = **10 cm^3**
volume of O_2 remaining = 100 – (45 + 30) = **25 cm^3**
Volume of gaseous mixture after burning = 50 + 10 + 25 = **85 cm^3**
Since CO_2 and SO_2 are acidic gases, they will be removed by NaOH (aq)
therefore, **Volume of gaseous mixture after adding NaOH (aq)** = 85 – 60 = **25 cm^3**

3 **Answer: A**

By considering change in oxidation number of element:

Reaction 1 $3F_2 + 4NH_3 \longrightarrow 3NH_4F + NF_3$

$\quad 0 \quad -3 \qquad\qquad -1 \quad +3$

NH_3 acts as reducing agent hence it is a stronger reducing agent than F_2.

Reaction 2 $3Cl_2 + 8NH_3 \longrightarrow 6NH_4Cl + N_2$

$\quad 0 \quad -3 \qquad\qquad -1 \quad 0$

NH_3 acts as reducing agent hence it is a stronger reducing agent than Cl_2.

F_2 oxidises N to a larger extent (from –3 in NH_3 to +3 in NF_3) as compared to Cl_2 (from –3 in NH_3 to 0 in N_2). **F_2 is a stronger oxidising agent and hence a weaker reducing agent as compared to Cl_2.**

NH_3 is the **strongest reducing agent** whereas **F_2** is the **weakest reducing agent**.

4 **Answer: A**

For element **L**: biggest increase between 6th and 7th ionisation energy.
(Largest difference in IE between 6th and 7th I.E.)
7th electron is removed from the inner quantum shell which is closer to the nucleus.
Thus the element has 6 valence electrons.
Element **L** belongs to **Group 16.**

For element **M**: biggest increase between 3rd and 4th ionisation energy.
(Largest difference in IE between 3rd and 4th I.E.)
4th electron is removed from the inner quantum shell which is closer to the nucleus.
Thus the element has 3 valence electrons.
Element M belongs to **Group 13**.

So the likely formula of the compound formed is **L_3M_2.**

5 **Answer: D**

	X	**Y**
Proton number, n	n	n + 1
No of electrons	n + 1	n
Charge	+1	+2

Option A is wrong
X and **Y** have different number of protons. Hence they can’t be isotopes.

Option B is wrong
X and **Y** have different number of protons. **X** atom has n electrons while **Y** has (n + 1) electrons. Hence **X** and **Y** atoms have different full electronic configurations.

Option C is wrong
Y has charge of +2 while it has same number of electrons as that of **X**. Hence, **Y** has smaller ionic radius. This leads to higher charge density.

Option D is correct
Y has charge of +2 while it has same number of electrons as that of **X**. Hence, **Y** has smaller ionic radius.

6 **Answer: B**

	First molecule	**Second molecule**
A	CO_2 *(2 bond pairs)* Shape: Linear Polarity: Non–polar Bond angle: 180°	F_2O *(2 bond pairs, 2 lone pair)* Shape: Bent Polarity: Polar Bond angle: 104.5°
B	NF_3 *(3 bond pairs, 1 lone pair)* Shape: Trigonal Pyramidal Polarity: Polarity: Polar Bond angle: 107°	SO_3 *(3 bond pairs, 0 lone pair)* Shape: Trigonal Planar Polarity: Non–polar Bond angle: 120°
C	SF_6 *(6 bond pairs, 0 lone pair)* Shape: Octahedral Polarity: Non–polar Bond angle: 90°	XeF_4 *(4 bond pairs, 2 lone pair)* Shape: Square Planar Polarity: Non–polar Bond angle: 90°
D	SO_2 *(2 bond pairs, 1 lone pair)* Shape: Bent Polarity: Polar Bond angle: 118°	NO_2 *(2 bond pairs, 1 lone electron)* Shape: Bent Polarity: Polar Bond angle: > 118 °
	Lone pair – bond pair repulsion > 1 unpaired electron – bond pair repulsion.	

7 **Answer: B**

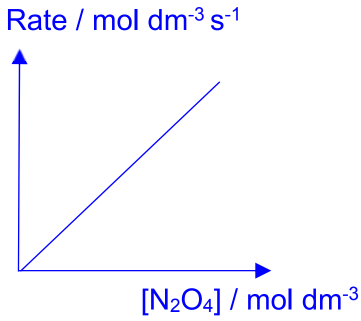
Statement **1** is correct as melting involves overcoming of the strong metallic bonds arising from the strong electrostatic forces attraction between the delocalised electrons and the residual metallic cations.

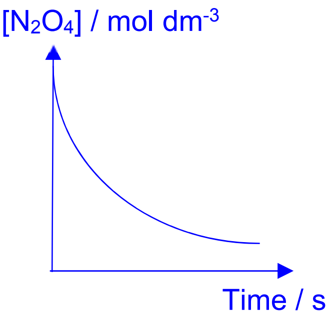
Statement **2** is correct as A*l* contribute more delocalised electrons than Na and this contributes to stronger metallic bonds.

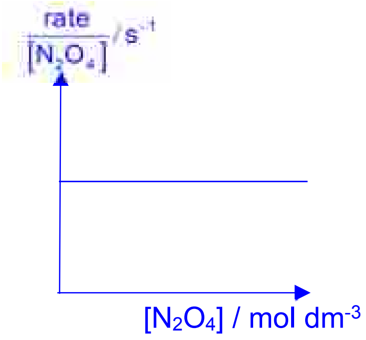
Statement **3** is incorrect as electrical conductivity in metals is due to the delocalised electrons, not mobile ions.

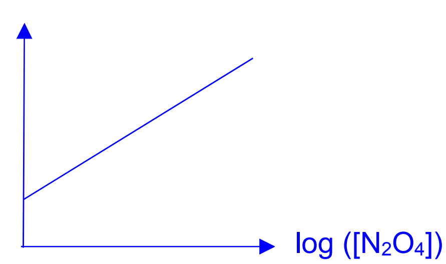
8 **Answer: C**

The graphs for first order reaction are shown as below:









9 **Answer: C**

$$\text{Half–life, } t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{\ln 2}{0.09} = 7.7 \text{ h}$$

$$\frac{C_t}{C_o} = \left(\frac{1}{2}\right)^n$$

$$\frac{18}{100} = \left(\frac{1}{2}\right)^n \Rightarrow n = 2.47$$

Time taken = half–life × n = 7.7 × n = **19.0 h**

10 **Answer: D**

$3O_2(g) + 4NH_3(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1248 \text{ kJ mol}^{-1}$

When pressure increases, by Le Chatelier's Principle, the equilibrium position shifts **left** to **reduce the number of moles of gas** to **decrease pressure**.

Therefore, Q represents products since the graphs show **decreasing %Q** when **pressure increases.**

Since forward reaction is exothermic, **$T_2 > T_1$**. By Le Chatelier's Principle, the equilibrium position shifts **left** towards the **endothermic** reaction to **absorb heat.**
T_2 has lower %Q than T_1

11 **Answer: D**

Option 1 is correct as it involves the formation of an intermediate.

Option 2 is correct as the potential energy of the intermediate is lower than that of the starting material.

Option 3 is correct as the catalyst will lower both E_a and E_a'

12 **Answer: B**

When temperature increases, based on Le Chatelier's principle, equilibrium position will shift right towards the endothermic reaction to absorb heat.

$[H^+]$ & $[OH^-]$ increases in magnitude

Since $K_w = [H^+][OH^-]$, K_w increases in magnitude.

$[H^+] = [OH^-]$ as 1 mol of water molecule dissociates to form 1 mol of H^+ and 1 mol of OH^-.

pH will decrease to a value below 7, as $[H^+]$ increases. ($pH = -\log[H^+]$)

13 **Answer: D**

Alkaline buffer consists of a weak base and its conjugate acid.

$$\text{pOH} = \text{p}K_b + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

Maximum buffer capacity occurs when pOH = $\text{p}K_b$, where $\frac{[\text{salt}]}{[\text{acid}]} = 1$

A → 0.003 mol NH_4^+ and 0.001 mol of NH_3
B → acidic buffer
C → 0.02 mol of $CH_3CH_2NH_3^+$
D → 0.0025 mol $CH_3NH_3^+$ and 0.0025 mol of CH_3NH_2

14 **Answer: A**

Bromophenol–blue appears purple (**pH > 4.6)** ⇒ Option **A** is **incorrect**
Phenol–red appears yellow (**pH < 6.8)** ⇒ Options **C and D** are **incorrect**.
The solution must be **weakly acidic and with 4.6 < pH < 6.8**.

15 **Answer: A**

The calculation could be completed using $\Delta H^{\ominus}_f$ of all compounds if $\Delta H^{\ominus}_f$ of $Cl\bullet$ is provided. Atomisation of $Cl–Cl$ molecule involves homolysis of the bond, forming Cl atoms with one unpaired electron each, i.e. Cl radicals.

16 **Answer: A**

$\Delta G = \Delta H - T\Delta S$
Reaction is exothermic ⇒ $\Delta H < 0$ ⇒ y–intercept is negative
Less gaseous products than reactants ⇒ $\Delta S < 0$ ⇒ $(-\Delta S) > 0$ ⇒ gradient of graph is positive

17 **Answer: D**

Explanation:
$BaCl_2$
$\Delta H^{\ominus}_{solution}$ = |Lattice energy| – $|\Delta H^{\ominus}_{hydration}\ Ba^{2+}| - 2|\Delta H^{\ominus}_{hydration}\ Cl^-|$
= 2053 – 1309 – 2(378) = –12 kJ mol^{-1}

18 **Answer: D**

Option A is incorrect.
Cathode is a positive electrode and accept electrons.

Option B is incorrect.

$E_{cell} = E_{red} - E_{ox} = 0.54 - (-3.04) = +3.58$ V

Option C is incorrect.
Ni is a metal which allows **electrons** to pass through and connect Li to I_2 complex.

Option D is correct.

Amount of Li^+, $\frac{5}{6.9} = \frac{0.8\times10^{-3}\times t}{1\times96500}$ ➔ $t = 8.73 \times 10^7$ s ➔ Time = 2.77 years

19 **Answer: B**

$Cr^{3+}(aq) + e \rightleftharpoons Cr^{2+}(aq)$ $\qquad$ $Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$

$E^\ominus_{red} = E^\ominus_{(Cr^{3+} | Cr^{2+})} = -0.41$ V $\qquad$ $E^\ominus_{ox} = E^\ominus_{(Fe^{2+} | Fe)} = -0.44$ V

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = -0.41 - (-0.44) = \underline{\mathbf{+0.03\ V}}$

For E_{cell} to be 0.00 V, E_{red} should decrease (more negative) ***OR***
E_{ox} should increase (more positive)

Change	*Effect*
increase [$FeSO_4$]	increase in [Fe^{2+} (aq)], $Fe^{2+} + 2e \rightleftharpoons Fe$ eqm position shifts right, $\underline{\mathbf{E_{ox}}\uparrow}$
decrease [$CrCl_2$]	decrease in [Cr^{2+} (aq)], $Cr^{3+} + e \rightleftharpoons Cr^{2+}$ eqm position shifts right, $E_{red}\uparrow$
decrease [$CrCl_3$]	decrease in [Cr^{3+} (aq)], $Cr^{3+} + e \rightleftharpoons Cr^{2+}$ eqm position shifts right, $\underline{\mathbf{E_{red}}\downarrow}$
increase surface area of Fe electrode	no effect to E_{red} value

20 **Answer: D**

Option **A** is wrong. Step 1 is reduction.

Option **B** is inconclusive. While the relative strength of H_2O, SCN^- and $EDTA^{4-}$ ligands can be concluded from the ligand exchange reactions in Step **4** and **5**, nothing can be concluded about the relative strength of H_2O and CN^- ligands.

Option **C** is incorrect. While $Fe(OH)_3$ can be formed, CO_2 (g) cannot be produced from this reaction. The correct reagent to be used in Step **2** should be Na_2CO_3.

Option **D** is correct.

21 **Answer: B**

Option 1 is correct.

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

$E^\ominus_{(S_2O_8^{2-}/SO_4^{2-})} = +2.01V$; $E^\ominus_{(I_2/I^-)} = +0.54V$

Hence, any transition metal ions catalyst with **$E^\ominus$ values between + 2.01 V and +0.54 V**

$E^\ominus_{(VO_2^+/VO^{2+})} = +1.00V$

Option 2 is incorrect.

When $VOSO_4(H_2O)_5$ dissolve in water to form an aqueous solution. $[VO(H_2O)_6]^{2+}$ is formed. The blue colour of the solution observed is due to the d-d transition caused by the splitting of the d-orbitals by the water ligands.

Option 3 is correct.

Zinc metal is functioning as a reducing agent. Assuming Zn is in excess,

$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(VO^{2+}/V^{2+})} = +0.34V$ (Reduction)	$Zn + 2VO^{2+} + 4H^+ \rightarrow Zn^{2+} + 2V^{3+} + 2H_2O$ $E^\ominus_{cell} = +0.34 - (-0.76) = +1.10\ V > 0$ (feasible)
$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(V^{3+}/V^{2+})} = -0.26V$(Reduction)	$Zn + 2V^{3+} \rightarrow Zn^{2+} + 2V^{2+}$ $E^\ominus_{cell} = -0.26 - (-0.76) = +0.50\ V > 0$ (feasible)
$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(V^{2+}/V)} = -1.20V$(Reduction)	$E^\ominus_{cell} = -1.20 - (-0.76) = -0.55\ V < 0$ (not feasible)

22 **Answer: B**

1	The oxide of **E** is amphoteric.	**E** is **aluminum**.
2	The oxide of **F** dissolves in water to form a strongly alkaline solution.	**F** is **sodium**.
3	The oxide of **G** reacts with dilute sodium hydroxide at room temperature.	**G** could either be **phosphorus or sulfur**.
4	The oxide of **H** is insoluble in water but is soluble in concentrated sodium hydroxide.	**H** is **silicon**.

In **increasing proton number**,
sodium, aluminium, silicon, phosphorus/sulfur

Option **B**: **F, E, H, G**

23 **Answer: D**

Element **A** has the **highest 3rd IE** ⇒ element **A** is in Group **2**.

A : Mg Group 2, **B : A*l*** Group 13,
C : Si Group 14, **E : S** Group 16

1 Mg is a strong reducing agent ($E^{\ominus}_{Mg^{2+}/Mg} = -2.38V$). (False)
2 Al_2O_3 does not dissolve in water, because of its extremely high lattice energy. Large amount of energy is required to break the strong ionic bonds. (False)
3 SiO_2 is an acidic oxide, even though it doesn't dissolve in water to form an acid. It reacts with hot conc. NaOH to from Na_2SiO_3. (True)
4 Sulfur is in Group 16, hence it can form a hydride of H_2S. (True)

24 **Answer: A**

Option 1 – *Comparing $BaCO_3$ and $CaCO_3$:*
Ionic radius: Ba^{2+} (0.135 nm) > Ca^{2+} (0.099 nm)

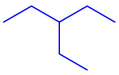
$$\boxed{|\text{Lattice energy}| \propto \frac{q_+ q_-}{r_+ + r_-}}$$

Magnitude of lattice energy: $CaCO_3 > BaCO_3$

Option 2 & 3 – *Comparing $BaCO_3$, $CuCO_3$ and $CaCO_3$:*

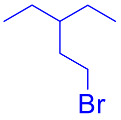
- Ionic radius: Cu^{2+} (0.073 nm) < Ca^{2+} (0.099 nm) < Ba^{2+} (0.135 nm)
- Charge density & polarising power of cation: $Cu^{2+} > Ca^{2+} > Ba^{2+}$
- Ability of cation to distort the CO_3^{2-} electron cloud, weakening and break the C–O bond for: $Cu^{2+} > Ca^{2+} > Ba^{2+}$
- Thermal Stability: $BaCO_3 > CaCO_3 > CuCO_3$

25 **Answer: C**



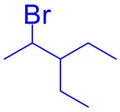
3-ethylpentane

9 Primary H atoms
6 Secondary H atoms
1 Tertiary H atom



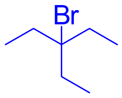
1-bromo-3-ethylpentane

9 x 1 = 9



2-bromo-3-ethylpentane

6 x 4 = 24

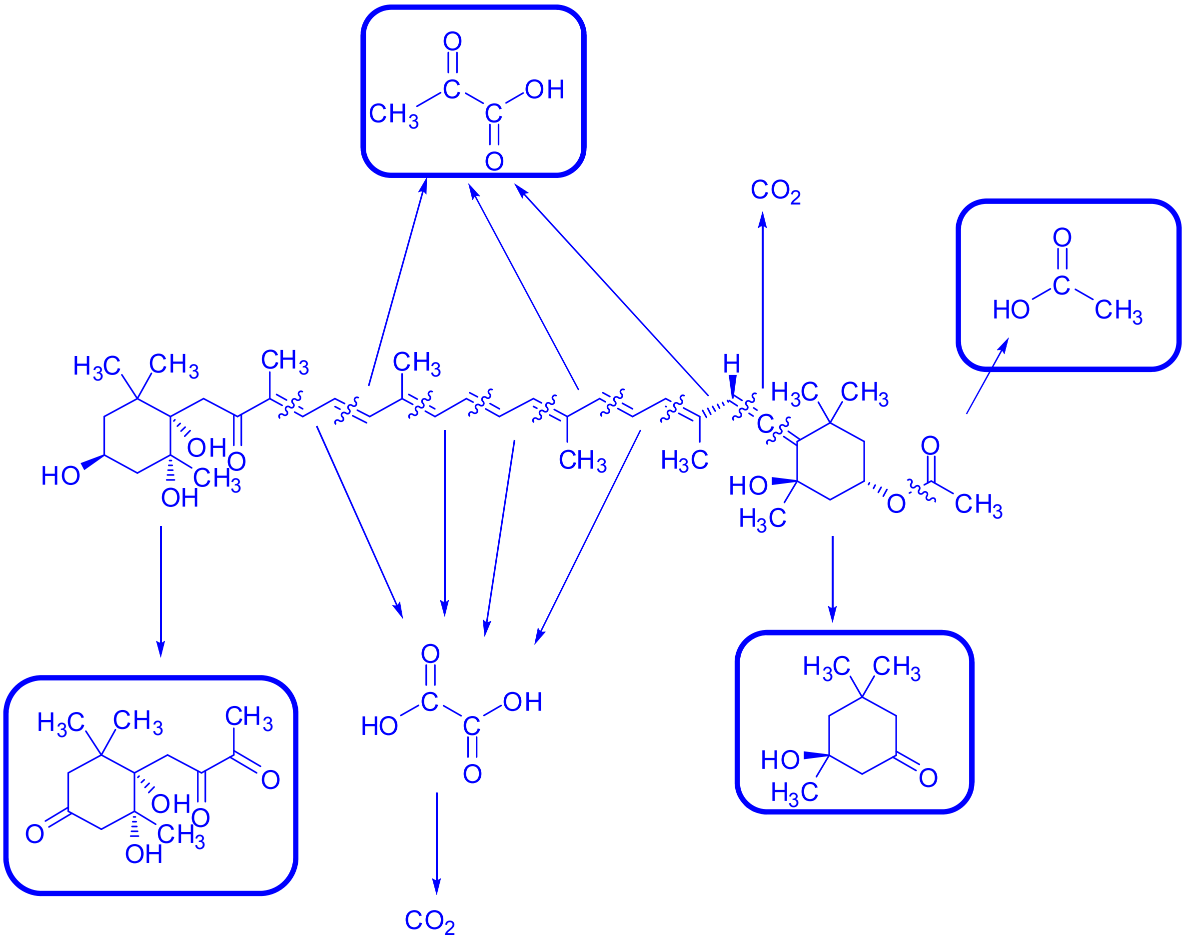


3-bromo-3-ethylpentane

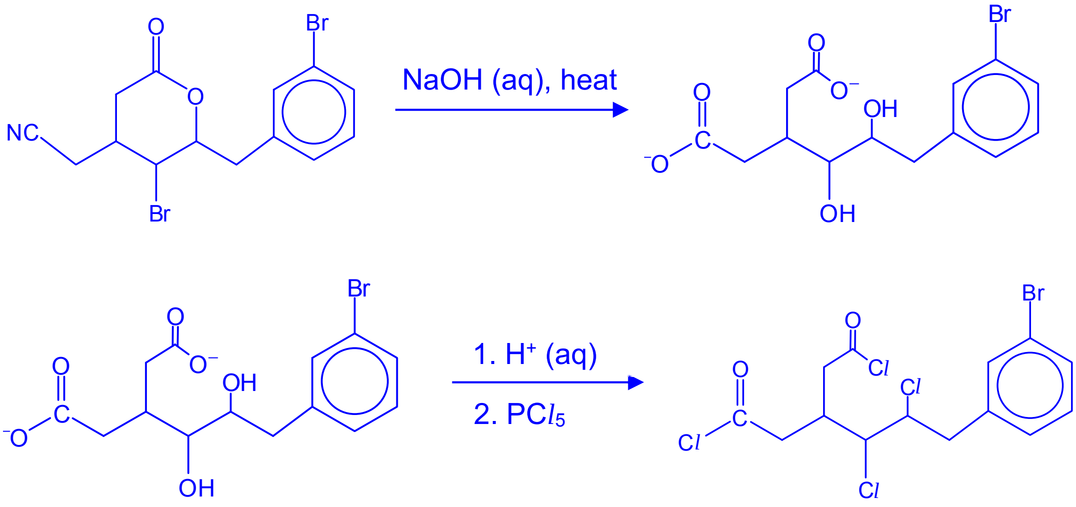
1 x 6 = 6

Ratio is 9 : 24 : 6
= 3 : 8 : 2

26 **Answer: B**

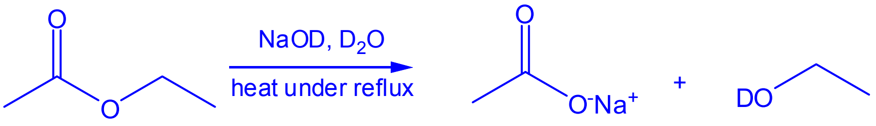


27 **Answer: C**

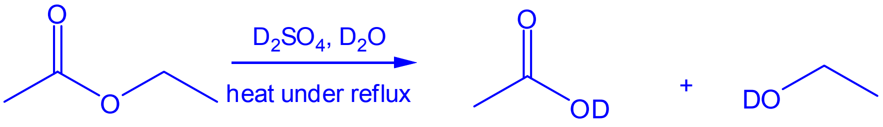


28 **Answer: C**

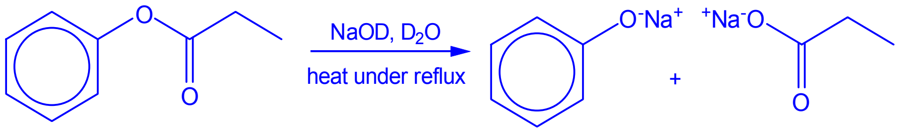
A



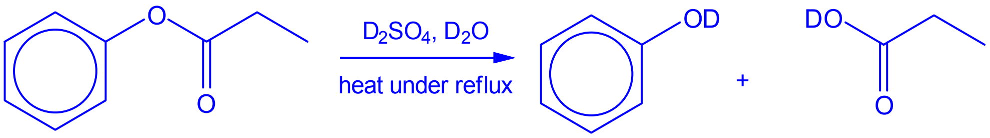
B



C

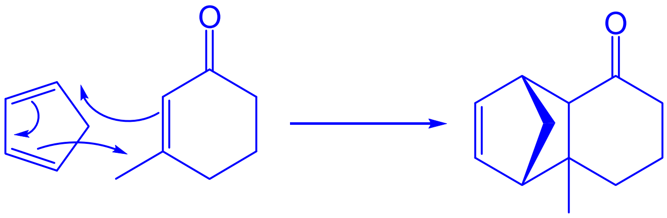


D



29 **Answer: A**

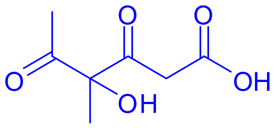
Explanation:



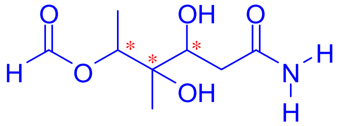
30 **Answer: C**

Explanation:

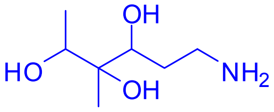
Option 1 is true: Compound A undergoes acidic hydrolysis (amide and ester) as well as oxidation.

Products are CO_2 +  + NH_4^+

Option 2 is false: Compound A has 3 chiral carbon atoms with no internal plane of symmetry. Total number of stereoisomers should be 2^3 = 8 (not 2 × 3 = 6)



Option 3 is false:

The products after reacting with LiA*l*H₄ are CH_3OH + 

END OF PAPER

Class	Reg Number
17	

Name: ____________________

MERIDIAN JUNIOR COLLEGE

JC2 Preliminary Examination

Higher 2

Calculator Model / No.

Chemistry

9729/02

Paper 2 Structured Questions

18 September 2018

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

Examiner's Use			
Paper 1	**MCQ**	**/ 30**	**/ 15 %**
Paper 2	**Q1**	**/ 13**	
	Q2	**/ 19**	
	Q3	**/ 14**	
	Q4	**/ 15**	
	Q5	**/14**	
	Total	**/ 75**	**/ 30%**
Paper 3	**Total**	**/ 80**	**/ 35%**
Paper 4	**Total**	**/ 55**	**/ 20%**
Total			**/ 100 %**
Grade			

This document consists of **17** printed pages (including this cover page).

1 Ammonia is one of the most highly produced inorganic chemicals. Modern chemical plants depend on Haber Process whereby hydrogen derived from natural gas reacts with atmospheric nitrogen using a catalyst under high pressure and temperature to produce anhydrous ammonia.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

(a) For the above reaction, a 1:3 ratio of N_2 and H_2 is passed over a catalyst. The resulting mixture is allowed to reach dynamic equilibrium. At equilibrium, 20% of the N_2 has reacted and the total pressure is 2.0 atm.

(i) Explain what is meant by the term *dynamic equilibrium*.

[1]

(ii) Calculate the partial pressures of N_2 and H_2 at equilibrium.

[2]

(iii) Write an expression for the equilibrium constant, K_p, and calculate its value.

[2]

(b) **(i)** Using relevant data in the *Data Booklet,* calculate the enthalpy change of reaction, ΔH_{rxn} of the Haber Process.

[2]

(ii) The enthalpy change of reaction calculated above in **(b)(i)** differs slightly from the actual value of –92.0 kJ mol^{-1}. Suggest a reason for this.

[1]

(c) Explain whether the formation of ammonia is favoured with

I high or low pressure,
II high or low temperature.

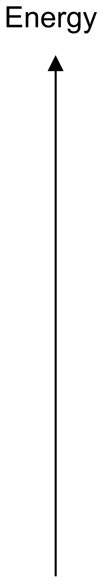
[3]

(d) Ammonium chloride, NH_4Cl is typically used in instant ice–packs. A crushing action activates the ice–pack as this mixes NH_4Cl with water. The ice–pack cools as the dissolution of NH_4Cl is endothermic.

Draw an energy level diagram to determine the standard enthalpy change of solution of ammonium chloride given the following information.

Lattice energy of ammonium chloride	–705 kJ mol^{-1}
Enthalpy change of hydration of NH_4^+	–307 kJ mol^{-1}
Enthalpy change of hydration of Cl^-	–381 kJ mol^{-1}

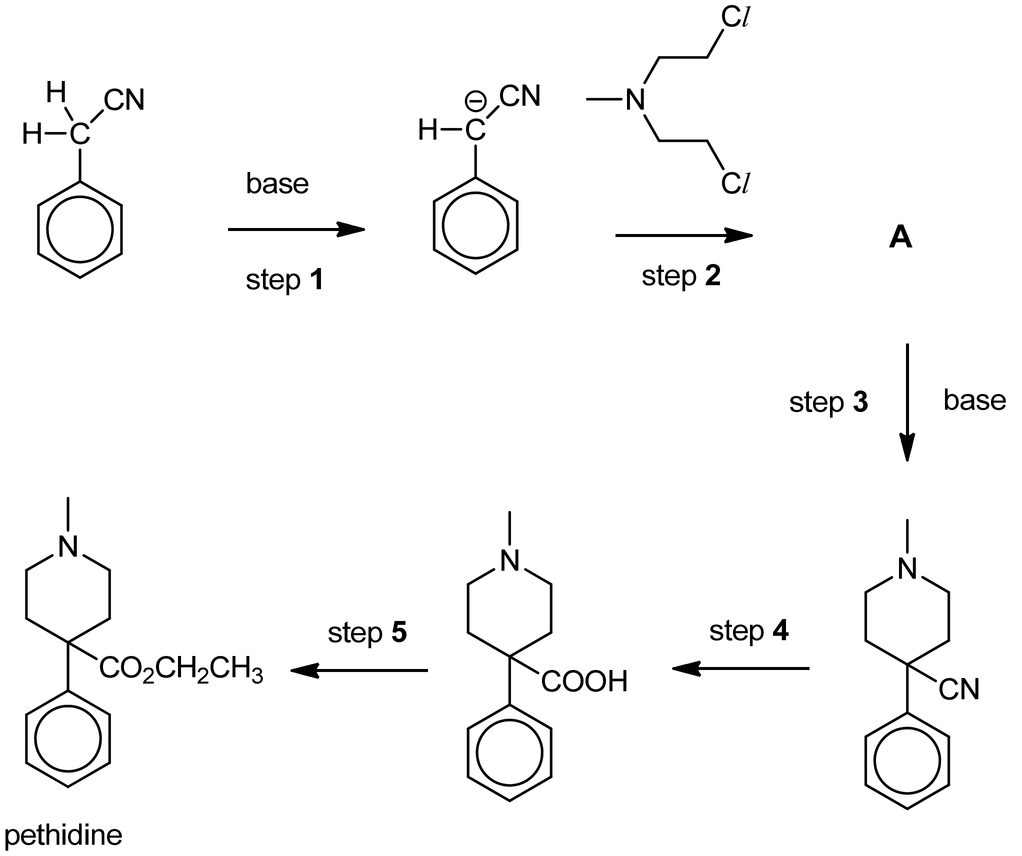
[2]



[Total: 13]

2 Nitrogen is an element commonly found in various major classes of drugs.

(a) The following is a reaction scheme for the synthesis of pethidine, a powerful painkilling drug.



(i) State the type of reaction for step **1** and step **2**. **[2]**

Step 1: ....

Step 2: ....

(ii) Suggest the structure of intermediate **A** **[1]**

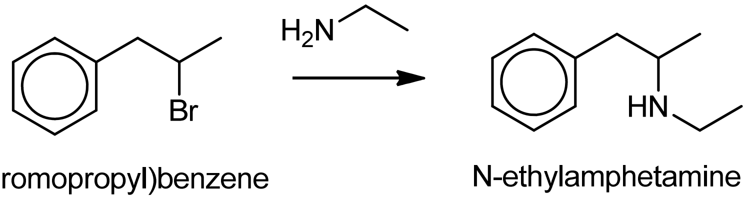
(iii) State the reagents and conditions needed for step **4** and step **5**. **[2]**

Step 4: ....

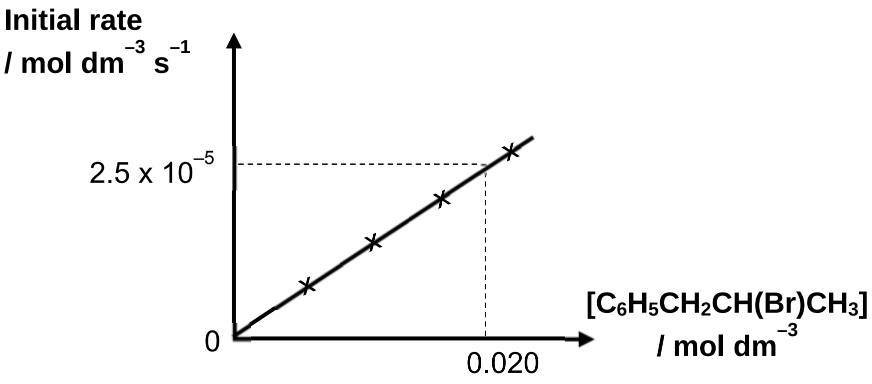
Step 5: ....

(b) Kinetics studies of organic reactions provide strong evidence in supporting the postulated mechanisms.

The results from the kinetics study of the nucleophilic substitution reaction involved in the synthesis of N–ethylamphetamine, a discontinued weight–loss drug, are presented below.



The graph was plotted based on data obtained from repeating the experiment several times by varying the concentration of $C_6H_5CH_2CH(Br)CH_3$ while maintaining that of $CH_3CH_2NH_2$ to be at 2.5 mol dm^{-3}.



(i) The rate equation for the reaction was found to be

$$\text{rate} = k\,[C_6H_5CH_2CH(Br)CH_3][CH_3CH_2NH_2]$$

Using the graph provided, justify why the order of reaction with respect to $C_6H_5CH_2CH(Br)CH_3$ is one.

[2]

(ii) Calculate the rate constant, k and state its units.

[2]

(iii) Given that this is a bimolecular reaction, outline the mechanism for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

(iv) Suggest why the rate of reaction decreases when $(CH_3)_3CNH_2$ is used instead of $CH_3CH_2NH_2$.

[1]

(v) Explain how the reactivity of (2–chloropropyl)benzene will differ towards $CH_3CH_2NH_2$ as compared to (2–bromopropyl)benzene.

[1]

(vi) With the aid of a Maxwell–Boltzmann Distribution curve, explain how heating the reaction mixture will increase the rate of the reaction.

[3]

(c) Investigating the optical activity of the product of a nucleophilic substitution reaction can also provide evidence on how the reaction may proceed.

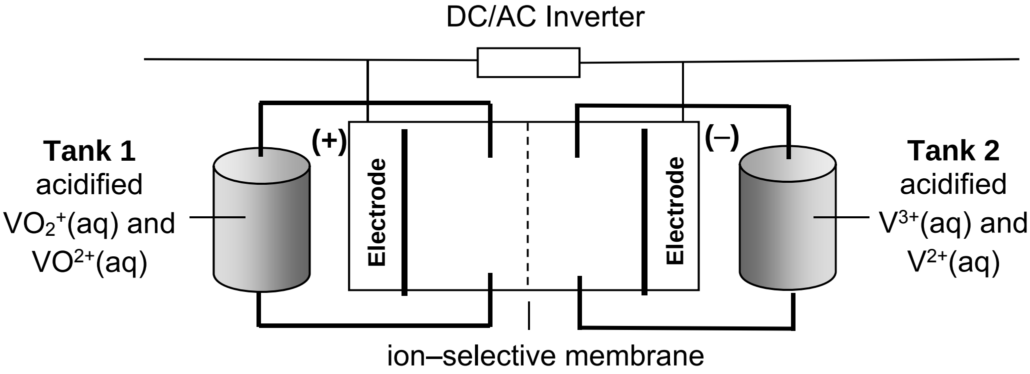
Consider the reaction between the (+) enantiomer of 2–bromobutane and hot NaOH (aq).

State the expected optical activity of the product if this reaction proceeds via S_N1 mechanism. Provide reasoning for your answer.

[2]

[Total: 19]

3 The vanadium flow battery (VFB) is a type of rechargeable battery that employs electrolyte containing vanadium ions in different oxidation states.



(a) Electricity is generated from the battery by half–cell reactions of these electrolytes that were pumped into the cell from separate storage tanks. The two electrolytes in the cell are separated by an ion selective membrane, which only allows H^+ ions to pass through.

(i) Write the two half equations for the reaction occurring at the anode and the cathode when the battery discharges. Hence, write the overall cell reaction.

[2]

Anode: ....

Cathode: ....

Overall: ....

(ii) Calculate the e.m.f of the battery.

[1]

(iii) Explain how the ion–selective membrane in VFB maintains electrical neutrality.

[1]

....

....

....

....

(iv) State and explain what happens to the overall e.m.f when a small amount of $OH^-(aq)$ ions were added to the electrolyte in **Tank 1**.

[2]

(b) The total concentration of vanadium ions in the 20 dm^3 electrolyte in **Tank 1** is 5.00 mol dm^{-3}. During the charging of the VFB, the percentage composition of VO_2^+ has to be increased from 5% to 90%.

(i) Calculate the amount of VO_2^+ that needs to be converted during this charging process.

[1]

(ii) Find the time taken, in hours, if a 120 A current is used in the charging process.

[2]

(c) Anodising of aluminum is an electrolytic process to increase the thickness of the alumnium oxide layer on the surface of aluminium, by passing a direct current through dilute sulfuric acid.

(i) Draw a labelled diagram of an electrolysis set–up during the anodising of aluminium.

[2]

(ii) Write the half–equations for the reactions taking place at the anode, cathode and hence write the overall equation.

[2]

Anode: ....

Cathode: ....

Overall: ....

(iii) State and explain any observations if copper(II) sulfate was used as the electrolyte instead.

[1]

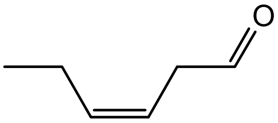
....

....

....

[Total: 14]

4(a) *cis*–3–hexenal, $CH_3CH_2CH=CHCH_2CHO$ is a compound with an intense smell of freshly cut grass and leaves.



cis–3–hexenal

Two isomers, **P** and **Q**, with the same molecular formula, $C_6H_{10}O$, as *cis*–3–hexenal show different types of isomerism. Both isomers decolourises aqueous bromine in the dark and both gives a positive test with Fehling's reagent.

Draw their structures and state their isomeric relationship to *cis*–3–hexenal.

[2]

isomer **P**	isomer **Q**
isomeric relationship to *cis*–3–hexenal:	isomeric relationship to *cis*–3–hexenal:

(b) Aldehydes and ketones (broadly classified as carbonyl compounds) can be reduced to alcohols using metal hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). These metal hydride reagents provide a source of hydride, H^- ions.

(i) The reaction between *cis*–3–hexenal, $CH_3CH_2CH{=}CHCH_2CHO$ and sodium borohydride in methanol is a nucleophilic addition reaction.

Draw the mechanism for this reaction, showing all charges, dipoles and curly arrows to represent the movement of electron pairs.

[3]

(ii) BH_3 is a side product of the earlier reaction in **(b)(i)**. BH_3 can form an addition product with Lewis bases, for example, with the alkoxide ion generated in the mechanism.

Draw the structure of this adduct formed and explain why the formation of the adduct is likely to happen.

[2]

(c) Both Li*Al*H_4 and $NaBH_4$ are sources of H^-. Hydride ions react vigorously with Bronsted–Lowry acids, releasing H_2 (g) and heat.

Li*Al*H_4 reacts violently with water or alcohols. When carrying out reactions with Li*Al*H_4, chemists often use solvents like anhydrous diethyl ether that has been treated to remove traces of water. On the other hand, $NaBH_4$ does not react that vigorously with water or alcohol.

Using the information provided or otherwise, suggest why Li*Al*H_4 is a better source of H^- than $NaBH_4$.

	Pauling Electronegativity
aluminium	1.61
boron	2.04
hydrogen	2.20

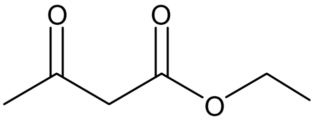
[1]

....

....

....

(d) A student proposed the following procedure to reduce ethyl acetoacetate ($C_6H_{10}O_3$),



using $NaBH_4$.

Procedures

1. Add 0.70 g of $NaBH_4$ to 25 cm^3 ethanol solvent in a 100 cm^3 round–bottomed flask. Cool the resulting mixture to 0 °C using an ice–bath.
2. To this mixture, slowly add 30 cm^3 of 40.8 g dm^{-3} ethyl acetoacetate solution. Stir the resulting solution at 0 °C for 15 minutes, then allow to warm to room temperature and stir for an additional 15 minutes.
3. Evaporate the solvent. Dissolve the resulting white solid in 30 cm^3 dichloromethane solvent, CH_2Cl_2.
4. Cool the flask in an ice–bath. Then, add 30 cm^3 of 1 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction by destroying any unreacted hydride. **Safety note*: The addition of HCl will release H_2 gas.*
5. Separate the organic layer from the aqueous layer.
6. Add powdered magnesium sulfate to the organic layer in excess, till no clumping of magnesium sulfate powder is observed. Filter off the magnesium sulfate and evaporate the dichloromethane solvent.
7. Weigh the product and record the actual yield.

(i) Explain why $NaBH_4$ is soluble in ethanol (in **step 1**) in terms of structure and bonding. **[2]**

(ii) One mole of $NaBH_4$ can reduce a maximum of four moles of carbonyl groups. Generally, in an experimental procedure, the reducing agent $NaBH_4$ should be used in excess.

Determine with relevant calculations, whether the student is correct with the quantities proposed in his procedures (**step 1 – 2**). **[2]**

(iii) In **step 4**, hydrochloric acid is added to quench the reaction, producing hydrogen gas and sodium boron chloride. Write an equation for the reaction that took place. **[1]**

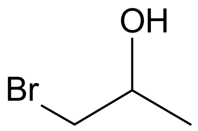
(iv) Draw the **skeletal** formula of the product isolated in the organic layer at the end of the experiment. **[1]**

(v) Suggest the function of magnesium sulfate in **step 6**. **[1]**

[Total: 15]

5 Organic reactions can lead to increased variation due to the direction–specific nature of covalent bonds, giving rise to much complexity from using only a small range of elements such as carbon, hydrogen and oxygen.

(a) Propene reacts with aqueous bromine to form a mixture of products, including molecule **A**.



Molecule **A**

(i) State the IUPAC name of molecule **A**.

[1]

(ii) Draw a mechanism for the reaction between propene and aqueous bromine to form Molecule **A** and hydrogen bromide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[3]

(iii) Molecule **A** is the major product of this reaction. Suggest the structure of two other organic by–products.

[2]

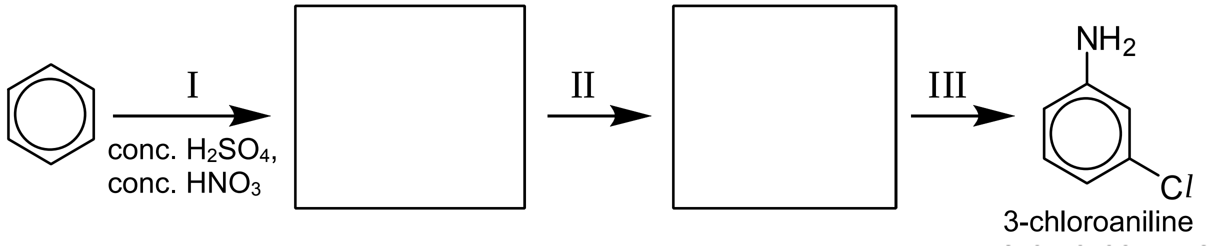
(iv) In the mechanism outlined in **(a)(ii)**, two stereoisomers of **A** are formed in equal amounts. Draw these two stereoisomers and name the type of isomerism displayed.

[2]

(b) 3–chloroaniline can be synthesised from benzene in a 3–step synthesis.

(i) Propose a synthetic route by suggesting the two intermediates compounds and state the reagents and conditions used for steps **II** and **III**.

[4]



Step II: ....

Step III: ....

(ii) One of the by–products from the synthesis in **(b)(i)** is HC*l*, which is a strong acid. The acid dissociation constant values, K_a of several hydrogen halides are shown below.

Compound	**K_a / mol dm^{-3}**
HC*l*	1.3×10^6
HBr	1.0×10^9
HI	3.2×10^9

Account for the relative K_a values.

[2]

....

....

....

....

[Total: 14]

END OF PAPER

Name: Suggested Solutions

Class	Reg Number
17	

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9729/02

Paper 2 Structured Questions

18 September 2018

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

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Paper 1	**MCQ**	**/ 30**	**/ 15 %**
Paper 2	**Q1**	**/ 13**	
	Q2	**/ 19**	
	Q3	**/ 14**	
	Q4	**/ 15**	
	Q5	**/14**	
	Total	**/ 75**	**/ 30%**
Paper 3	**Total**	**/ 80**	**/ 35%**
Paper 4	**Total**	**/ 55**	**/ 20%**
Total			**/ 100 %**
Grade			

This document consists of **17** printed pages (including this cover page).

1 Ammonia is one of the most highly produced inorganic chemicals. Modern chemical plants depend on Haber Process whereby hydrogen derived from natural gas reacts with atmospheric nitrogen using a catalyst under high pressure and temperature to produce anhydrous ammonia.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

(a) For the above reaction, a 1:3 ratio of N_2 and H_2 is passed over a catalyst. The resulting mixture is allowed to reach dynamic equilibrium. At equilibrium, 20% of the N_2 has reacted and the total pressure is 2.0 atm.

(i) Explain what is meant by the term *dynamic equilibrium*.

[1]

A dynamic equilibrium is a chemical equilibrium where the rate of forward reaction is equal to the rate of backward reaction and the substances are still reacting together although the concentrations of the reactants and products remain constant.

(ii) Calculate the partial pressures of N_2 and H_2 at equilibrium.

[2]

	$N_2(g)$ +	**$3H_2(g)$ $\rightleftharpoons$**	**$2NH_3(g)$**
Initial no. of mole	x	$3x$	0
Change in no. of mole	$-0.2\,x$	$-0.6\,x$	$+0.4\,x$
No. of mole at equilibrium	$0.8\,x$	$2.4\,x$	$0.4\,x$

Total no. of moles at equilibrium = $0.8\,x + 2.4\,x + 0.4\,x = 3.6\,x$

Mole fraction at equilibrium	$0.8\,x / 3.6\,x$ $= 0.222$	$2.4\,x / 3.6\,x$ $= 0.667$	$0.4\,x / 3.6\,x$ $= 0.111$
Partial Pressure at equilibrium/ atm	0.222 x 2.0 = 0.444	0.667 x 2.0 = 1.33	0.111 x 2.0 = 0.222

Partial pressure of N_2 at equilibrium = 0.444 atm
Partial pressure of H_2 at equilibrium = 1.33 atm

(iii) Write an expression for the equilibrium constant, K_p, and calculate its value.

[2]

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3} = \frac{(0.222)^2}{(0.444)(1.33)^3} = 0.0472\ \text{atm}^{-2}$$

(b) **(i)** Using relevant data in the *Data Booklet,* calculate the enthalpy change of reaction, ΔH_{rxn} of the Haber Process.

[2]

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\begin{aligned}\Delta H_{rxn} &= [BE(N{\equiv}N) + 3BE(H–H) – [6BE(N–H)] \\ &= [(944) + 3(436)] – [6(390)] \\ &= – 88.0 \text{ kJ mol}^{-1}\end{aligned}$$

(ii) The enthalpy change of reaction calculated above in **(b)(i)** differs slightly from the actual value of –92.0 kJ mol^{-1}. Suggest a reason for this.

[1]

The bond energy calculation is an approximation method as the N–H bond energy value / bond energy values for polyatomic molecules from the *Data Booklet* are average values.

(c) Explain whether the formation of ammonia is favoured with

I high or low pressure,
II high or low temperature.

[3]

I High pressure favours ammonia formation.
By Le Chatelier's Principle, with an increase in pressure, the equilibrium position will shift right to decrease the number of moles of gas to decrease pressure.

New equilibrium mixture contains less reactants, N_2 and H_2 and more products, NH_3. Yield of ammonia increases.

II Low temperature favours ammonia formation.
By Le Chatelier's Principle, with a decrease in temperature, the equilibrium position will shift right towards exothermic reaction to release heat.

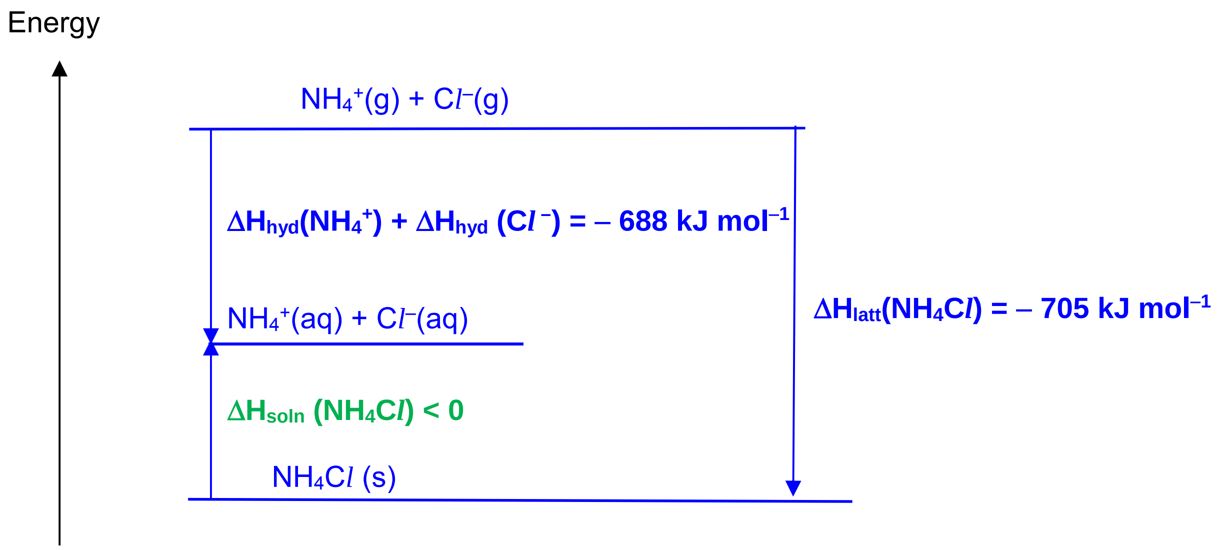
New equilibrium mixture contains less reactants, N_2 and H_2 and more products, NH_3. Yield of ammonia increases.

(d) Ammonium chloride, NH_4Cl is typically used in instant ice–packs. A crushing action activates the ice–pack as this mixes NH_4Cl with water. The ice–pack cools as the dissolution of NH_4Cl is endothermic.

Draw an energy level diagram to determine the standard enthalpy change of solution of ammonium chloride given the following information.

Lattice energy of ammonium chloride	-705 kJ mol^{-1}
Enthalpy change of hydration of NH_4^+	-307 kJ mol^{-1}
Enthalpy change of hydration of Cl^-	-381 kJ mol^{-1}

[2]



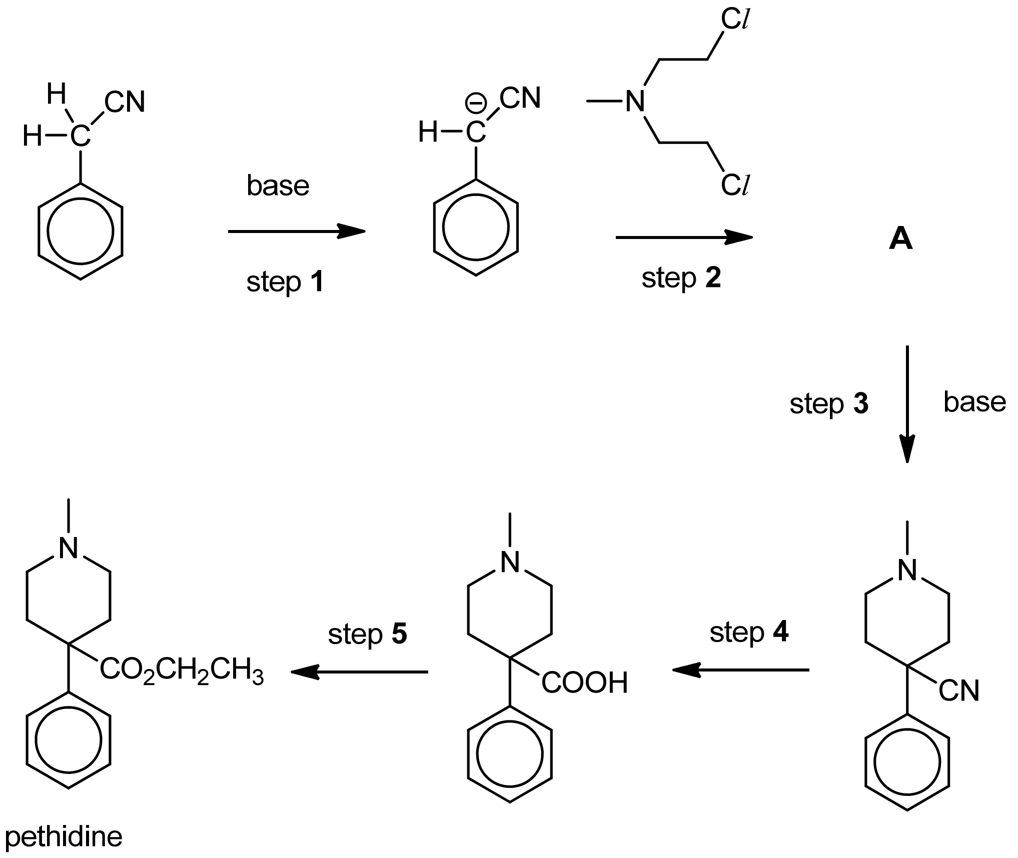
By Hess' Law,

$$\begin{aligned}\Delta H_{soln}(NH_4Cl) &= -\Delta H_{latt}(NH_4Cl) + \Delta H_{hyd}(NH_4^+) + \Delta H_{hyd}(Cl^-)\\ &= -(-705) + (-307) + (-381)\\ &= +17.0 \text{ kJ mol}^{-1}\end{aligned}$$

[Total: 13]

2 Nitrogen is an element commonly found in various major classes of drugs.

(a) The following is a reaction scheme for the synthesis of pethidine, a powerful painkilling drug.

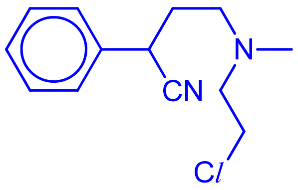


(i) State the type of reaction for step **1** and step **2**. **[2]**

Step 1: acid–base reaction / neutralisation

Step 2: nucleophilic substitution

(ii) Suggest the structure of intermediate **A** **[1]**



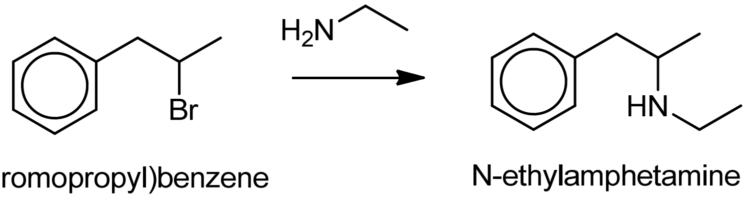
(iii) State the reagents and conditions needed for step **4** and step **5**. **[2]**

Step 4: HCl (aq) / H_2SO_4 (aq), heat under reflux

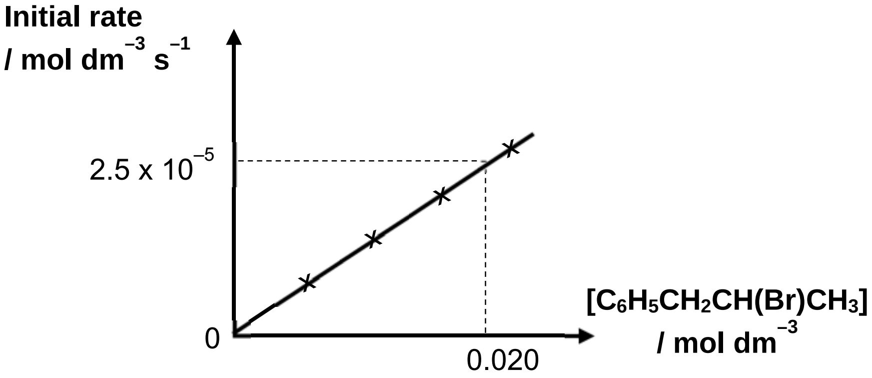
Step 5: CH_3CH_2OH, conc. H_2SO_4, heat OR PCl_5 followed by CH_3CH_2OH

(b) Kinetics studies of organic reactions provide strong evidence in supporting the postulated mechanisms.

The results from the kinetics study of the nucleophilic substitution reaction involved in the synthesis of N–ethylamphetamine, a discontinued weight–loss drug, are presented below.



The graph was plotted based on data obtained from repeating the experiment several times by varying the concentration of $C_6H_5CH_2CH(Br)CH_3$ while maintaining that of $CH_3CH_2NH_2$ to be at 2.5 mol dm^{-3}.



(i) The rate equation for the reaction was found to be

$$\text{rate} = k\,[C_6H_5CH_2CH(Br)CH_3][CH_3CH_2NH_2]$$

Using the graph provided, justify why the order of reaction with respect to $C_6H_5CH_2CH(Br)CH_3$ is one.

[2]

The graph of rate against $[C_6H_5CH_2CH(Br)CH_3]$ is a positively sloped straight line passing through the origin hence the initial rate is directly proportional to $[C_6H_5CH_2CH(Br)CH_3]$.

(ii) Calculate the rate constant, k and state its units.

[2]

Using data from the graph,

Rate = $k\,[C_6H_5CH_2CH(Br)CH_3]\,[CH_3CH_2NH_2]$

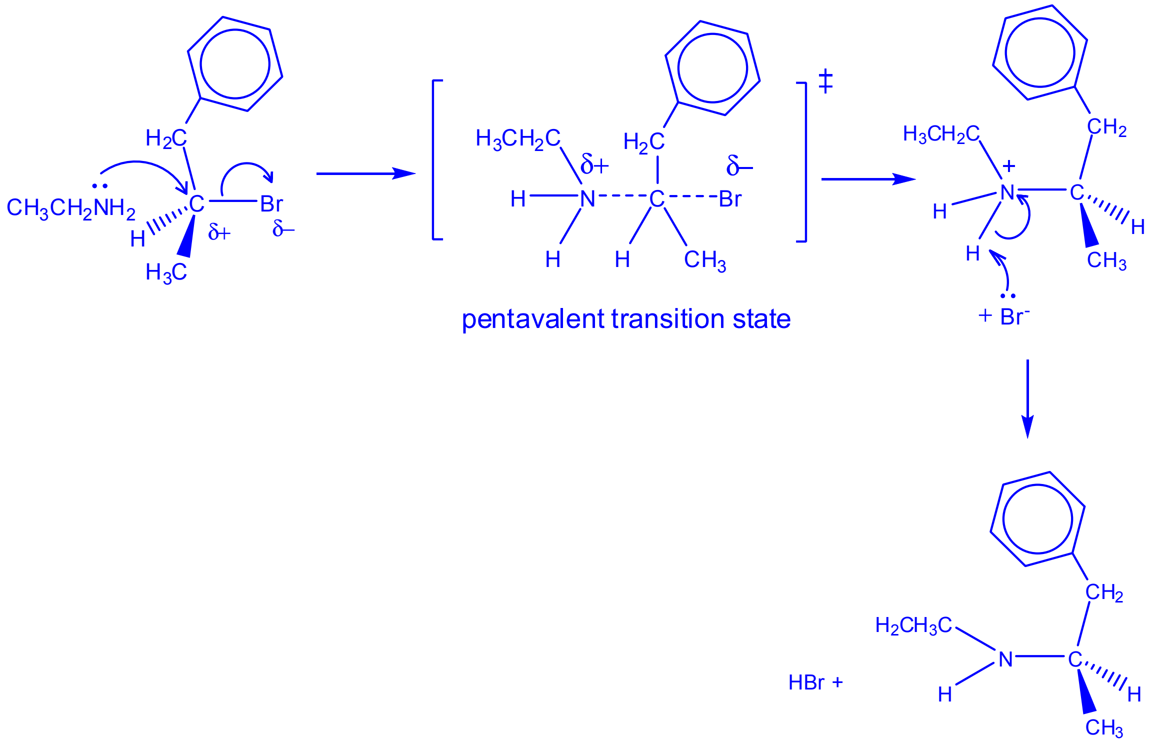
$2.5 \times 10^{-5} = k\,(0.020)(2.5)$

$k = 5.00 \times 10^{-4}$ mol^{-1} dm^{3} s^{-1}

(iii) Given that this is a bimolecular reaction, outline the mechanism for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

Nucleophilic Substitution (**<u>S_N2</u>**)



(iv) Suggest why the rate of reaction decreases when $(CH_3)_3CNH_2$ is used instead of $CH_3CH_2NH_2$.

[1]

The alkyl group of $(CH_3)_3CNH_2$ is bulkier than that of $CH_3CH_2NH_2$ hence there will be steric hindrance. The rate of reaction will decrease.

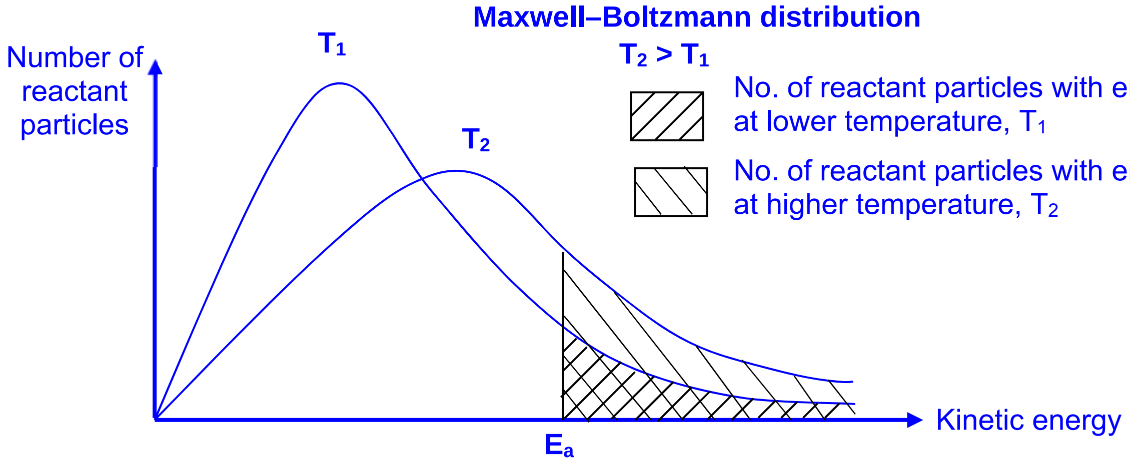
(v) Explain how the reactivity of (2–chloropropyl)benzene will differ towards $CH_3CH_2NH_2$ as compared to (2–bromopropyl)benzene.

[1]

C–C*l* bond is stronger than C–Br. Hence (2–chloropropyl)benzene will be less reactive towards $CH_3CH_2NH_2$.

(vi) With the aid of a Maxwell–Boltzmann Distribution curve, explain how heating the reaction mixture will increase the rate of the reaction.

[3]



- When temperature is increased, number of reactant particles with energy ≥ E_a increases,
- Frequency of effective collisions increases.
- Since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

(c) Investigating the optical activity of the product of a nucleophilic substitution reaction can also provide evidence on how the reaction may proceed.

Consider the reaction between the (+) enantiomer of 2–bromobutane and hot NaOH (aq).

State the expected optical activity of the product if this reaction proceeds via S_N1 mechanism. Provide reasoning for your answer.

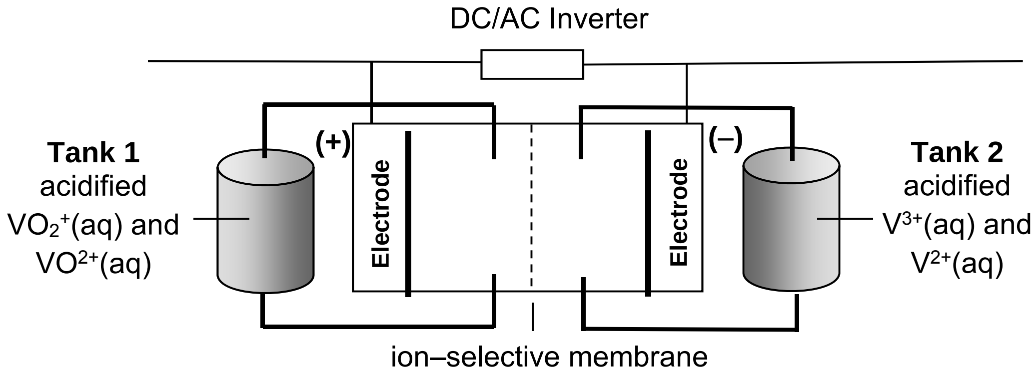
[2]

If the reaction proceeds via a S_N1 mechanism, the product obtained is likely going to be optically inactive.

Since S_N1 mechanism involves the formation of a carbocation intermediate, the nucleophile (OR OH^-) can attack the sp^2 hybridised (OR trigonal planar) carbocation (OR $[CH_3CH(CH_2CH_3)]^+$) intermediate from either top and bottom of the plane with equal probability giving rise to equal amount of both enantiomers of the product (OR racemic mixture).

[Total: 19]

3 The vanadium flow battery (VFB) is a type of rechargeable battery that employs electrolyte containing vanadium ions in different oxidation states.



(a) Electricity is generated from the battery by half–cell reactions of these electrolytes that were pumped into the cell from separate storage tanks. The two electrolytes in the cell are separated by an ion selective membrane, which only allows H^+ ions to pass through.

(i) Write the two half equations for the reaction occurring at the anode and the cathode when the battery discharges. Hence, write the overall cell reaction.

[2]

Anode: $V^{2+}(aq) \longrightarrow V^{3+}(aq) + e$

Cathode: $VO_2^+(aq) + 2H^+(aq) + e \longrightarrow VO^{2+}(aq) + H_2O(l)$

Overall: $V^{2+}(aq) + VO_2^+(aq) + 2H^+(aq) \longrightarrow V^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$

(ii) Calculate the e.m.f of the battery.

[1]

Cathode (Tank 1): $VO_2^+(aq) + 2H^+(aq) + e \longrightarrow VO^{2+}(aq) + H_2O(l)$ $E^\ominus_{ox} = +1.00$ V

Anode (Tank 2): $V^{2+}(aq) \longrightarrow V^{3+}(aq) + e$ $E^\ominus_{ox} = -0.26$ V

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxid} = +1.00 - (-0.26)$$
$$= +1.26 \text{ V}$$

(iii) Explain how the ion–selective membrane in VFB maintains electrical neutrality.

[1]

As the reaction proceeds, the anode/Tank 2 becomes more positively charged (formation of more positively charged ion) whilst the cathode/Tank 1 becomes more negatively charged (due to consumption of H^+).

The membrane allows H^+ ions to migrate from Tank 2/anode to Tank 1/cathode so as to maintain electrical neutrality.

(iv) State and explain what happens to the overall e.m.f when a small amount of OH^-(aq) ions were added to the electrolyte in **Tank 1**.

[2]

When OH^-(aq) ions were added, $[H^+]$ decreases in electrolyte in Tank 1

$VO_2^+ (aq) + 2H^+ (aq) + e \rightleftharpoons VO^{2+} (aq) + H_2O (l)$ —— (1) $E^\ominus_{red}$

By Le Chatelier's Principle, the equilibrium position in (1) will shift left to increase $[H^+]$. Hence, E_{red} becomes less positive

Since, $E_{cell} = E_{red} - E_{oxid}$; E_{cell} becomes less positive/more negative.

(b) The total concentration of vanadium ions in the 20 dm^3 electrolyte in **Tank 1** is 5.00 mol dm^{-3}. During the charging of the VFB, the percentage composition of VO_2^+ has to be increased from 5% to 90%.

(i) Calculate the amount of VO_2^+ that needs to be converted during this charging process.

[1]

Change in amount of VO_2^+ required = $\left(\frac{90}{100} - \frac{5}{100}\right) \times 20.0 \times 5.00 = 85.0$ mol

(ii) Find the time taken, in hours, if a 120 A current is used in the charging process.

[2]

$VO_2^+(aq) + 2H^+(aq) + e^- \longrightarrow VO^{2+} (aq) + H_2O (l)$

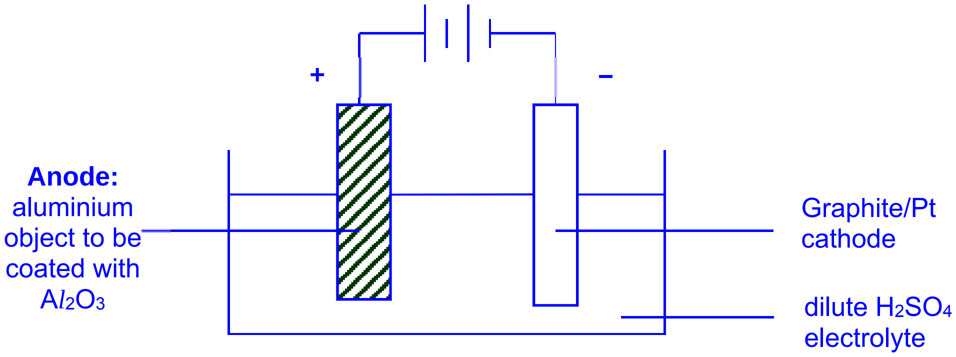
Amount of VO_2^+ = $\frac{It}{nF}$

$85.0 = \frac{120 \times t}{1 \times 96500}$ $\Rightarrow$ $t = 68354$ s $= 19.0$ h

(c) Anodising of aluminum is an electrolytic process to increase the thickness of the alumnium oxide layer on the surface of aluminium, by passing a direct current through dilute sulfuric acid.

(i) Draw a labelled diagram of an electrolysis set–up during the anodising of aluminium.

[2]



(ii) Write the half–equations for the reactions taking place at the anode, cathode and hence write the overall equation.

[2]

Anode: $2Al\,(s) + 3H_2O(l) \longrightarrow Al_2O_3\,(s) + 6H^+\,(aq) + 6e$

Cathode: $2H^+\,(aq) + 2e \longrightarrow H_2\,(g)$

Overall: $2Al\,(s) + 3H_2O(l) \longrightarrow Al_2O_3\,(s) + 3H_2\,(g)$

(iii) State and explain any observations if copper(II) sulfate was used as the electrolyte instead.

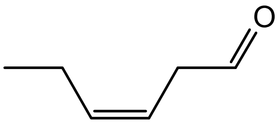
[1]

Pink Cu solid will be deposited on the cathode; blue $CuSO_4$ solution/electrolyte fades.

Cu^{2+} will be preferentially reduced/discharged at the cathode instead of H^+, as $E^\theta_{Cu^{2+}/Cu}$ is more positive compared to $E^\theta_{H_2/H^+}$

[Total: 14]

4(a) *cis*–3–hexenal, $CH_3CH_2CH{=}CHCH_2CHO$ is a compound with an intense smell of freshly cut grass and leaves.

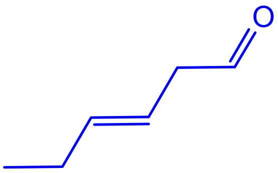


cis–3–hexenal

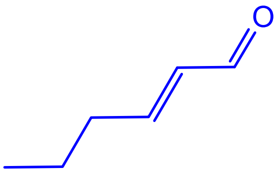
Two isomers, **P** and **Q**, with the same molecular formula, $C_6H_{10}O$, as *cis*–3–hexenal show different types of isomerism. Both isomers decolourises aqueous bromine in the dark and both gives a positive test with Fehling's reagent.

Draw their structures and state their isomeric relationship to *cis*–3–hexenal.

[2]



isomer **P**



isomer **Q**

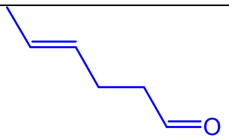
isomeric relationship to *cis*–3–hexenal:

cis–trans isomerism

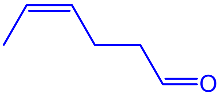
isomeric relationship to *cis*–3–hexenal:

constitutional isomerism

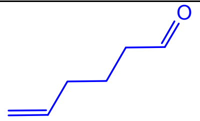
Other possible answers



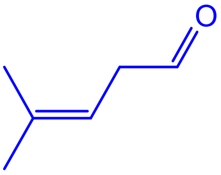
trans–4–hexenal



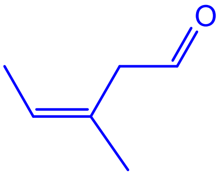
cis–4–hexenal



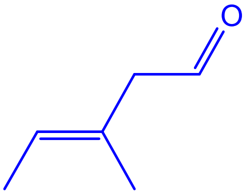
5–hexenal



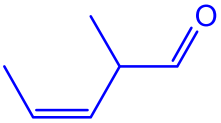
5–methyl–4–hexenal



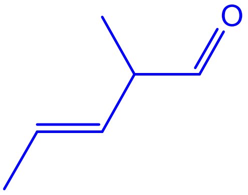
trans–3–methyl–4–hexenal



cis–3–methyl–4–hexenal



cis–2–methyl–4–hexenal



trans–2–methyl–4–hexenal

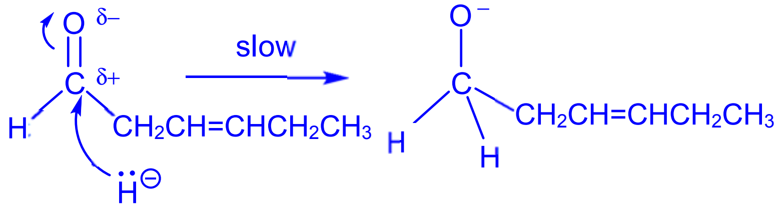
(b) These metal hydride reagents provide a source of hydride, H^- ions.

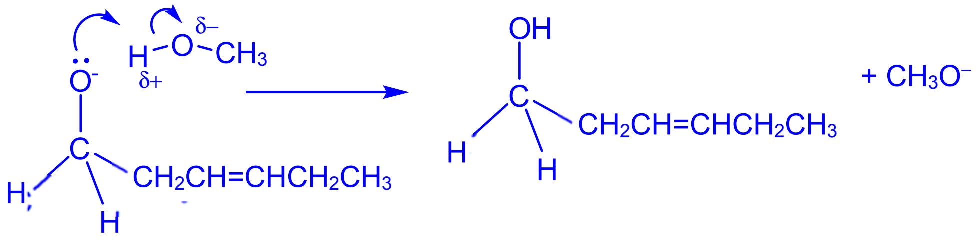
(i) The reaction between *cis*–3–hexenal, $CH_3CH_2CH=CHCH_2CHO$ and sodium borohydride in methanol is a nucleophilic addition reaction.

Draw the mechanism for this reaction, showing all charges, dipoles and curly arrows to represent the movement of electron pairs.

[3]

Nucleophilic addition



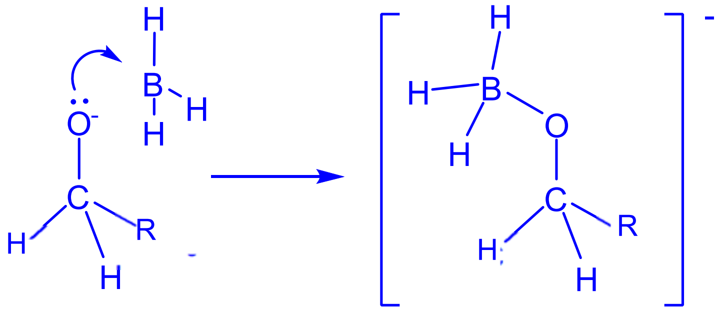


(ii) BH_3 is a side product of the earlier reaction in **(b)(i)**. BH_3 can form an addition product with Lewis bases, for example, with the alkoxide ion generated in the mechanism.

Draw the structure of this adduct formed and explain why the formation of the adduct is likely to happen.

[2]

- B in BH_3 is electron deficient or B has only 6 electrons.
- B readily accepts lone pair of electron from Lewis bases to form complexes to attain stable octet structure / configuration.



(c) Both $LiAlH_4$ and $NaBH_4$ are sources of H^-. Hydride ions react vigorously with Bronsted–Lowry acids, releasing H_2 (g) and heat.

$LiAlH_4$ reacts violently with water or alcohols. When carrying out reactions with $LiAlH_4$, chemists often use solvents like anhydrous diethyl ether that has been treated to remove traces of water. On the other hand, $NaBH_4$ does not react that vigorously with water or alcohol.

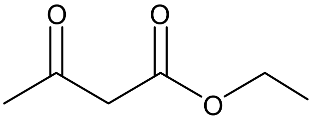
Using the information provided or otherwise, suggest why $LiAlH_4$ is a better source of H^- than $NaBH_4$.

	Pauling Electronegativity
aluminium	1.61
boron	2.04
hydrogen	2.20

[1]

The difference between the electronegativities of B and H is smaller than the difference between the electronegativities of A*l* and H, so there is a greater degree of ionic character in A*l*–H bonds than in B–H bonds

(d) A student proposed the following procedure to reduce ethyl acetoacetate ($C_6H_{10}O_3$),



using $NaBH_4$.

Procedures

1. Add 0.70 g of $NaBH_4$ to 25 cm^3 ethanol solvent in a 100 cm^3 round–bottomed flask. Cool the resulting mixture to 0 °C using an ice–bath.
2. To this mixture, slowly add 30 cm^3 of 40.8 g dm^{-3} ethyl acetoacetate solution. Stir the resulting solution at 0 °C for 15 minutes, then allow to warm to room temperature and stir for an additional 15 minutes.
3. Evaporate the solvent. Dissolve the resulting white solid in 30 cm^3 dichloromethane solvent, CH_2Cl_2.
4. Cool the flask in an ice–bath. Then, add 30 cm^3 of 1 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction by destroying any unreacted hydride. **Safety note*: The addition of HCl will release H_2 gas.*
5. Separate the organic layer from the aqueous layer.
6. Add powdered magnesium sulfate to the organic layer in excess, till no clumping of magnesium sulfate powder is observed. Filter off the magnesium sulfate and evaporate the dichloromethane solvent.
7. Weigh the product and record the actual yield.

(i) Explain why $NaBH_4$ is soluble in ethanol (in **step 1**) in terms of structure and bonding. **[2]**

- $NaBH_4$ has a giant ionic lattice structure.
- The formation of ion–dipole interactions between polar ethanol molecules and the ions results in the release of energy causes the detachment of ions from the crystal lattice for solvation/hydration.
- Hence, $NaBH_4$ is soluble in ethanol.

(ii) One mole of $NaBH_4$ can reduce a maximum of four moles of carbonyl groups. Generally, in an experimental procedure, the reducing agent $NaBH_4$ should be used in excess.

Determine with relevant calculations, whether the student is correct with the quantities proposed in his procedures (**step 1 – 2**). **[2]**

Amount of $NaBH_4$ available = $\dfrac{0.70}{23.0+10.8+4.0}$ = 0.01852 mol

Amount of ethyl acetoacetate available = $\dfrac{40.8\times\frac{30}{1000}}{12.0\times6+10.0+16.0\times3}$ = 9.415×10^{-3} mol

Since $NaBH_4$ can reduced a maximum of 4 carbonyl groups,
mole ratio could be $NaBH_4 \equiv 4$ carbonyl groups

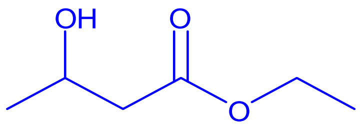
Theoretical amount of $NaBH_4$ required if all carbonyl groups are used up
= $9.415 \times 10^{-3} / 4 = 0.00235$ mol

Amount of $NaBH_4$ available > Amount of $NaBH_4$ required
$\Rightarrow$ $NaBH_4$ is in large excess; the student is correct.

(iii) In **step 4**, hydrochloric acid is added to quench the reaction, producing hydrogen gas and sodium boron chloride. Write an equation for the reaction that took place. **[1]**

$NaBH_4 + 4HCl \longrightarrow NaBCl_4 + 4H_2$

(iv) Draw the **skeletal** formula of the product isolated in the organic layer at the end of the experiment. **[1]**



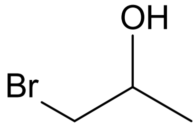
(v) Suggest the function of magnesium sulfate in **step 6**. **[1]**

$MgSO_4$: drying agent to remove water in the organic layer

[Total: 15]

5 Organic reactions can lead to increased variation due to the direction–specific nature of covalent bonds, giving rise to much complexity from using only a small range of elements such as carbon, hydrogen and oxygen.

(a) Propene reacts with aqueous bromine to form a mixture of products, including molecule **A**.



Molecule **A**

(i) State the IUPAC name of molecule **A**.

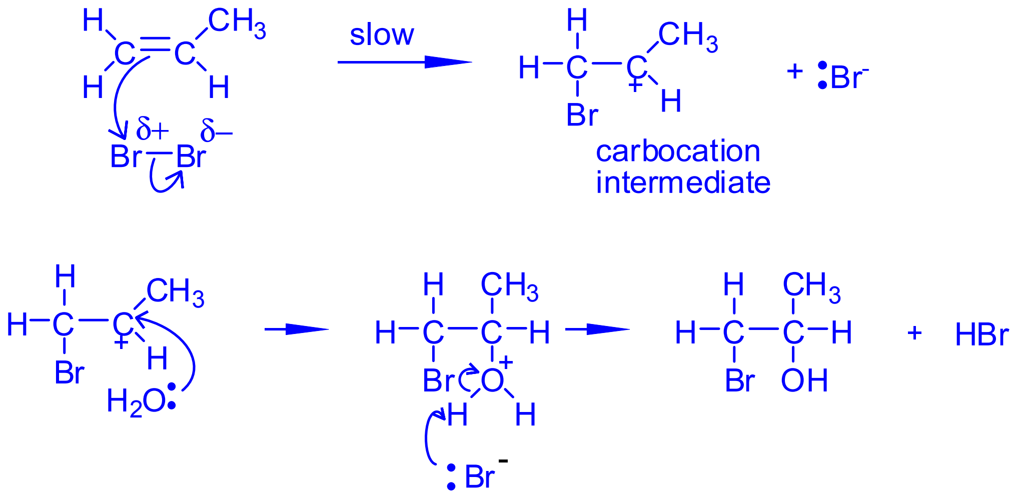
[1]

1–bromopropan–2–ol or 1-bromo-2-propanol

(ii) Draw a mechanism for the reaction between propene and aqueous bromine to form Molecule **A** and hydrogen bromide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

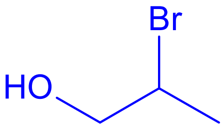
[3]

Electrophilic Addition

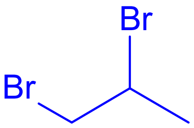


(iii) Molecule **A** is the major product of this reaction. Suggest the structure of two other organic by–products.

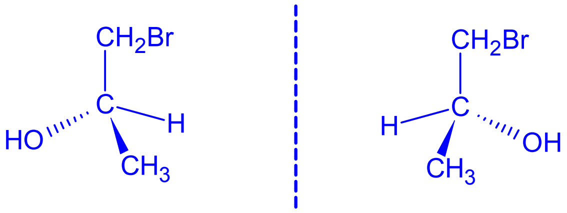
[2]



and



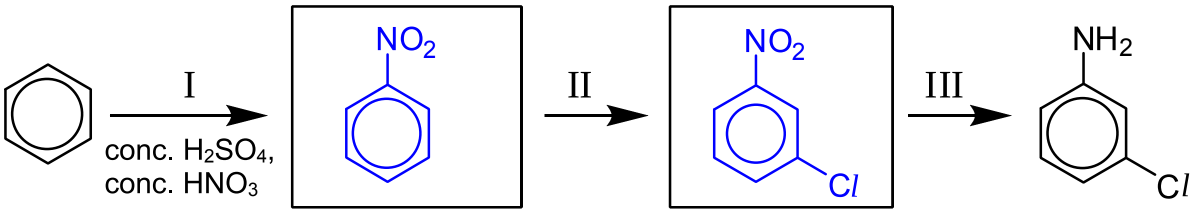
(iv) In the mechanism outlined in **(a)(ii)**, two stereoisomers of **A** are formed in equal amounts. Draw these two stereoisomers and name the type of isomerism displayed. **[2]**



Enantiomerism

(b) 3–chloroaniline can be synthesised from benzene in a 3–step synthesis.

(i) Propose a synthetic route by suggesting the two intermediates compounds and state the reagents and conditions used for steps **II** and **III**. **[4]**



3-chloroaniline

Step II: Cl_2, anhydrous $AlCl_3$, heat

Step III: Sn, in excess conc HC*l*, heat followed by NaOH (aq)

(ii) One of the by–products from the synthesis in **(b)(i)** is HC*l*, which is a strong acid. The acid dissociation constant values, K_a of several hydrogen halides are shown below.

Compound	K_a / mol dm^{-3}
HC*l*	1.3×10^6
HBr	1.0×10^9
HI	3.2×10^9

Account for the relative K_a values. **[2]**

Down the group, the K_a value of HX increases. This means HX dissociates more readily to give H^+. This is because H–X bond strength decreases and becomes easier to break.

[Total: 14]

Name ______________________ **Class: 17S**______ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry **9729/03**

Paper 3 Free Response **13 September 2018**

2 hour

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

This document consists of **17** printed pages (including this cover page).

Section A

Answer **all** questions in this section.

1(a) Explain the variation in melting point of the oxides of the elements in Period 3 (sodium to sulfur), using oxides of three different structure as examples.

Indicate clearly the type of structure and bonding present in the examples you have selected.

[3]

(b) With the aid of the *Data Booklet*, explain the difference in observed melting points of $NaCl$ (801 °C) and MgO (2852 °C).

[2]

(c) Instead of melting like chlorides or oxides, Group 2 nitrates decompose upon heating.

(i) Write an equation, including state symbols, for the thermal decomposition of magnesium nitrate, $Mg(NO_3)_2$.

[1]

(ii) Predict, with reasoning, whether barium nitrate, $Ba(NO_3)_2$, is more or less thermally stable compared with $Mg(NO_3)_2$.

[2]

(d) Chlorides of Period 3 elements dissolve in water to form solutions of differing pH values.

(i) Sketch a graph to illustrate how the pH of the resultant solutions vary across the period (from sodium to phosphorus).

[1]

(ii) Write an equation to illustrate the reaction of PCl_5 with water.

[1]

(iii) Lithium is a Group 1 element. Its chloride, $LiCl$ however behaves similarly to that of a chloride of a Group 2 element when dissolved in water.

Suggest a reason why this would be so.

[1]

(e) Disulfur dichloride, S_2Cl_2 is one of three chlorides of sulfur. It is a liquid at room temperature with a pungent odour. It has a structure in which the central sulfur atoms are bonded by a single covalent bond.

Draw clear diagrams of two possible molecular arrangements of S_2Cl_2, showing clearly the electron pairs around the sulfur atoms. Apply the principles of the VSEPR theory to suggest which arrangement would result in a molecule which could be more stable.

[3]

(f) CCl_4, an important commercial solvent is prepared by the reaction of Cl_2 gas with a sulfur–containing carbon compound. S_2Cl_2 is produced as a by–product. The reaction for the production is shown below.

$$CS_2\,(l) + 3Cl_2\,(g) \longrightarrow CCl_4\,(l) + S_2Cl_2\,(l)$$

(i) Using appropriate data in **Table 1.2** and the energy cycle provided, determine the enthalpy change, $\Delta H^{\ominus}_{rxn}$ for the above reaction.

Table 1.2

	$\Delta H^{\ominus}$ / kJ mol^{-1}
Standard enthalpy change of formation of $CCl_4\,(l)$	–135.4
Standard enthalpy change of combustion of C (s)	–393.5
Standard enthalpy change of formation of $S_2Cl_2\,(l)$	–58.2
Standard enthalpy change of formation of $SO_2\,(g)$	–296.8
$CS_2\,(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g)$	–1077.0
$SO_2\,(g) + Cl_2\,(g) \longrightarrow SO_2Cl_2\,(l)$	+97.3

[2]

$$\begin{tikzcd}
CS_2\,(l) + 3Cl_2\,(g) \arrow[rr, "\Delta H^{\ominus}_{rxn}"] \arrow[d] & & CCl_4\,(l) + S_2Cl_2\,(l) \arrow[dd] \\
CO_2\,(g) + 2SO_2\,(g) + 3\,Cl_2\,(g) & & \\
& 2S\,(s) + 3Cl_2\,(g) + C\,(s) \arrow[ul] &
\end{tikzcd}$$

(ii) CCl_4 could be reacted with limited oxygen according to the following reaction.

$$CCl_4\,(l) + O_2\,(g) \longrightarrow COCl_2\,(g) + Cl_2O\,(g) \qquad \Delta H^{\ominus} = -5.2 \text{ kJ mol}^{-1}$$

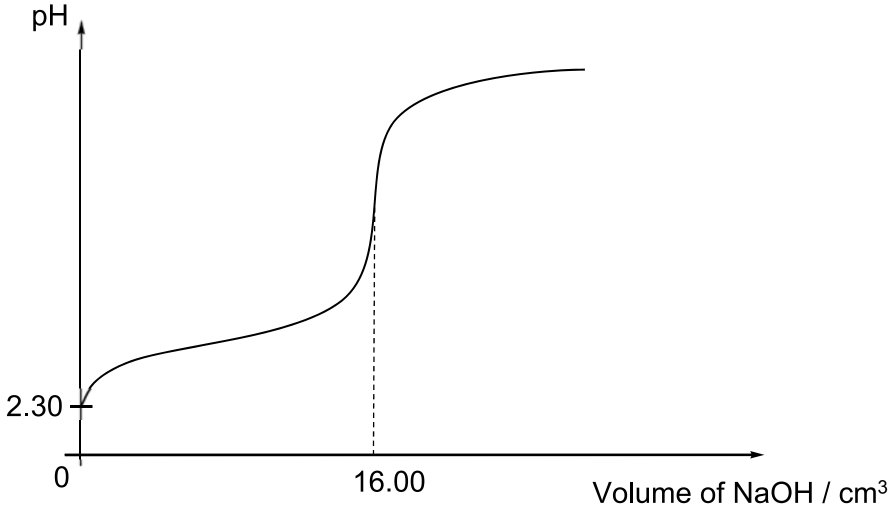
Predict the sign of entropy change, $\Delta S^{\ominus}$ for this reaction and explain whether the reaction would be spontaneous at all temperatures.

[2]

[Total: 18]

2 In analytical chemistry, both quantitative and qualitative information about chemical reactions are established through the use of various chemical methods.

(a) Glycolic acid, $HOCH_2COOH$ is a weak acid used in many cosmetic skin–care products. When a student titrated 25.0 cm^3 of a glycolic acid against 0.250 mol dm^{-3} NaOH, the following titration curve was obtained.



(i) Suggest an appropriate indicator for the titration, giving a reason for your choice.

[1]

(ii) Use the above titration data to calculate the K_a value of glycolic acid.

[2]

(b) The pH levels of skin–care products need to be regulated to prevent degradation of the active ingredients. A buffer solution containing ethanoic acid and its sodium salt, sodium ethanoate can be added to control the pH. The pK_a of ethanoic acid is 4.76.

(i) With the aid of a balanced equation, briefly explain how a solution of ethanoic acid and sodium ethanoate can maintain a fairly constant pH when a small amount of acid is added to this solution.

[1]

(ii) Determine the resulting pH of a 100.0 cm^3 solution containing 0.10 mol dm^{-3} of ethanoic acid and 0.10 mol dm^{-3} of sodium ethanoate when 5.0 x 10^{-4} mol of H_2SO_4 is added to this solution.

[2]

(c) Another student performed a series of thermometric experiments to determine the enthalpy change of neutralisation involving several acids and sodium hydroxide. Her experimental results are summarised in the table below.

Acid	**Enthalpy change of neutralisation, $\Delta H^{\ominus}_{n}$ / kJ mol^{-1}**
hydrochloric acid, HCl	– 57.2
hydrofluoric acid, HF	– 68.6
glycolic acid, $HOCH_2COOH$	– 53.2

(i) Explain why the neutralisation reaction involving glycolic acid is less exothermic than that involving hydrochloric acid.

[1]

Deducing the strength of acids solely from the enthalpy change of neutralisation may not be appropriate as there are exceptions. For instance, the neutralisation reaction between HF, a weak acid and NaOH is significantly more exothermic than that of HC*l* and NaOH.

(ii) Suggest why the neutralisation reaction between HF and NaOH is unexpectedly more exothermic.

[1]

(d) Argentometric titration can be used to determine the amount of sodium chloride present in skin–care products by titrating the sample against silver nitrate, $AgNO_3$. A suitable indicator is one that forms a precipitate of a different colour after all the chloride ions have reacted.

The following are relevant K_{sp} values of some sparingly soluble silver compounds.

	K_{sp}
$AgCl$	1.8×10^{-10} mol^2 dm^{-6}
AgI	7.7×10^{-17} mol^2 dm^{-6}
Ag_3PO_4	1.3×10^{-20} mol^4 dm^{-12}

(i) Write an expression for the solubility product, K_{sp} of Ag_3PO_4.

[1]

(ii) Given that Ag_3PO_4 precipitate is yellow in appearance, by means of suitable calculations, suggest whether potassium phosphate, K_3PO_4 can be used as an indicator in the argentometric titration for the determination of chloride content.

[2]

(iii) With the aid of appropriate equations, explain why silver chloride, AgC*l* is soluble in excess aqueous ammonia.

[3]

(iv) Hence, briefly explain why silver iodide, AgI remains insoluble even in concentrated ammonia solution.

[1]

(e) The distinctive reactions of solid halides with hot concentrated sulfuric acid also provide useful basis for further analysis.

These halides react with hot concentrated sulfuric acid to form white fumes of hydrogen halides.

$$\mathrm{Na}\mathbf{X}\,(s) + H_2SO_4\,(l) \longrightarrow \mathrm{H}\mathbf{X}\,(g) + NaHSO_4\,(s)$$

where **X** = C*l*, Br or I

However, only HBr and HI formed will further react with concentrated H_2SO_4. The main products for these reactions are recorded in the table below.

HC*l*	HBr	HI
no further reaction	red–brown gas	violet fumes
	acidic gas that decolourises acidified purple $KMnO_4$	pungent H_2S gas

(i) Suggest an identity for both the red–brown gas and the acidic gas formed when HBr further reacts with concentrated H_2SO_4.

[1]

(ii) Hence, write an equation for the reaction between HBr and concentrated H_2SO_4.

[1]

(iii) By considering the reactions of HC*l* and HI with concentrated sulfuric acid and the change in oxidation number of sulfur, explain which halide ion is a stronger reducing agent.

[2]

[Total: 19]

3 Transition elements show typical properties that distinguish them from s–block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron, copper and cadmium.

property	calcium	iron	copper	cadmium
relative atomic mass	40.1	55.8	63.5	112.4
atomic radius (metallic) / nm	0.197	0.126	0.128	0.151
ionic radius (2+) / nm	0.099	0.076	0.069	0.097
melting point / ^oC	839	1535	1085	322
density / g cm^{-3}	1.54	7.86	8.92	8.65

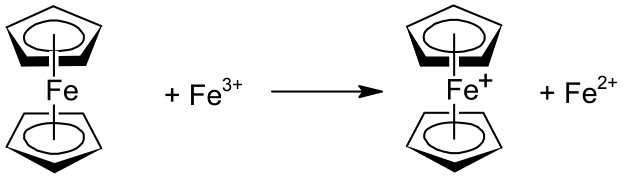
(a) **(i)** Explain why the atomic radii of iron and copper are similar to each other.

[2]

(ii) The melting point of iron is significantly higher than that of calcium and cadmium. Explain this using relevant data from the table and in terms of the structure and bonding in each metal.

[3]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange organometallic solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3*d* orbitals of Fe. A chemist suggested that ferrocene would react with aqueous iron(III) ions to form iron(II) ions as shown below.



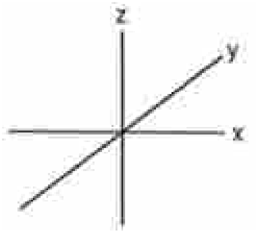
ferrocene

(i) The chemist found the reduction potential of ferrocene, $E^\ominus_{Fe(C_5H_5)_2^+ / Fe(C_5H_5)_2}$ to be +0.63V. Predict if the reaction between ferrocene and iron(III) ions will occur. Calculate $\Delta G^\ominus$ for this reaction.

[2]

(ii) Iron(II) ion forms octahedral complexes, the orbitals are split into two energy levels. Using the Cartesian axes shown below, draw separate labelled diagrams of

1. one of the *d* orbitals at the **lower** energy level in an octahedral complex,
2. one of the *d* orbitals at the **higher** energy level in an octahedral complex.



[2]

(iii) Using your diagrams in **(b)(ii)**, explain why the *d* subshell of a transition metal ion is split into two energy levels in an octahedral complex.

[2]

Most transition element complexes are coloured.

(iv) Explain why ferrocene is orange in colour.

[2]

(v) Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger or smaller split between the two groups of 3*d* orbitals as compared to $C_5H_5^-$.

[2]

(vi) The reaction between $S_2O_8^{2-}$ and I^- is slow in the absence of catalyst. Fe^{2+}(aq) can be used as catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

Explain with the aid of equations how it works.

[3]

(c) Cadmium ions form complexes with primary amines and with 1,2–diaminoethane.

(1) $Cd(H_2O)_6^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 3.6 \times 10^6$

(2) $Cd(H_2O)_6^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 4.2 \times 10^{10}$

K_{stab} is an equilibrium constant that accounts for the formation of a complex. It is a measure of the strength of the interactions between the ligands and the metal centre that come together to form the complex.

The values for $\Delta H^\ominus$ and $\Delta G^\ominus$ for equilibria **(1)** and **(2)**, and the value of $\Delta S^\ominus$ for equilibrium **(1)**, are given in the table below. All values are determined at a temperature of 298 K.

Equilibrium	**$\Delta H^\ominus$ / kJ mol^{-1}**	**$\Delta G^\ominus$ / kJ mol^{-1}**	**$\Delta S^\ominus$ / J mol^{-1} K^{-1}**
(1)	– 57.3	– 37.4	– 66.8
(2)	– 56.5	– 60.7	**–**

(i) Suggest a reason why the $\Delta H^\ominus$ values for the two equilibria are very similar.

[1]

(ii) Calculate the standard entropy change of reaction, $\Delta S^\ominus$ in equilibrium **(2)**.

[2]

(iii) Suggest a reason for the difference between the $\Delta S^\ominus$ you have calculated for equilibrium **(2)** and that for equilibrium **(1)** given in the table.

[1]

(iv) Which of the two complexes is more stable? Give a reason for your answer.

[1]

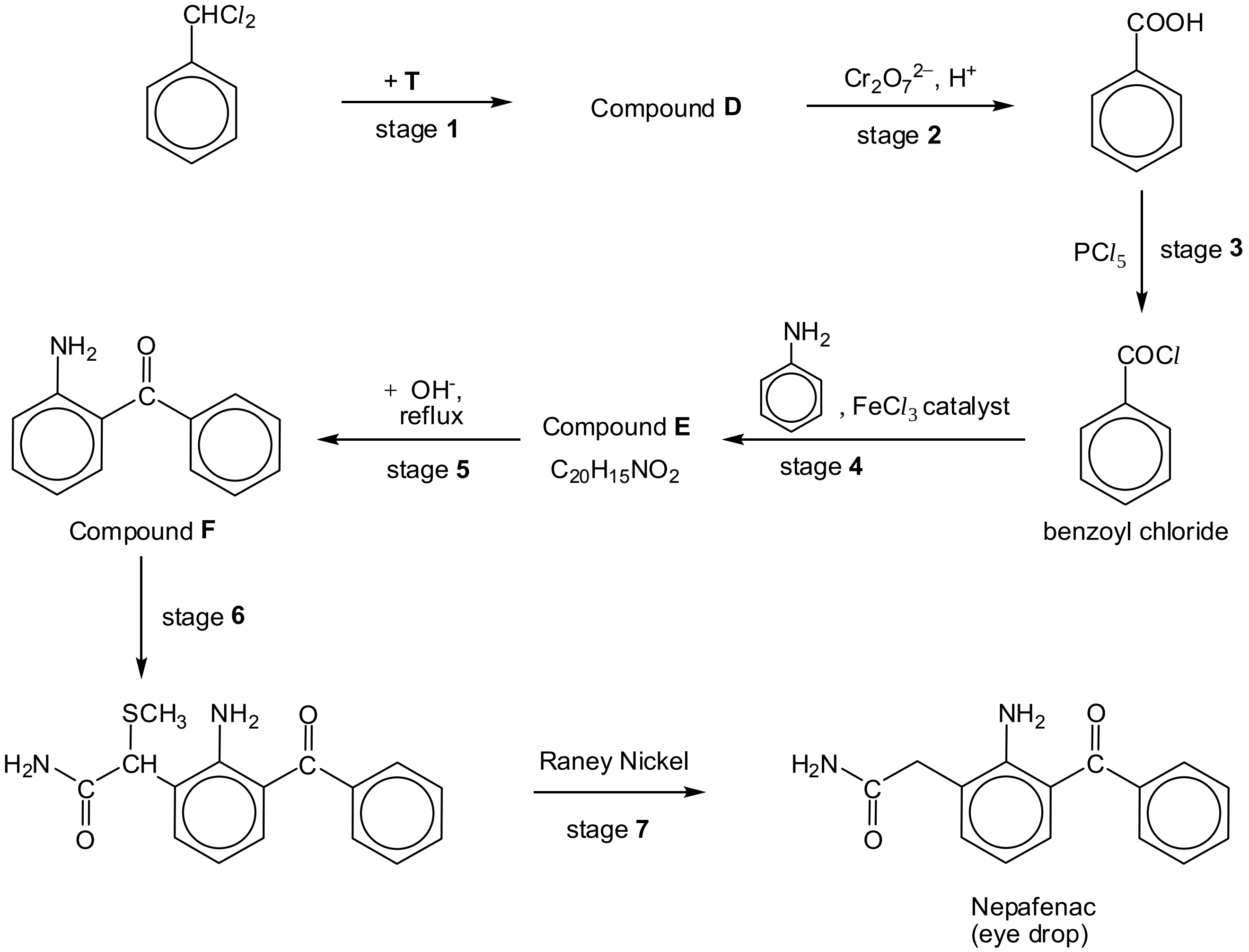
[Total: 23]

Section B

Answer **one** question from this section.

4(a) *Nepafenac* is a prescription eye drop that is used to treat pain and inflammation associated with eye surgery.

The following scheme shows a synthesis of *Nepafenac*.



(i) State the type of reaction occurring in stage **3** and stage **7**.

[2]

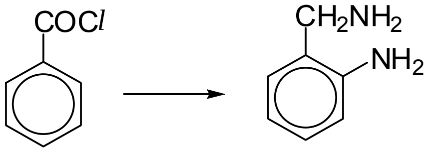
(ii) Draw the structure of compound **D**. Suggest the reagent and conditions required in stage **1**.

[2]

(iii) In stage **4**, two reactions are involved. Draw the structure of compound **E** and state the reactions that occurred.

[2]

(iv) Benzoyl chloride can be converted into 2–aminobenzylamine, an important starting material in the synthesis of quinazoline, a source of useful pharmacophores for new drug development.

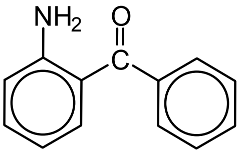


benzoyl chloride 2-aminobenzylamine

Suggest a 4–step synthesis of 2–aminobenzylamine from benzoyl chloride. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[4]

(v) A student made a statement regarding a reaction with compound **F**: *"Cyanide, CN^-, is acting as a **Bronsted–Lowry base** to attack the carbonyl group of compound **F** to form a cyanohydrin."*

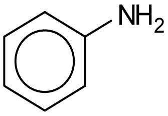
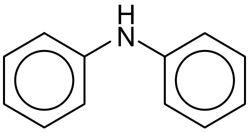


Compound **F**

Based on your understanding of a *Bronsted–Lowry* base, explain why the student's statement is wrong.

[1]

(vi) Data about phenylamine and diphenylamine are given in the table below.

Compound	 phenylamine	 diphenylamine
pK_b value	9.39	13.21

Give **two** reasons, why pK_b of phenylamine is lower than that of diphenylamine.

[2]

(b) Compound **J**, $C_{10}H_8O_3$, does not decolourise bromine water nor give effervescence with magnesium strip. **J** gives a silver mirror with Tollens' reagent but does not give a precipitate with hot alkaline Cu^{2+} solution.

On prolonged heating with acidified $KMnO_4$, **J** gives benzene–1,2–3–tricarboxylic acid as the only organic product. When heated with dilute H_2SO_4, **J** forms compound **K**, $C_{10}H_{10}O_4$. **K** gives a yellow precipitate with alkaline aqueous iodine.

J reacts with Li*Al*H_4 to form compound **L** (with an internal plane of symmetry), $C_{10}H_{14}O_3$. However, **J** forms compound **M**, $C_{10}H_{10}O_3$ with $NaBH_4$.

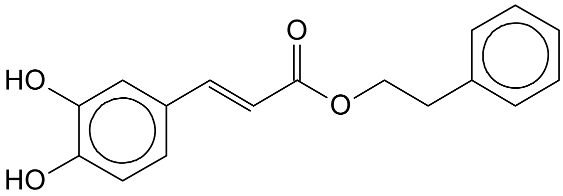
All compounds are optically active but only **K** reacts with sodium carbonate.

Suggest the structure for **J**, **K**, **L** and **M** and explain the reactions described.

[7]

[Total: 20]

5 Caffeic acid phenethyl ester (CAPE) is a natural occurring compound, found in propolis from honeybee hives. It is currently being studied for its anti–carcinogenic and anti–inflammatory properties. It is the ester of caffeic acid and 2–phenylethanol.



caffeic acid phenethyl ester (CAPE)

(a) Till date, there has been two well–established reaction schemes to synthesise CAPE. Study **Fig. 2.1** and **Fig 2.2** carefully and answer the questions that follow.

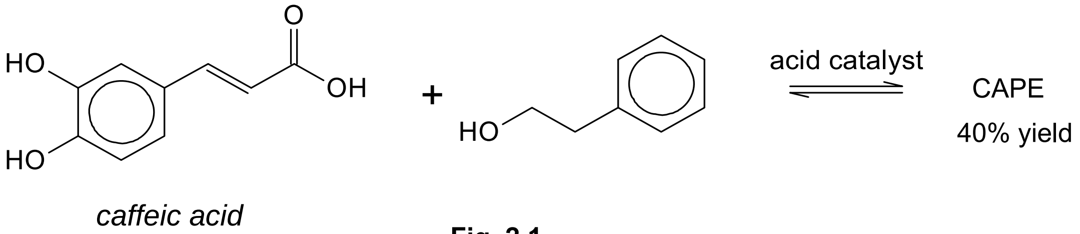


Fig. 2.1

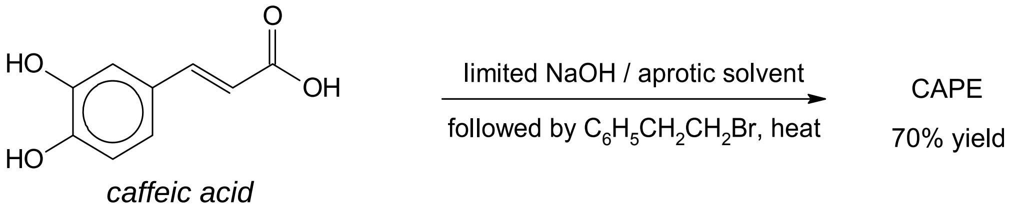


Fig. 2.2

(i) State the type of reaction occurring in each of the above synthesis method.

[2]

(ii) To improve the yield of CAPE in **Fig 2.1**, a student suggested using the acyl chloride derivative of caffeic acid instead. Comment on the validity of his suggestion.

[2]

(iii) Explain why NaOH has to be added in limited amount rather than in large excess in **Fig 2.2**.

[1]

(iv) A protic solvent is one that has labile proton(s) and readily donates its proton(s). Conversely an aprotic solvent does not have any labile proton. Suggest why is it important to use an aprotic solvent in **Fig 2.2**.

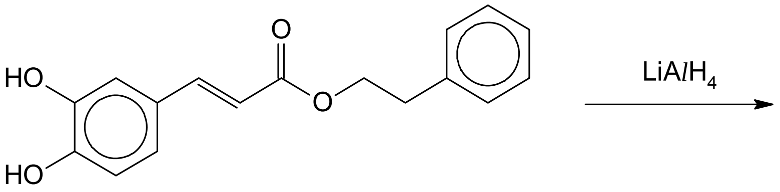
[1]

(v) The reported yield in **Fig. 2.2** is only 70%, as there are other by–products. Draw the skeletal formula of one possible by–product, assuming that caffeic acid reacts with $C_6H_5CH_2CH_2Br$ in a 1:1 ratio.

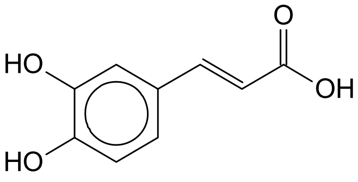
[1]

(vi) Draw the structure of the resultant product(s) when CAPE is reacted with $LiAlH_4$.

[1]



(b) The structure of *caffeic acid* is shown below.



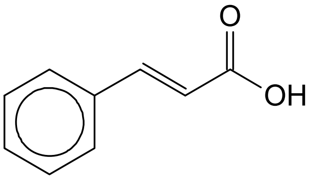
caffeic acid

(i) *Caffeic acid* contains two organic functional groups with pK_a values lower than that of an alcohol. Identify these functional groups.

Compare and account for the relative pK_a values of these two organic groups.

[3]

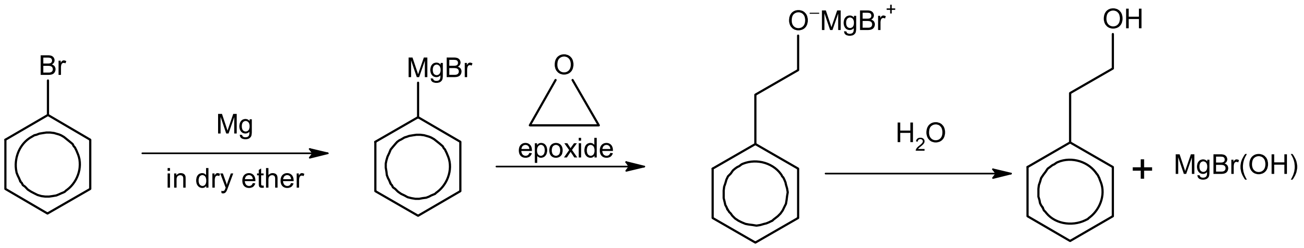
(ii) Suggest a chemical test that can be carried out to distinguish between a sample of *caffeic acid* and *cinnamic acid.*



cinnamic acid

[2]

(c) The synthesis of 2–phenylethanol from bromobenzene is shown below.



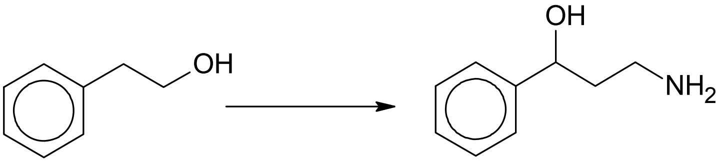
In the above synthesis, a Grignard reagent, C_6H_5MgBr is generated. Once generated, the Grignard reagent behaves as a nucleophile. The C_6H_5 in C_6H_5MgBr behaves like an anion, $C_6H_5^-$ and is a strong Lewis base. The Grignard reagent is useful for the formation of carbon–carbon bonds.

The reaction between the Grignard reagent, C_6H_5MgBr and the epoxide, C_2H_4O is a bimolecular reaction and the intermediate formed will subsequently react with water to form 2–phenylethanol.

From the information provided, outline the mechanism to account for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons by curly arrows.

[2]

(d) Suggest a 4–step synthesis of 3–amino–1–phenylpropan–1–ol from 2–phenylethanol.



3-amino-1-phenylpropan-1-ol

The synthesis involves an intermediate compound that decolourises aqueous bromine in the dark. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[3]

(e) A 0.460 g sample of gaseous methanoic acid, HCOOH was found to only occupy a volume of 173 cm^3 at a temperature of 160°C and a pressure of 1.04×10^5 Pa.

Using the ideal gas equation and the above information, determine the molar mass of this gaseous sample. Hence, draw a possible structure at this temperature.

[2]

[Total: 20]

END OF PAPER

Cover Page for P3 Q1 & 2

Name ___________________________ Class: 17S_______ Reg Number: _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

13 September 2018

INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer **all** questions in Section **A.**

Answer **only ONE** question in Section **B.**

Begin each question on a ***fresh page*** of writing paper.

Fasten your answers for Q1 & 2 behind this Cover Page.

You are advised to spend about **30 min each question.**

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded the need for good English and clear presentation in your answers.

Examiner's Use		
Paper 3	**Q1**	**/ 18**
	Q2	**/ 19**

Cover Page for P3 Q3 & 4 or 5

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Write your name, class and register number in the spaces provided at the top of this page.

Answer **all** questions in Section **A.**

Answer **only ONE** question in Section **B. CIRCLE the question that you have attempted.**

Begin each question on a ***fresh page*** of writing paper.

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Examiner's Use		
Paper 3	**Q3**	**/ 23**
	Q4	**/ 20**
	Q5	**/ 20**

Name Suggested Solutions **Class: 17S_______** **Reg Number: _____**

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry **9729/03**

Paper 3 Free Response **13 September 2018**

2 hour

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets [ ] at the end of each question or part question.

You are reminded of the need for good English and clear presentation in your answers.

This document consists of **15** printed pages (including this cover page).

Section A

Answer **all** questions in this section.

1(a) Explain the variation in melting point of the oxides of the elements in Period 3 (sodium to sulfur), using oxides of three different structure as examples.

Indicate clearly the type of structure and bonding present in the examples you have selected.

[3]

High melting point for NaO_2, MgO_2 (or Al_2O_3)
– giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged ions

High melting point (intermediate between that of NaO_2 and MgO) for SiO_2
– giant (3D) molecular structure with strong covalent bonds between (Si and O) atoms

Low melting point (lower than that of NaO_2) for P_4O_{10}, SO_3
– simple molecular structure with weak instantaneous dipole – induced dipole attractive forces between molecules.

(b) With the aid of the *Data Booklet*, explain the difference in observed melting points of NaC*l* (801 °C) and MgO (2852 °C)

[2]

$$\text{Lattice energy} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Charge of cation, q_+: $Na^+ < Mg^{2+}$
Radius of cation, r_+: Na^+ (0.095 nm) > Mg^{2+} (0.065 nm)

Charge of anion, q_-: $Cl^- < O^{2-}$
Radius of anion, r_-: Cl^- (0.181 nm) > O^{2-} (0.140 nm)

Lattice energy of NaC*l* is less exothermic than that of MgO ⇒ Melting point: NaC*l* < MgO

(c) Instead of melting like chlorides or oxides, Group 2 nitrates decompose upon heating.

(i) Write an equation, including state symbols, for the thermal decomposition of magnesium nitrate, $Mg(NO_3)_2$.

[1]

$$Mg(NO_3)_2\,(s) \longrightarrow MgO\,(s) + 2NO_2\,(g) + \frac{1}{2}O_2\,(g)$$

(ii) Predict, with reasoning, whether barium nitrate, $Ba(NO_3)_2$, is more or less thermally stable compared with $Mg(NO_3)_2$.

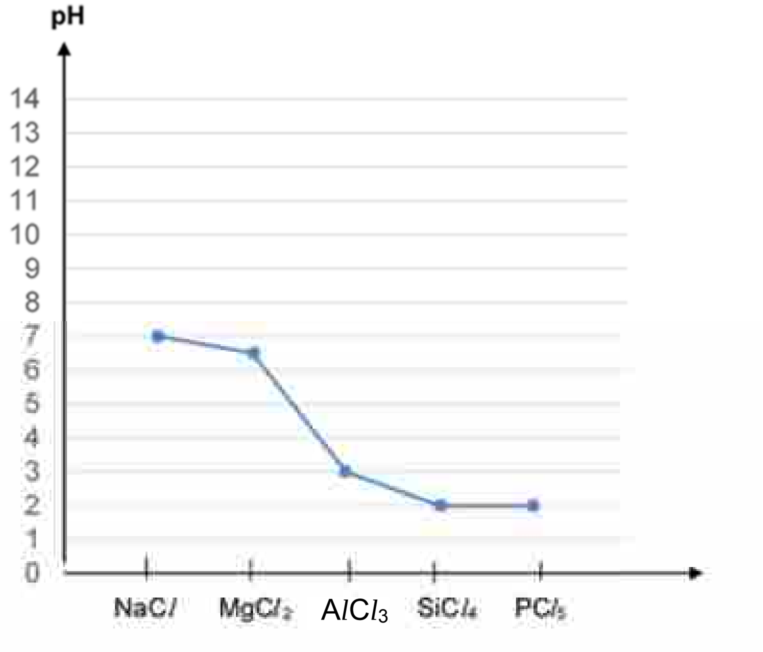
[2]

$Ba(NO_3)_2$ is more thermally stable compared with $Mg(NO_3)_2$.
Ba^{2+} is less polarising due to lower charge density than Mg^{2+}, hence it is less able to polarise electron cloud of NO_3^- to a significant extent.

(d) Chlorides of Period 3 elements dissolve in water to form solutions of differing pH values.

(i) Sketch a graph to illustrate how the pH of the resultant solutions vary across the period (from sodium to phosphorus).

[1]



(ii) Write an equation to illustrate the reaction of PCl_5 with water.

[1]

(iii) Lithium is a Group 1 element. Its chloride, $LiCl$ however behaves similarly to that of a chloride of a Group 2 element when dissolved in water.

Suggest a reason why this would be so.

[1]

Similar to $MgCl_2$ as the metal cations have similar charge densities (hence diagonal relationship)

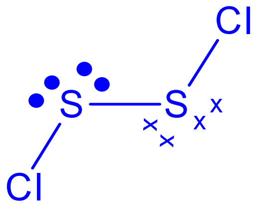
(e) Disulfur dichloride, S_2Cl_2 is one of three chlorides of sulfur. It is a liquid at room temperature with a pungent odour. It has a structure in which the central sulfur atoms are bonded by a single covalent bond.

Draw clear diagrams of two possible molecular arrangements of S_2Cl_2, showing clearly the electron pairs around the sulfur atoms. Apply the principles of the VSEPR theory to suggest which arrangement would result in a molecule which could be more stable.

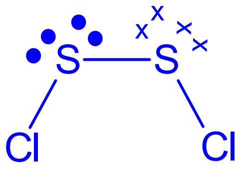
[3]

To minimise repulsion and maximise stability, the 4 electron pairs are directed to corners of a regular tetrahedron. Since lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion, the shape is bent about each S atom.

Arrangement 1 is more stable over arrangement 2 as the lone pairs of electrons are pointed away from each other (in opposite directions), which minimises the repulsion.



Arrangement 1



Arrangement 2

(f) CCl_4, an important commercial solvent is prepared by the reaction of Cl_2 gas with a sulfur–containing carbon compound. S_2Cl_2 is produced as a by–product. The reaction for the production is shown below.

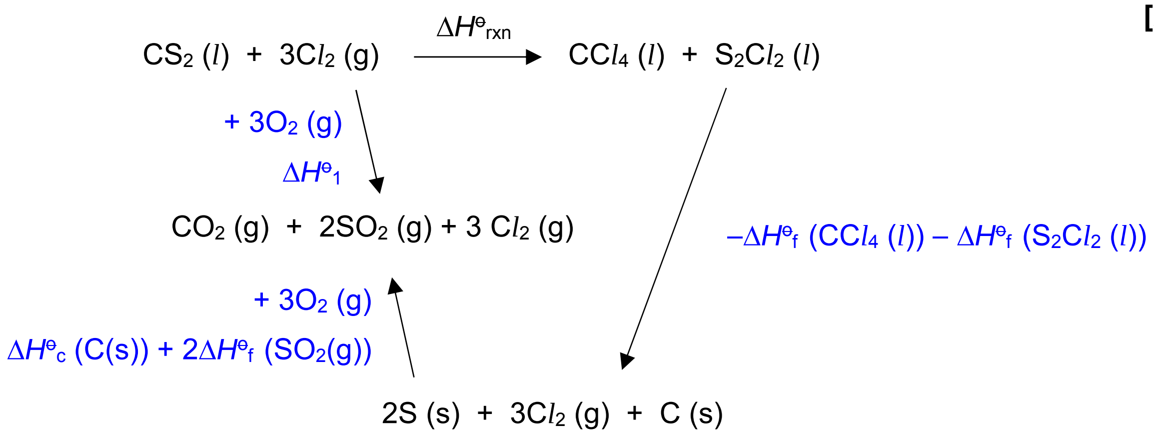
$$CS_2\,(l) + 3Cl_2\,(g) \longrightarrow CCl_4\,(l) + S_2Cl_2\,(l)$$

(i) Using appropriate data in **Table 1.2** and the energy cycle provided, determine the enthalpy change, ΔH°_{rxn} for the above reaction.

Table 1.2

	ΔH° / kJ mol^{-1}
Standard enthalpy change of formation of $CCl_4\,(l)$	–135.4
Standard enthalpy change of combustion of C (s)	–393.5
Standard enthalpy change of formation of $S_2Cl_2\,(l)$	–58.2
Standard enthalpy change of formation of SO_2 (g)	–296.8
$CS_2\,(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g)$	–1077.0
$SO_2\,(g) + Cl_2\,(g) \longrightarrow SO_2Cl_2\,(l)$	+97.3

[2]



By Hess' Law,

$$\Delta H^\circ_{rxn} = \Delta H^\circ_1 - \Delta H^\circ_c\,(C(s)) - 2\Delta H^\circ_f\,(SO_2(g)) \;\; -\Delta H^\circ_f\,(CCl_4\,(l)) - \Delta H^\circ_f\,(S_2Cl_2\,(l))$$

$$\Delta H^\circ_{rxn} = (-1077) - (-393.5) - 2(-296.8) + (-135.4) + (-58.2)$$
$$= -283.5 \text{ kJ mol}^{-1}$$

(ii) CCl_4 could be reacted with limited oxygen according to the following reaction.

$$CCl_4\,(l) + O_2\,(g) \longrightarrow COCl_2\,(g) + Cl_2O\,(g) \qquad \Delta H^\circ = -5.2 \text{ kJ mol}^{-1}$$

Predict the sign of entropy change, ΔS° for this reaction and explain whether the reaction would be spontaneous at all temperatures.

[2]

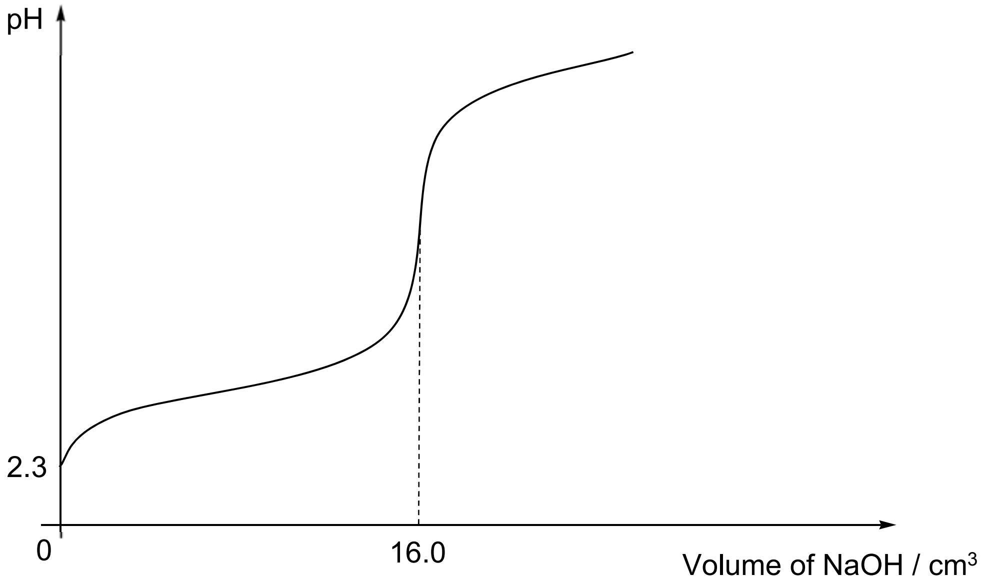
ΔS is positive as there is to an increase in number of moles of gas (from 1 to 2), hence an increase in the entropy / disorder of the system.

$\Delta G = \Delta H - T\Delta S$
When $\Delta S = +ve$, then $-T\Delta S = -$ve, ➔ Both ΔH and $-T\Delta S$ are negative
$\Delta G < 0$ (–ve) $\Rightarrow$ spontaneous for all temperature.

[Total: 18]

2 In analytical chemistry, both quantitative and qualitative information about chemical reactions are established through the use of various chemical methods.

(a) Glycolic acid, $HOCH_2COOH$ is a weak acid used in many cosmetic skin–care products. When a student titrated 25.0 cm^3 of a glycolic acid against 0.250 mol dm^{-3} NaOH, the following titration curve was obtained.



(i) Suggest an appropriate indicator for the titration, giving a reason for your choice.

[1]

Phenolphthalein
The pH transition range of the indicator lies within the rapid pH change over the equivalence point

(ii) Use the above titration data to calculate the K_a value of glycolic acid.

[2]

$HA \equiv OH^-$
Amount of NaOH = Amount of HA in 25.0 cm^3 of solution

$$= \frac{16.0}{1000} \times 0.250 = 4.00 \times 10^{-3} \text{ mol}$$

$$[HA] = \frac{4.00\times10^{-3}}{\frac{25.0}{1000}} = 0.160 \text{ mol dm}^{-3}$$

$$[H^+] = 10^{-2.3} = 5.01 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_a = \frac{\left(5.01\times10^{-3}\right)^2}{0.160} = 1.57 \times 10^{-4} \text{ mol dm}^{-3}$$

(b) The pH level of skin–care products need to be regulated to prevent degradation of the active ingredients. A buffer solution containing ethanoic acid and its sodium salt, sodium ethanoate can be added to control the pH. The pK_a of ethanoic acid is 4.76.

(i) With the aid of a balanced equation, briefly explain how a solution of ethanoic acid and sodium ethanoate can maintain a fairly constant pH when a small amount of acid is added to this solution.

[1]

When a small amount of H^+ is added, $CH_3COO^- + H^+ \longrightarrow CH_3COOH$

H^+ added is removed as CH_3COOH. $[H^+]$ slightly changed and pH remains fairly constant

(ii) Determine the resultant pH of a 100.0 cm^3 solution containing 0.10 mol dm^{-3} of ethanoic acid and 0.10 mol dm^{-3} of sodium ethanoate when 5.0 x 10^{-4} mol of H_2SO_4 is added to this solution.

[2]

$H_2SO_4 \equiv 2H^+$
Amount of H^+ added = 1.0 x 10^{-3} mol

$[H^+]$ = 1.0 x 10^{-2} mol dm^{-3}

$[CH_3COOH]_{new}$ = 0.10 + 0.010 = 0.110 mol dm^{-3}
$[CH_3COO^-]_{new}$ = 0.10 – 0.010 = 0.09000 mol dm^{-3}

$$pH = pK_a + \log_{10}\frac{\left[CH_3COO^-\right]_{new}}{[CH_3COOH]_{new}} = 4.76 + \log_{10}\left(\frac{0.0900}{0.110}\right) = 4.67 \text{ (2 d.p.)}$$

(c) Another student performed a series of thermometric experiments to determine the enthalpy change of neutralisation involving several acids and sodium hydroxide. Her experimental results are summarised in the table below.

Acid	**Enthalpy change of neutralisation, $\Delta H^\ominus_n$ / kJ mol^{-1}**
hydrochloric acid, HC*l*	– 57.2
hydrofluoric acid, HF	– 68.6
glycolic acid, $HOCH_2COOH$	– 53.2

(i) Explain why the neutralisation reaction involving glycolic acid is less exothermic than that involving hydrochloric acid.

[1]

Glycolic acid is a weak acid and is only slightly dissociated in aqueous solution. Some of the energy evolved from the neutralisation process is used to further dissociate the weak acid completely.

Deducing the strength of acids solely from the enthalpy change of neutralisation may not be appropriate as there are exceptions. For instance, the neutralisation reaction between HF, a weak acid and NaOH is significantly more exothermic than that of HC*l* and NaOH.

(ii) Suggest why the neutralisation reaction between HF and NaOH is unexpectedly more exothermic.

[1]

On dissociation, the small F^- ions can form strong ion–dipole interactions with water molecules that releases high amount of heat.

OR

The enthalpy change of hydration of F^- ions is very exothermic.

(d) Argentometric titration can be used to determine the amount of sodium chloride present in skin–care products by titrating the sample against silver nitrate, $AgNO_3$. A suitable indicator is one that forms a precipitate of a different colour after all the chloride ions have reacted.

The following are relevant K_{sp} values of some sparingly soluble silver compounds.

	K_{sp}
AgC*l*	1.8×10^{-10} mol^2 dm^{-6}
AgI	7.7×10^{-17} mol^2 dm^{-6}
Ag_3PO_4	1.3×10^{-20} mol^4 dm^{-12}

(i) Write an expression for the solubility product, K_{sp} of Ag_3PO_4.

[1]

K_{sp} of $Ag_3PO_4 = [Ag^+]^3\,[PO_4^{3-}]$

(ii) Given that Ag_3PO_4 precipitate is yellow in appearance, by means of suitable calculations, suggest whether potassium phosphate, K_3PO_4 can be used as an indicator in the argentometric titration for the determination of chloride content.

[2]

Let the solubility of AgC*l* be *s*.

$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$

$K_{sp}\ (AgCl) = [Ag^+][Cl^-] = s^2$

Solubility of AgC*l* = $[Ag^+] = \sqrt{1.8\times10^{-10}} = 1.34 \times 10^{-5}$ mol dm^{-3}

Let the solubility of Ag_3PO_4 be *s*.

$Ag_3PO_4\ (s) \rightleftharpoons 3Ag^+\ (aq) + PO_4^{3-}\ (aq)$

$K_{sp}\ (Ag_3PO_4) = [Ag^+]^3\,[PO_4^-] = (3s)^3\,(s) = 27s^4$

Solubility of $Ag_3PO_4 = \sqrt[4]{\dfrac{1.3\times10^{-20}}{27}} = 4.68 \times 10^{-6}$ mol dm^{-3}

Since solubility of Ag_3PO_4 is lower, it has the tendency to precipitate out first before most Cl^- has been precipitated therefore it is not suitable to be used as an indicator.

(iii) With the aid of appropriate equations, explain why silver chloride, Ag*Cl* is soluble in excess aqueous ammonia.

[3]

When aqueous ammonia is added, a soluble complex cation $[Ag(NH_3)_2]^+(aq)$ is formed, hence decreasing $[Ag^+ (aq)]$.

$$Ag^+(aq) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+ (aq) \text{ ——— } (1)$$

By Le Chatelier's Principle, the equilibrium position in (2) shifts right to increase $[Ag^+(aq)]$ but Ag^+ will be used to form more $[Ag(NH_3)_2]^+$.

$$AgCl\,(s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq) \text{ ——— } (2)$$

Overall, $[Ag^+(aq)]$ decreases and ionic product of $[Ag^+][Cl^-]$ decreases to a value lower than its relatively higher K_{sp}. Hence white ppt of Ag*Cl* dissolves.

(iv) Hence, briefly explain why silver iodide, AgI, remains insoluble even in concentrated ammonia solution.

[1]

K_{sp} of AgI is relatively much lower than that of Ag*Cl*. AgI remains insoluble in concentrated NH_3 as its ionic product, $[Ag^+][I^-]$ which decreases will still be higher than its K_{sp} value.

(e) The distinctive reactions of solid halides with hot concentrated sulfuric acid also provide useful basis for further analysis.

These halides react with hot concentrated sulfuric acid to form white fumes of hydrogen halides.

$$Na\mathbf{X}\,(s) + H_2SO_4\,(l) \longrightarrow H\mathbf{X}\,(g) + NaHSO_4\,(s)$$

where **X** = C*l*, Br or I

However, only HBr and HI formed will further react with concentrated H_2SO_4. The main products for these reactions are recorded in the table below.

HC*l*	HBr	HI
no further reaction	red–brown gas	violet fumes
	acidic gas that decolourises acidified purple $KMnO_4$	pungent H_2S gas

(i) Suggest an identity for both the red–brown gas and the acidic gas formed when HBr further reacts with concentrated H_2SO_4.

[1]

Red–brown gas is Br_2 and acidic gas is SO_2.

(ii) Hence, write an equation for the reaction between HBr and concentrated H_2SO_4.

[1]

$$2HBr\,(g) + H_2SO_4\,(l) \longrightarrow Br_2\,(g) + SO_2\,(g) + 2H_2O\,(l)$$

(iii) By considering the reactions of HC*l* and HI with concentrated sulfuric acid and the change in oxidation number of sulfur, explain which halide ion is a stronger reducing agent.

[2]

Cl^- is a weaker reducing agent OR I^- is a stronger reducing agent.

Cl^- does not react with H_2SO_4 so there is no change in oxidation number of sulfur.

I^- is able to reduce H_2SO_4 to H_2S. There is a decrease in the oxidation number of S from +6 in H_2SO_4 to –2 in H_2S.

[Total: 19]

3 Transition elements show typical properties that distinguish them from s–block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron, copper and cadmium.

property	calcium	iron	copper	cadmium
relative atomic mass	40.1	55.8	63.5	112.4
atomic radius (metallic) / nm	0.197	0.126	0.128	0.151
ionic radius (2+) / nm	0.099	0.076	0.069	0.097
melting point / °C	839	1535	1085	322
density / g cm^{-3}	1.54	7.86	8.92	8.65

(a) **(i)** Explain why the atomic radii of iron and copper are similar to each other.

[2]

- Nuclear charge increases from Fe to Cu. The electrons in Cu are added to the inner 3d orbitals and provide more shielding for the 4s electrons.
- Increase in nuclear charge slightly outweighs the increase in shielding effect. Effective nuclear charge increases only slightly.
- Hence, atomic radius of Fe and Cu are similar.

(ii) The melting point of iron is significantly higher than that of calcium and cadmium. Explain this using relevant data from the table and in terms of the structure and bonding in each metal.

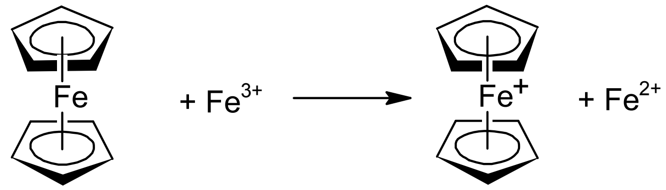
[3]

Fe, Cd and Ca have giant metallic structure. Both 3d and 4s electrons of Fe and Cd are involved in the delocalized in metallic bonding while only the 4s electrons for Ca is involved.

The ionic radius of Fe^{2+} is also smaller than that of Ca^{2+} and Cd^{2+} resulting in higher charge density. This results in stronger electrostatic forces of attraction between the Fe^{2+} cations and sea of delocalised electrons.

Hence, Fe has a higher melting point than Ca and Cd.

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange organometallic solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3*d* orbitals of Fe. A chemist suggested that ferrocene would react with aqueous iron(III) ions to form iron(II) ions as shown below.



ferrocene

(i) The chemist found the reduction potential ferrocene, $E^\ominus_{Fe(C_5H_5)_2^+ / Fe(C_5H_5)_2}$ to be +0.63V. Predict if the reaction between ferrocene and iron(III) ions will occur. Calculate $\Delta G^\ominus$ for this reaction.

(ii) **[2]**

$Fe(C_5H_5)_2^+ + e \rightleftharpoons Fe(C_5H_5)_2$ $E^\ominus = +0.63$ V (Oxidation)

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V (Reduction)

Overall: $Fe^{3+} + Fe(C_5H_5)_2 \longrightarrow Fe^{2+} + Fe(C_5H_5)_2^+$

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxid}$$
$$= 0.77 - 0.63$$
$$= +0.14\ \text{V}$$

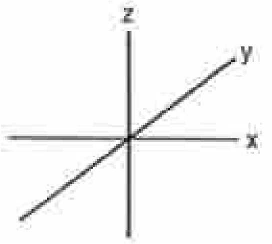
Since $E^\ominus_{cell} > 0 \Rightarrow$ Reaction is spontaneous

$$\Delta G^\theta = -nFE^\theta_{cell}$$
$$= -(1 \times 96500 \times 0.14) = -13.51\ \text{kJ mol}^{-1}$$

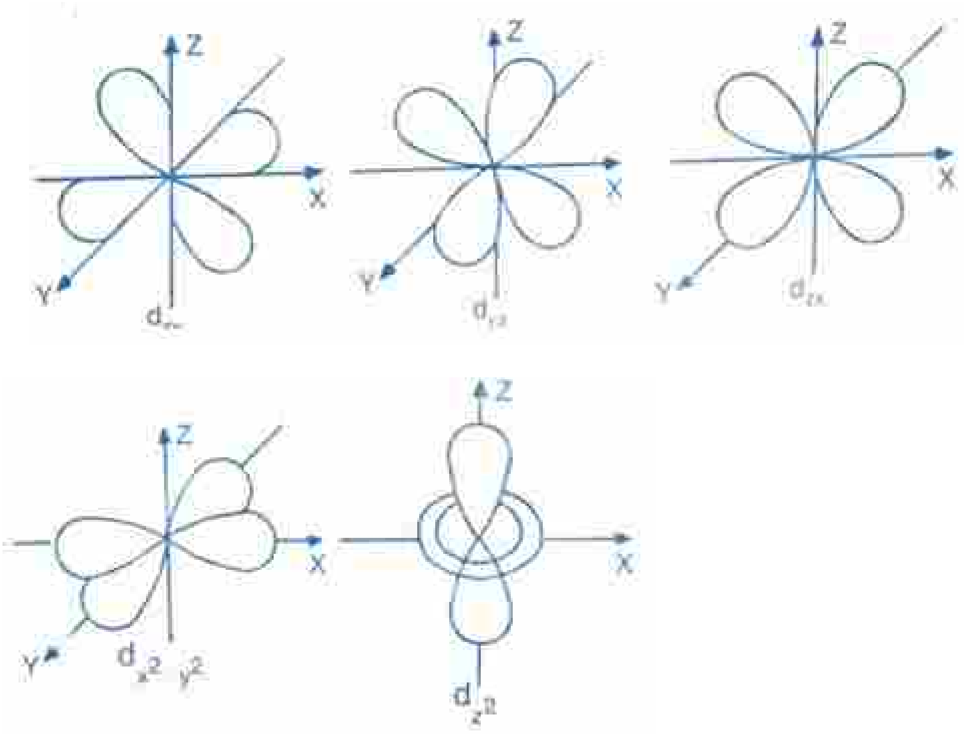
(iii) Iron(II) ion forms octahedral complexes, the orbitals are split into two energy levels. Using the Cartesian axes shown below, draw separate labelled diagrams of

1. one of the *d* orbitals at the **lower** energy level in an octahedral complex,

2. one of the *d* orbitals at the **higher** energy level in an octahedral complex.



[2]



(iii) Using your diagrams in **(b)(ii)**, explain why the *d* subshell of a transition metal ion is split into two energy levels in an octahedral complex.

- The $d_{x^2-y^2}$ orbital and the d_{z^2} orbitals have their lobes pointing at the ligands along the x and y axes, and z axis respectively, hence they experience greater repulsion from the ligands. On the other hand, the d_{xy}, d_{xz} and d_{yz} orbitals experienced less repulsion as their lobes are in between the coordinate axes.

- As a result, the five d orbitals are split into 2 energy levels, with the $d_{x^2-y^2}$ and d_{z^2} orbitals having the higher energy level and the d_{xy}, d_{xz} and d_{yz} orbitals having the lower energy level.

Most transition element complexes are coloured.

(iv) Explain why ferrocene is orange in colour.

[2]

Fe^{2+} ion has partially filled *d* orbitals. In the presence of $C_2H_5^-$ ligands, the *d* orbitals are split into two groups with an energy gap, ΔE. This effect is known as *d* orbital splitting.

During the d–d transition, the *d* electrons from the lower energy d orbitals absorb a blue wavelength of light from the visible spectrum and gets promoted to a *higher* energy *d* orbital. The orange colour observed in ferrocene is complementary of the blue colour absorbed.

(v) Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger or smaller split between the two groups of 3*d* orbitals as compared to $C_5H_5^-$.

[2]

With H_2O ligands, the green Fe^{2+}(aq) ion absorbed red which has a longer wavelength and lower ΔE than the blue absorbed when $C_5H_5^-$ is the ligand.

Hence, H_2O ligands causes a smaller splitting of the 3*d* orbitals of Fe^{2+}.

(vi) The reaction between $S_2O_8^{2-}$ and I^- is slow in the absence of catalyst. Fe^{2+}(aq) can be used as catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

Explain with the aid of equations how it works.

[3]

With Fe^{2+} (aq) catalyst:

Step 1: Fe^{2+} intermediate reacts with $S_2O_8^{2-}$

Equation 1 : $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$E^\ominus_{cell} = 2.01 - 0.77 = +1.24 \text{ V} > 0 \Rightarrow$ reaction is spontaneous

Step 2: Fe^{3+} reacts with I^-.

Equation 2 : $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$

$E^\ominus_{cell} = 0.77 - 0.54 = +0.23 \text{ V} > 0 \Rightarrow$ reaction is spontaneous

Overall equation : $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

Both steps are spontaneous since oppositely charged ions are involved and attract each other. Activation energy is lowered and thus reaction is faster (or kinetically feasible).

(c) Cadmium ions form complexes with primary amines and with 1,2–diaminoethane.

(1) $Cd(H_2O)_6^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 3.6 \times 10^6$

(2) $Cd(H_2O)_6^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 4.2 \times 10^{10}$

K_{stab} is an equilibrium constant that accounts for the formation of a complex. It is a measure of the strength of the interactions between the ligands and the metal centre that come together to form the complex.

The values for $\Delta H^\ominus$ and $\Delta G^\ominus$ for equilibria **(1)** and **(2)**, and the value of $\Delta S^\ominus$ for equilibrium **(1)**, are given in the table below. All values are determined at a temperature of 298 K.

Equilibrium	**$\Delta H^\ominus$ / kJ mol^{-1}**	**$\Delta G^\ominus$ / kJ mol^{-1}**	**$\Delta S^\ominus$ / J mol^{-1} K^{-1}**
(1)	– 57.3	– 37.4	– 66.8
(2)	– 56.5	– 60.7	**–**

(i) Suggest a reason why the $\Delta H^\ominus$ values for the two equilibria are very similar.

[1]

Each complex is formed by making four N–Cd bonds and breaking six O–Cd bonds

OR

same types of / similar bonds forming / breaking

OR

same number of bonds forming / breaking

(ii) Calculate the standard entropy change of reaction, $\Delta S^\ominus$ in equilibrium **(2)**.

[2]

$$\Delta S = (\Delta H - \Delta G) / T$$
$$= (60.7 - 56.5) \times 1000 / 298$$
$$= +14.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

(iii) Suggest a reason for the difference between the $\Delta S^\ominus$ you have calculated for equilibrium **(2)** and that for equilibrium **(1)** given in the table.

[1]

For equilibrium (1), 5 moles of reactants react to form 7 moles of products while equilibrium (2), 3 moles of reactants react to form 7 moles of products. Hence, there is more disorder in equilibrium (2) than equilibrium (1) and hence ΔS^θ for equilibrium (2) is more positive.

(iv) Which of the two complexes is more stable? Give a reason for your answer.

[1]

The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ in equilibrium 2 is more stable because either K_{stab} is larger in magnitude or $\Delta G^{\ominus}$ is more negative.

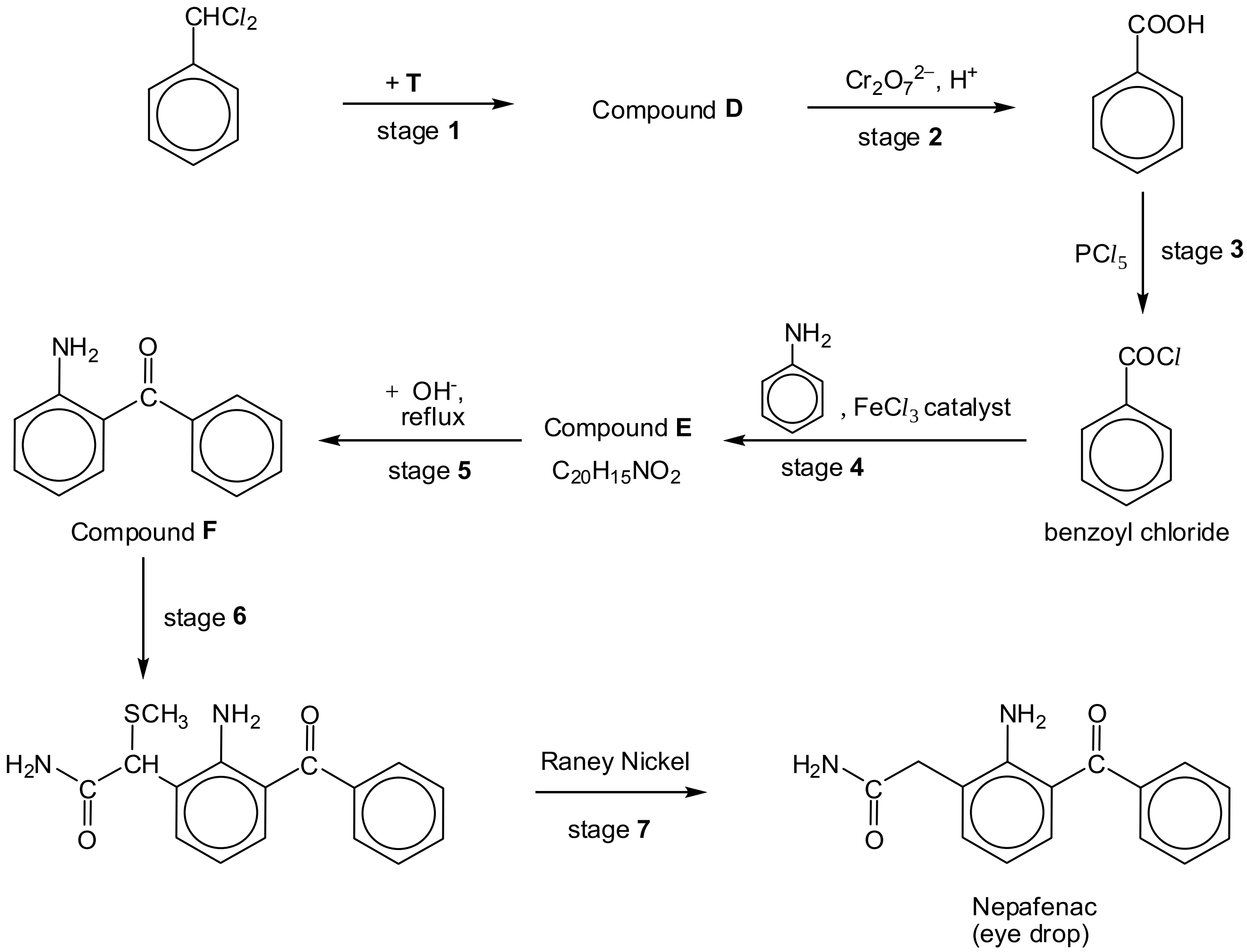
[Total: 23]

Section B

Answer **one** question from this section.

4(a) *Nepafenac* is a prescription eye drop that is used to treat pain and inflammation associated with eye surgery.

The following scheme shows a synthesis of *Nepafenac*.



(i) State the type of reaction occurring in stage **3** and stage **7**.

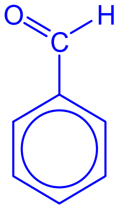
[2]

Stage 3: Nucleophilic acyl substitution

Stage 7: Reduction

(ii) Draw the structure of compound **D**. Suggest the reagent and conditions required in stage **1**.

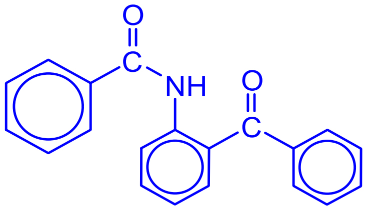
[2]



NaOH (aq), heat

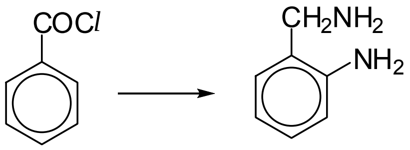
(iii) In stage **4**, two reactions are involved. Draw the structure of compound **E** and state the reactions that occurred.

[2]



Electrophilic substitution and Condensation / Nucleophilic acyl substitution

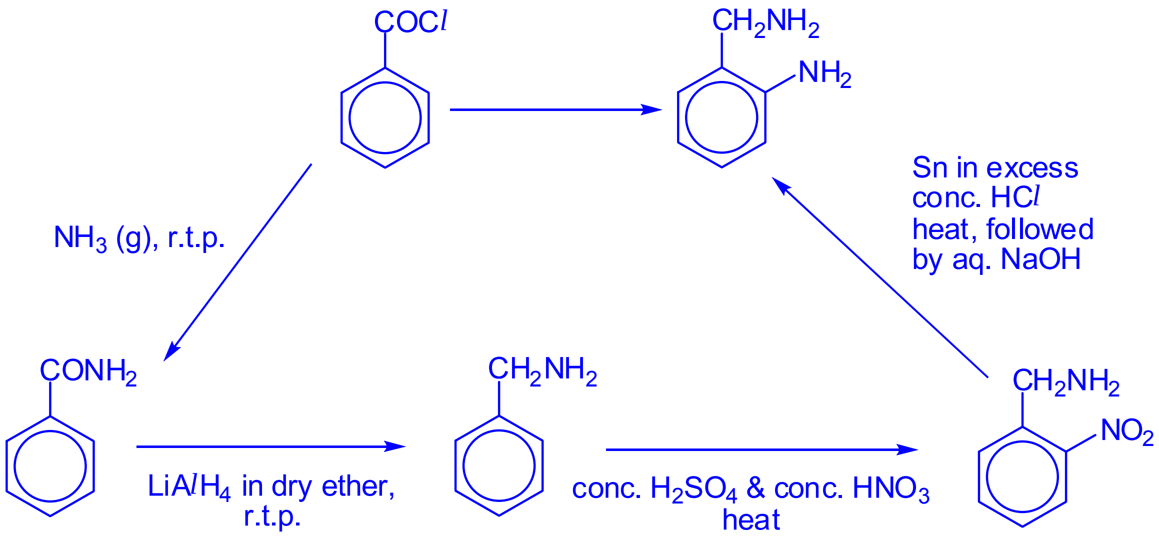
(iv) Benzoyl chloride can be converted into 2–aminobenzylamine, an important starting material in the synthesis of quinazoline, a source of useful pharmacophores for new drug development.



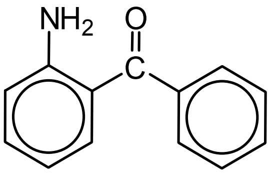
benzoyl chloride 2-aminobenzylamine

Suggest a 4–step synthesis of 2–aminobenzylamine from benzoyl chloride. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[4]



(v) A student made a statement regarding a reaction with compound **F**: *"Cyanide, CN^-, is acting as a* ***Bronsted–Lowry base*** *to attack the carbonyl group of compound* ***F*** *to form a cyanohydrin."*



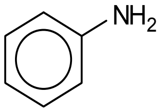
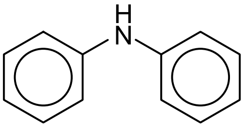
Compound **F**

Based on your understanding of a *Bronsted–Lowry* base, explain why the student's statement is wrong.

[1]

A *Bronsted–Lowry* base is a proton acceptor. In this reaction, the cyanide is behaving as a Lewis base that act as an electron–pair donor.

(vi) Data about phenylamine and diphenylamine are given in the table below.

Compound	 phenylamine	 diphenylamine
pK_b value	9.39	13.21

Give **two** reasons, why pK_b of phenylamine is lower than that of diphenylamine.

[2]

Phenylamine is a stronger base than diphenylamine. There is greater delocalisation of lone pair of electrons on N atom into the two benzene ring of diphenylamine as compare to phenylamine.

There is also greater steric hindrance of the 2 R group of diphenylamine.
The lone pair on N atom of diphenylamine is less available to accept a proton.

(b) Compound **J**, $C_{10}H_8O_3$, does not decolourise bromine water nor give effervescence with magnesium strip. **J** gives a silver mirror with Tollens' reagent but does not give a precipitate with hot alkaline Cu^{2+} solution.

On prolonged heating with acidified $KMnO_4$, **J** gives benzene–1,2–3–tricarboxylic acid as the only organic product. When heated with dilute H_2SO_4, **J** forms compound **K**, $C_{10}H_{10}O_4$. **K** gives a yellow precipitate with alkaline aqueous iodine.

J reacts with $LiAlH_4$ to form compound **L** (with an internal plane of symmetry), $C_{10}H_{14}O_3$. However, **J** forms compound **M**, $C_{10}H_{10}O_3$ with $NaBH_4$.

All compounds are optically active but only **K** reacts with sodium carbonate.

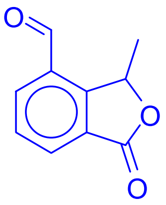
Suggest the structure for **J**, **K**, **L** and **M** and explain the reactions described.

[7]

- J has comparable number of C and H atoms and no. of carbon atoms > 6 ➔ J contains a benzene ring.
- J does not undergo electrophilic substitution (or electrophilic addition) with aqueous bromine. J *does not contain* phenol (or alkene group).
- J does not undergo acid metal displacement with Mg. J does not contain alcohol/phenol/carboxylic acid group.
- J undergoes oxidation with Tollens' reagent but does not undergoes oxidation with Fehling's reagent. ➔ J contains an aromatic aldehyde.
- J undergoes oxidation with hot acidified $KMnO_4$ to give benzene–1,2,3–tricarboxylic acid as the only organic product. Substituents the on benzene ring are on 1, 2 and 3 position.
- When heated with dilute H_2SO_4, J undergoes acidic hydrolysis to form K. Since only one compound is formed / no decrease in no. of carbon atoms.
  - J contains cyclic ester.
  - K contains carboxylic acid and alcohol group.
- K undergoes oxidation with alkaline aqueous iodine. ➔ K contains $RCHOH(CH_3)$
- J undergoes reduction with $LiAlH_4$ to form compound L and 6 H atoms are added to L.
  - J contains aldehyde and cyclic ester.
  - L contains 3 alcohol groups
- J undergoes reduction with $NaBH_4$ to form compound L and only 2 H atoms are added to M.
  - J contains aldehyde and cyclic ester.
  - L contains 1 alcohol group
- K undergoes acid–base / neutralisation with sodium carbonate. ➔ K contains carboxylic acid group.

- All compound contains chiral carbon and does not an internal plane of symmetry.

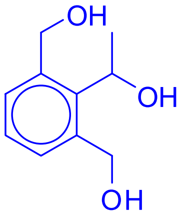
Compound **J:**



Chemical Formula: $C_{10}H_8O_3$

- No phenol, carboxylic acid, alcohol FGs
- Aromatic aldehyde
- Cyclic ester
- Forms benzene–1,2,3–tricarboxylic acid on strong oxidation
- Undergoes reduction to form **L** (gain of 6 H atoms)

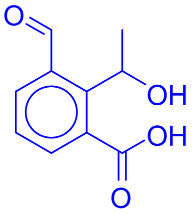
Compound **L**:



Chemical Formula: $C_{10}H_{14}O_3$

- Product of reduction of **J** (using $LiAlH_4$)
- Reduction of ester in **J** to alcohols in **L** (gain of 4 H)
- Reduction of aldehyde in **J** to primary alcohol in **L** (gain of 2H)
- Internal plane of symmetry

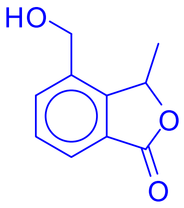
Compound **K**:



Chemical Formula: $C_{10}H_{10}O_4$

- Contains carboxylic acid
- Acidic hydrolysis product of **J** (ester linkage)
- Contains a $CH_3CH(OH)$–

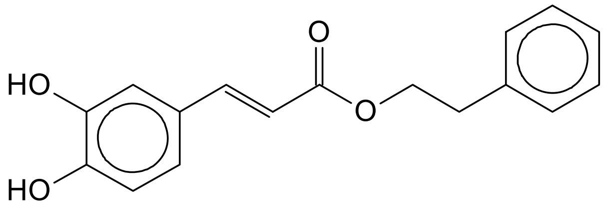
Compound **M**:



Chemical Formula: $C_{10}H_{10}O_3$

- Product of reduction of **J** (using $NaBH_4$)
- Reduction of aldehyde in **J** to primary alcohol in **L** (gain of 2 H)

5 Caffeic acid phenethyl ester (CAPE) is a natural occurring compound, found in propolis from honeybee hives. It is currently being studied for its anti–carcinogenic and anti–inflammatory properties. It is the ester of caffeic acid and 2–phenylethanol.



caffeic acid phenethyl ester (CAPE)

(a) Till date, there has been two well–established reaction schemes to synthesise CAPE. Study **Fig. 2.1** and **Fig 2.2** carefully and answer the questions that follow.

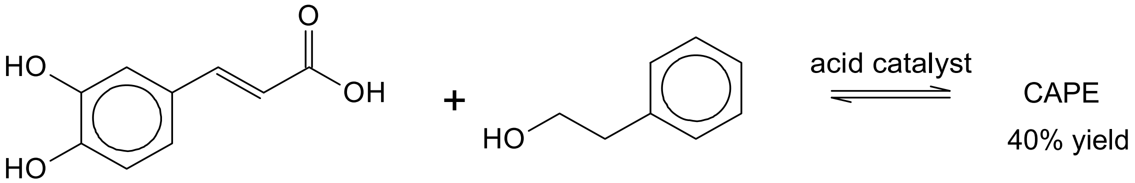


Fig. 2.1

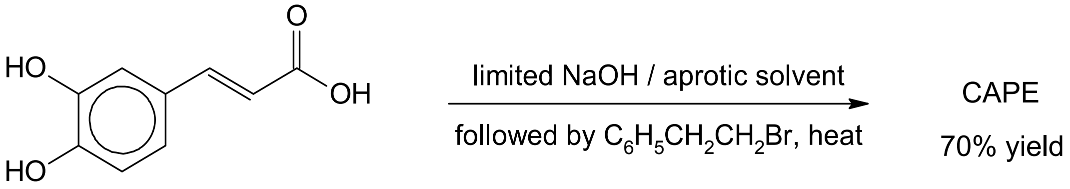


Fig. 2.2

(i) State the type of reaction occurring in each of the above synthesis method.

[2]

Fig 2.1: Condensation / Nucleophilic Acyl Substitution
Fig 2.2: Nucleophilic substitution

(ii) To improve the yield of CAPE in **Fig 2.1**, a student suggested using the acyl chloride derivative of caffeic acid instead. Comment on the validity of his suggestion.

[2]

Yes, his suggestion is valid. The reaction between an acyl chloride and an alcohol to form ester is irreversible, hence a higher yield is expected. There are two very electronegative atoms O and C*l* bonded to highly electron deficient carbonyl C atom in an acyl chloride. Hence, the carbonyl C atom in an acyl chloride is more susceptible to nucleophilic acyl substitution.

OR

No, his suggestion is invalid.An acyl chloride functional groups can undergo condensation / nucleophilic acyl substitution with the phenol functional groups to form other esters (side products), hence a lower yield is expected.

(iii) Explain why NaOH has to be added in limited amount rather than in large excess in **Fig 2.2**.

[1]

This is to prevent the halogenoalkane from undergoing nucleophilic substitution with NaOH to form the corresponding alcohols.

(iv) A protic solvent is one that has labile proton(s) and readily donates its proton(s). Conversely an aprotic solvent does not have any labile proton. Suggest why is it important to use an aprotic solvent in **Fig 2.2**.

[1]

This is to prevent the carboxylate anion from being protonated to form carboxylic acid, hence reducing its ability to function as the nucleophile for nucleophilic substitution with the halogenoalkane.

OR

This is to prevent the generation of phenoxide, another nucleophile which can undergo nucleophilic substitution with $C_6H_5CH_2CH_2Br$ to form the corresponding ether.

(v) The reported yield in **Fig. 2.2** is only 70%, as there are other by–products. Draw the skeletal formula of one possible by–product, assuming that caffeic acid reacts with $C_6H_5CH_2CH_2Br$ in a 1:1 ratio.

[1]

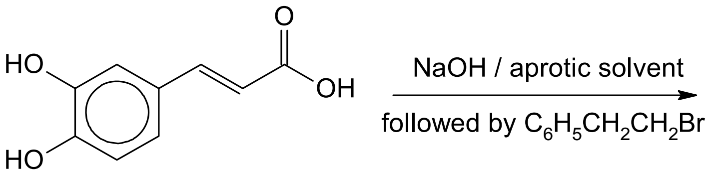
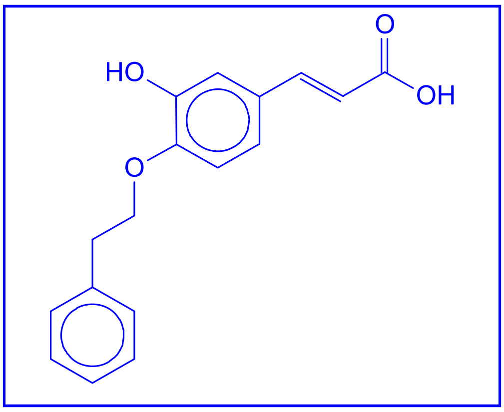
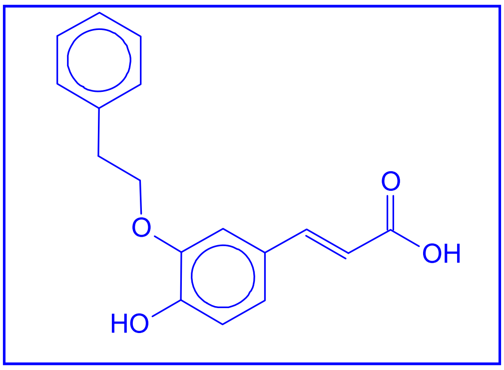


Fig. 2.2

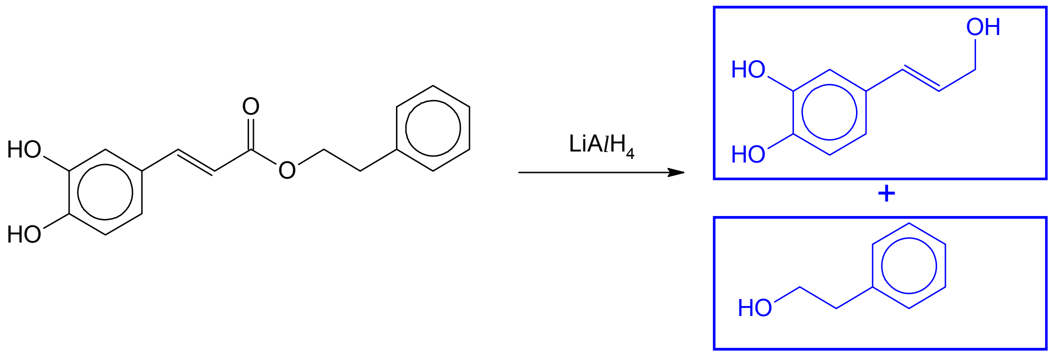


OR

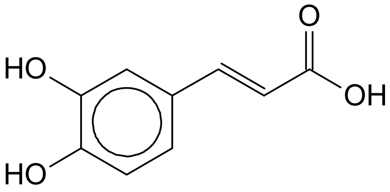


(vi) Draw the structure of the resultant product(s) when CAPE is reacted with $LiAlH_4$.

[1]



(b) The structure of *caffeic acid* is shown below.



caffeic acid

(i) *Caffeic acid* contains two organic functional groups with pK_a values lower than that of an alcohol. Identify these functional groups.

Compare and account for the relative pK_a values of these two organic groups.

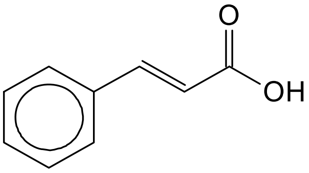
[3]

The carboxylic acid functional group has a lower pK_a value than the phenol functional group. Carboxylic acid is a stronger acid than phenol.

The phenoxide ion is stabilised by charge delocalisation, where the lone pair of electrons on the oxygen atom of the phenoxide ion is delocalised into the benzene ring. This reduces the intensity of the negative charge on the oxygen atom of the phenoxide ion, hence stabilising the phenoxide ion. Phenol is stronger acid than alcohol with a higher tendency to dissociate in aqueous medium to give H^+.

The carboxylate anion ($RCOO^-$) is resonance stabilised by the delocalisation of the negative charge over the C atom and both electronegative oxygen atoms in the carboxylate anion. Hence, the carboxylate anion is more stable than phenoxide ion. There is a greater tendency for the carboxylic acid to dissociate in aqueous medium to give H^+ as compared to phenol.

(ii) Suggest a chemical test that can be carried out to distinguish between a sample of *caffeic acid* and *cinnamic acid.*



cinnamic acid

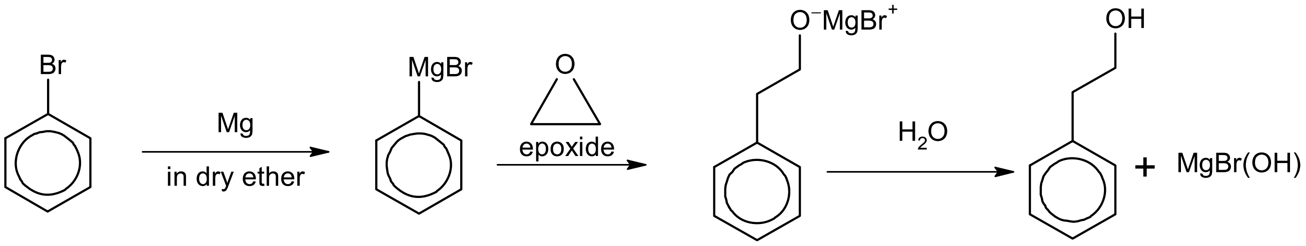
[2]

Test: Add aqueous neutral $FeCl_3$ to each compound separately at r.t.p.

Observations:

Caffeic acid:	Violet complex / colouration will be formed.
Cinnamic acid:	No violet complex will be formed.

(c) The synthesis of 2–phenylethanol from bromobenzene is shown below.

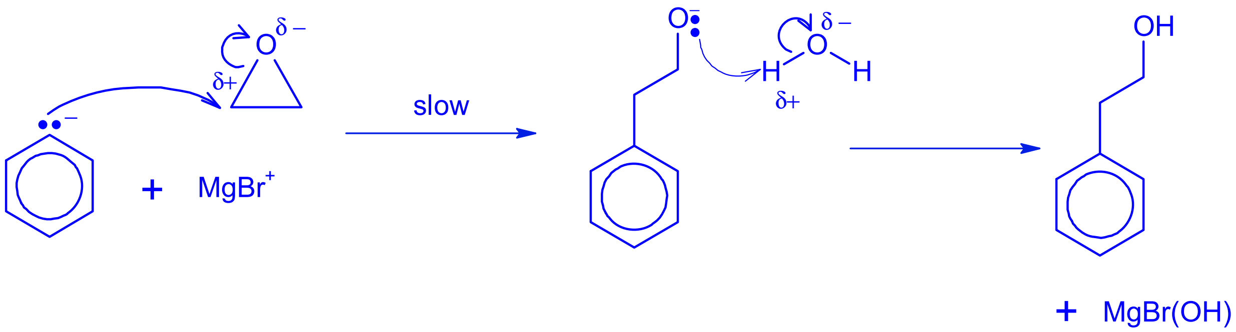


In the above synthesis, a Grignard reagent, C_6H_5MgBr is generated. Once generated, the Grignard reagent behaves as a nucleophile. The C_6H_5 in C_6H_5MgBr behaves like an anion, $C_6H_5^-$ and is a strong Lewis base. The Grignard reagent is useful for the formation of carbon–carbon bonds.

The reaction between the Grignard reagent, C_6H_5MgBr and the epoxide, C_2H_4O is a bimolecular reaction and the intermediate formed will subsequently react with water to form 2–phenylethanol.

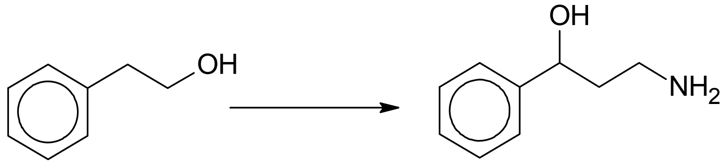
From the information provided, outline the mechanism to account for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons by curly arrows.

[2]



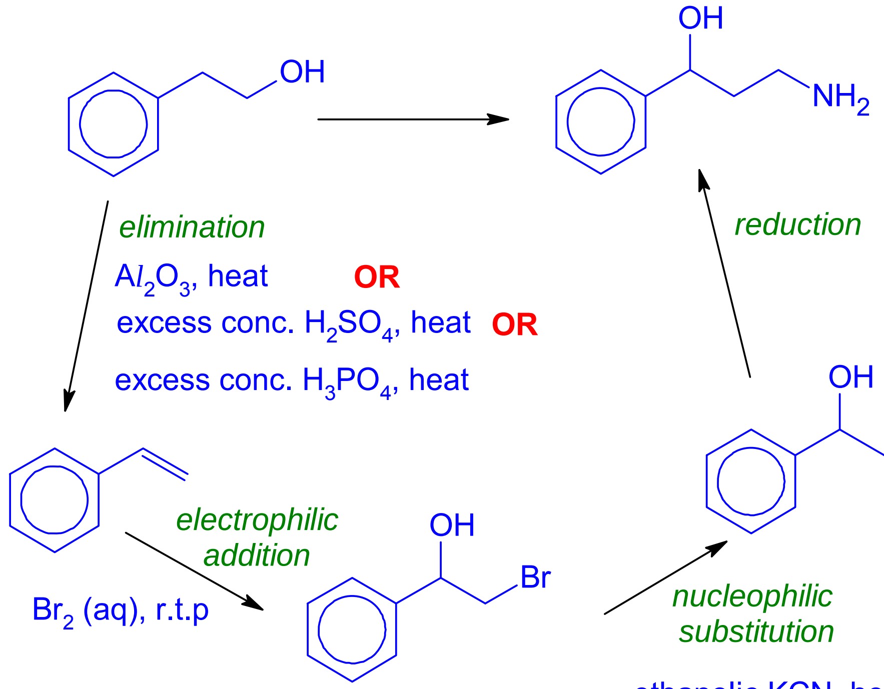
(d) Suggest a 4–step synthesis of 3–amino–1–phenylpropan–1–ol from 2–phenylethanol.

The synthesis involves an intermediate compound that decolourises aqueous bromine in the dark. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.



3-amino-1-phenylpropan-1-ol

[3]



elimination

Al_2O_3, heat **OR**

excess conc. H_2SO_4, heat **OR**

excess conc. H_3PO_4, heat

electrophilic addition

Br_2 (aq), r.t.p

nucleophilic substitution

ethanolic KCN, heat (under reflux)

reduction

$LiAlH_4$ in dry ether, r.t.p. **OR**

H_2 (g), Ni catalyst, high temp. and pressure **OR**

H_2 (g), Pt / Pd catalyst, r.t.p.

(e) A 0.460 g sample of gaseous methanoic acid, HCOOH was found to only occupy a volume of 173 cm^3 at a temperature of 160°C and a pressure of 1.04×10^5 Pa.

Using the ideal gas equation and the above information, determine the molar mass of this gaseous sample. Hence, draw a possible structure at this temperature.

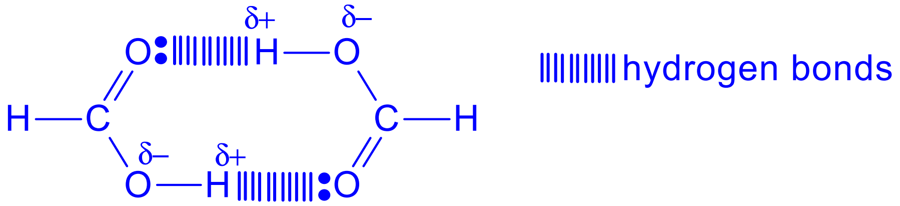
[2]

Applying **pV = nRT**

$$pV = \frac{m}{M}RT$$

Molar mass, **M** = $= \frac{mRT}{pV} = \frac{0.460 \times 8.31 \times (160+273)}{(1.04 \times 10^5)(173 \times 10^{-6})} = 92.0 \text{ g mol}^{-1}$

The molar mass of 92.0 g mol^{-1} is **doubled** of the expected molar mass of HCOOH (46.0 g mol^{-1})



[Total: 20]

END OF PAPER

Name **Suggested Solutions**

Class	Reg Number
17S	

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9729/04

Paper 4

11 September 2018

2 hours 30 minutes

READ THESE INSTRUCTIONS FIRST

Write your name, register number and class in the space provided above.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.
Do not use correction fluid.

Answer **all** questions in the space provided on the Question Paper.

The use of approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are provided on Pages **23** and **24**.
At the end of the examination, fasten all your work accurately together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

Examiner's Use	
Q1	**/ 21**
Q2	**/ 19**
Q3	**/ 15**
Total	**/ 55**

This document consists of **24** printed pages (including this cover page).

1 In this experiment, you are to determine the number of water of crystallisation (value of x) in an iron(II) salt, $(NH_4)_2Fe(SO_4)_2.\ x\ H_2O$ by titration with potassium manganate(VII).

You are provided with the following reagents.

FA 1 is potassium manganate(VII), $KMnO_4$ solution, of an approximate concentration 0.02 mol dm^{-3}
FA 2 is 0.0780 mol dm^{-3} ethanedioate ions $C_2O_4^{2-}$
FA 3 is a solution of the iron(II) salt containing 38.4 g dm^{-3} of $(NH_4)_2Fe(SO_4)_2.\ x\ H_2O$.
FA 4 is dilute sulfuric acid

Before using the provided solution of manganate(VII) ions, it is important to accurately determine its concentration. The exact concentration of **FA 1** can be determined with the given **FA 2** solution.

In an acidic medium, ethanedioate ions $C_2O_4^{2-}$ reacts with manganate(VII) ions MnO_4^- to form Mn^{2+} and CO_2 gas.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

As this reaction is very slow initially, MnO_4^- should only be added to a pre–heated $C_2O_4^{2-}$ solution in the presence of excess dilute acid. Subsequently, as the reaction proceeds, the rate of reaction will speed up and hence eliminating the need to continue heating.

Method

(a) (i) Standardisation of FA 1 solution

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 10.0 cm^3 of **FA 2** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 25 cm^3 of **FA 4** to the same conical flask.
4. Heat this solution to about 65 °C using the Bunsen burner.
5. **Turn off your Bunsen burner.**

Caution: Use the heat–resistant foam to handle the neck of the heated flask.

6. Run **FA 1** from the burette into this flask until a **permanent** pale pink colour is obtained.

Initially, the colour of the **FA 1** will take some time to disappear. Subsequently, as the reaction proceeds, the rate of reaction will speed up

7. Record your titration results in the space provided on page **3**. Make certain that your recorded results show the precision of your working.
8. Repeat steps **1** to **7** as necessary until consistent results are obtained.

Results

	1	**2**
Final burette reading / cm^3	**15.10**	**15.10**
Initial burette reading / cm^3	**0.30**	**29.90**
Volume of **FA 1** / cm^3	**14.80**	**14.80**
	✓	✓

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

[2]

Average volume of **FA 1** used = (14.80 + 14.80) ÷ 2 = **14.80 cm^3** **(2 d.p.)**

volume of **FA 1** = ...

(iii) Determine the concentration of MnO_4^- in **FA 1**.

[1]

Amount of $C_2O_4^{2-}$ used (in 10.0 cm^3) $= 0.0780 \times \frac{10.0}{1000} = 7.80 \times 10^{-4}$ mol

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

$\mathbf{2MnO_4^- \equiv 5C_2O_4^{2-}}$

Amount of MnO_4^- reacted (in 14.80 cm^3) $= \frac{2}{5} \times 7.80 \times 10^{-4} = 3.12 \times 10^{-4}$ mol

$[MnO_4^-] = 3.12 \times 10^{-4} \div \frac{14.80}{1000} = \underline{\mathbf{0.0211\ mol\ dm^{-3}}}$ **(3 s.f.)**

Concentration of MnO_4^- in **FA 1** = ...

M1	M2	M3

(iv) For the titration in **(a)(i)** between ethanedioate ions $C_2O_4^{2-}$ and manganate(VII) ions MnO_4^-, the ethanedioate solution needs to be at about 60 °C at the start.

However, during the titration, as **FA 1** is added, the temperature of the mixture decreases. This decrease in temperature did not cause the rate of reaction between $C_2O_4^{2-}$ and MnO_4^- added from the burette to decrease.

Suggest an explanation for this.

[1]

The rate of reaction between MnO_4^- and $C_2O_4^{2-}$ is slow initially due to the electrostatic repulsion between the two negatively charged ions resulting in high activation energy.

As the reaction proceeds, Mn^{2+}, an autocatalyst is generated which helps to increase the rate of the reaction.

M4	

(v) Calculate the maximum total percentage uncertainty for your titration in **(a)(i)** if the associated uncertainty associated with each reading using a 10.0 cm^3 pipette and a burette are ±0.03 cm^3 and ±0.05 cm^3 respectively.

% uncertainty due to pipette = $\frac{\pm 0.03}{10.0}$ x 100% = **±0.3000%**

% uncertainty due to burette used in titration = $\frac{\pm 0.05 \times 2}{14.80}$ x 100% **= ±0.6920%**

Maximum total percentage uncertainty = 0.3000 + 0.6920 = **±0.992% (3 s.f.)**

Percentage uncertainty = ……………………..……. **[1]**

M5	

(b) **(i)** **Titration**

1. Fill the burette with **FA 1**.
2. Pipette 25.0 cm^3 of **FA3** into a conical flask and add 25 cm^3 of **FA 4** using a measuring cylinder.
3. Titrate **FA 3** with **FA 1** until the end–point is reached.
4. Carry out as many accurate titrations as you think necessary to obtain consistent results. Record your titration results in the space provided below.

	1	**2**
Final burette reading / cm^3	**26.55**	**35.90**
Initial burette reading / cm^3	**2.90**	**12.20**
Volume of **FA 1** / cm^3	**23.65**	**23.70**
	✓	✓

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

[3]

Average volume of **FA 1** used = (23.65 + 23.70) ÷ 2 = **23.68 cm^3 (2 d.p.)**

volume of **FA 1** = ……………………………….

M6	M7	M8

(c) Calculations

(i) The two half–equations for the reaction between the iron(II) salt and manganate(VII) ions are shown below.

$MnO_4^- + 8\,H^+ + 5\,e \longrightarrow Mn^{2+} + 4\,H_2O$; $Fe^{2+} \longrightarrow Fe^{3+} + e$

Calculate the amount of iron(II) ion present in 1.00 dm^3 of **FA 3**.

[1]

Amount of $KMnO_4$ in **23.68** cm^3 $= \frac{23.68}{1000} \times 0.02108 =$ **4.992 x 10^{-4} mol**

$MnO_4^- + 8\,H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$

$5Fe^{2+} \equiv MnO_4^-$

Amount of Fe^{2+} in 25.0 cm^3 of **FA 3** $= 5 \times 4.992 \times 10^{-4}$ = **2.496 x 10^{-3} mol**

Amount of Fe^{2+} in 1.00 dm^3 of **FA 3** $= 2.496 \times 10^{-3} \times \frac{1000}{25.0}$ = **0.0998 mol (3 s.f.)**

Amount of iron(II) ions in 1.00 dm^3 of **FA 3** = ...

M9	

(ii) Using your answer in **(c)(i)**, determine the value of x, the number of water of crystallisation in the iron(II) salt, $(NH_4)_2Fe(SO_4)_2 . x\,H_2O$.

[A$_r$: Fe, 55.8; H, 1.0; N, 14.0; O, 16.0; S, 32.1]

[3]

$Fe^{2+} \equiv$ iron(II) salt ➔ Amount of iron(II) salt in 1.00 dm^3 of **FA 3** = 0.09983 mol

Relative formula mass of iron(II) salt $= \frac{38.4}{0.09983} = 384.6$

Formula mass of iron(II) salt $= 2\,(14.0 + 4.0) + 55.8 + 2\,(32.1 + 64.0) + x\,(2.0 + 16.0)$
$384.6 = 284.0 + 18\,x$
$100.6 = 18\,x$
$x = 5.59 \approx$ **6 (to nearest integer)**

x = ...

M10	M11	M12

(d) In the titration of the iron(II) salt and manganate(VII) ion in **(b)(i)**, it was observed that the colour of the mixture in the conical flask gradually changes before an excess drop of manganate(VII) turns the mixture pale pink at the end point.

State and explain the colour changes you observed in the titration, in terms of the complex ions involved.

[2]

As the titration proceeds, the colour of the mixture in the conical flask changes from pale green ($[Fe(H_2O)_6]^{2+}$) to yellow ($[Fe(H_2O)_6]^{3+}$).

As the electronic configuration of the metal changes, the amount of splitting of the d orbitals (energy gap, ΔE) also changes, resulting in different wavelength of light being absorbed during the d-d transitions.

M13	M14

(e) **Planning**

A saturated aqueous solution of magnesium methanoate, $Mg(HCOO)_2$, has a solubility of approximately **150 g dm^{-3}** at room temperature. Its exact solubility can be determined by titrating magnesium methanoate against aqueous potassium manganate(VII).

During the titration, methanoate ion, $HCOO^-$ reacts with manganate(VII) ion, MnO_4^- in an acidic medium as shown in the equation below.

$$2MnO_4^- + 5HCOO^- + 11H^+ \longrightarrow 2Mn^{2+} + 5CO_2 + 8H_2O$$

You may assume that you are provided with:

- 100 g of solid magnesium methanoate, $Mg(HCOO)_2$
- 0.0200 mol dm^{-3}aqueous potassium manganate(VII), $KMnO_4$
- 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
- the apparatus and equipment normally found in a school or college laboratory.

In order to obtain a reliable and feasible titre value, the saturated solution of magnesium methanoate needs to be diluted accurately (~**50 times** dilution) before titration.

(i) Plan an investigation to determine the effect of temperature on the solubility of magnesium methanoate, $Mg(HCOO)_2$. Your plan must enable you to plot a graph that includes data from the experiment.

Your plan should include details of:

- the preparation of 50 cm^3 of **saturated** aqueous solutions of $Mg(HCOO)_2$ at different temperatures
- the preparation of diluted solutions of $Mg(HCOO)_2$ for titration
- an outline of how the titration could be carried out
- a sketch of the graph you would expect to obtain
- an outline how the results can be used to determine the effect of temperature on the solubility of $Mg(HCOO)_2$

[6]

YOU ARE NOT REQUIRED TO PERFORM THIS EXPERIMENT.

Preparation of saturated solution of $HCOO^-$

1) Weigh approximately 8.0 g of solid $Mg(HCOO)_2$ and transfer the solid to 50 cm^3 of water in a beaker. Stir to ensure even mixing such that the obtained solution is saturated. Ensure solid deposits can be seen in the beaker.
2) Place this beaker in a thermostatically controlled water bath set at 30°C.
3) Use a thermometer to measure the temperature of the solution in the beaker.-Record the temperature of the solution.

Preparation of diluted solution

4) Quickly decant the saturated solution into a burette.
5) Using the burette, dispense 5.00 cm^3 of the saturated $HCOO^-$ solution into a 250 cm^3 volumetric flask.
6) Top up to the mark with deionized water, and invert the flask to ensure even mixing to obtain a homogenous solution. Label this as diluted solution at 30°C.

Titration

7) Fill another burette with $KMnO_4$ (aq)
8) Pipette 25.0 cm^3 of the diluted $HCOO^-$ solution into a conical flask and add 20 cm^3 of dilute H_2SO_4 using a measuring cylinder.
9) Note the initial reading of the burette.
10) Titrate with $KMnO_4$ until a permanent pale pink colour is obtained. Note the final reading of the burette.
11) Carry out accurate titrations to obtain consistent results. Record your titration results.

Repeat Step 1 to 11 at different temperatures (i.e. 35°C, 40°C, 45°C, 50°C) by adjusting the temperature of the thermostatically controlled water bath.

Analysis of Results

Determine the average titre value of $KMnO_4$ used and determine the amount of MnO_4^- used, which can be used to determine the amount of $HCOO^-$ in the diluted solution and hence the concentration of $HCOO^-$ in the diluted and saturated solution. This can be correlated to determine the solubility of Mg(HCOO).

Presentation of sample calculations

Amount of MnO_4^- = $\dfrac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200$

$2\ MnO_4^- \equiv 5HCOO^-$

Amount of $HCOO^-$ in 25.0 cm^3 (diluted solution) = $\dfrac{5}{2} \times \dfrac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200$

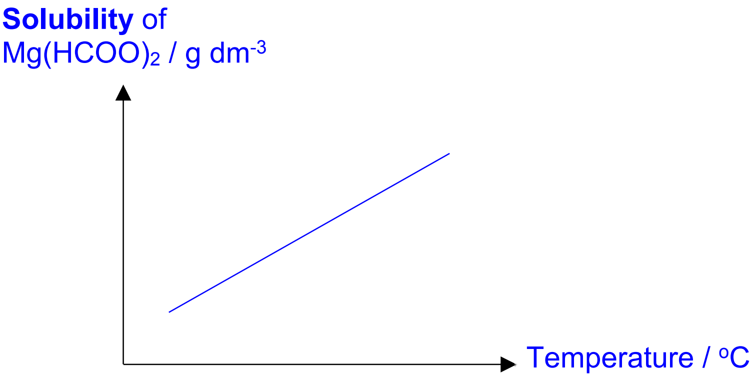
Amount of $HCOO^-$ in 5.00 cm^3 (saturated) = $\dfrac{250}{25.0} \times \dfrac{5}{2} \times \dfrac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200$

$$[HCOO^-]\text{ (saturated)} = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200}{\left(\frac{5.00}{1000}\right)}$$

$$[Mg(HCOO)_2]\text{ (saturated)} = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200}{\left(\frac{5.00}{1000}\right) \times 2}$$

$$\text{Solubility of } Mg(HCOO)_2\text{ (saturated)} = \frac{\frac{250}{25.0} \times \frac{5}{2} \times \frac{\text{Volume of } KMnO_4 \text{ used}}{1000} \times 0.0200}{\left(\frac{5.00}{1000}\right) \times 2} \times 114.3$$

Repeat the above for each different temperature. Plot a graph of solubility of $Mg(HCOO)_2$ against temperature to see how temperature affects the solubility of $Mg(HCOO)_2$.



M15 – M20

(ii) A student used the same titration method, this time to measure the concentration of a saturated solution of barium methanoate. Explain why the acidification of the solution with dilute sulfuric acid might make the titration difficult to do.

[1]

A precipitate of $BaSO_4$ will be formed thus obstructing an accurate judgement of the end-point of the titration.

M21	

[Total: 21]

2 Strong acids, such as hydrochloric acid, HC*l*, are completely ionised in aqueous solution. Weak acids, such as ethanoic acid, CH_3COOH, are partially ionised in aqueous solution.

You will investigate the enthalpy change for the reaction of an excess of each of these acids with magnesium and hence determine the energy needed to cause the weak acid to ionise completely.

(a) **Experiment 1**

FA 5 is 1.0 mol dm^{-3} hydrochloric acid, HC*l*.
FA 6 is magnesium, Mg.

1. Weigh the magnesium strip, **FA 6**, and record the mass reading.
2. Support the Sytrofoam cup in the 250 cm^3 beaker.
3. Coil the magnesium strip loosely so that it fits into the bottom of the Sytrofoam cup and then remove the strip.
4. Use the measuring cylinder to transfer 25 cm^3 of the acid, **FA 5**, into the Sytrofoam cup.
5. Place the thermometer in the acid and read the initial temperature. This is the temperature at time zero (t = 0).
6. Start timing and do not stop the stop watch until the whole experiment has been completed.
7. Read the temperature of the acid every half minute for two minutes.
8. At time t = 2.5 minutes drop the magnesium strip, **FA 6**, into the acid and stir the mixture. **Do not try to read the temperature at this time**.
9. Measure and record, the temperature of the mixture at t = 3.0 minutes and then every half minute until t = 8.0 minutes. Stir the mixture continuously between thermometer readings.
10. Rinse the Sytrofoam cup for use in **Experiment 2**. Shake to remove excess water.

In the space provided below, record all measurements of mass. Record all your results of temperature and time in a table.

Results

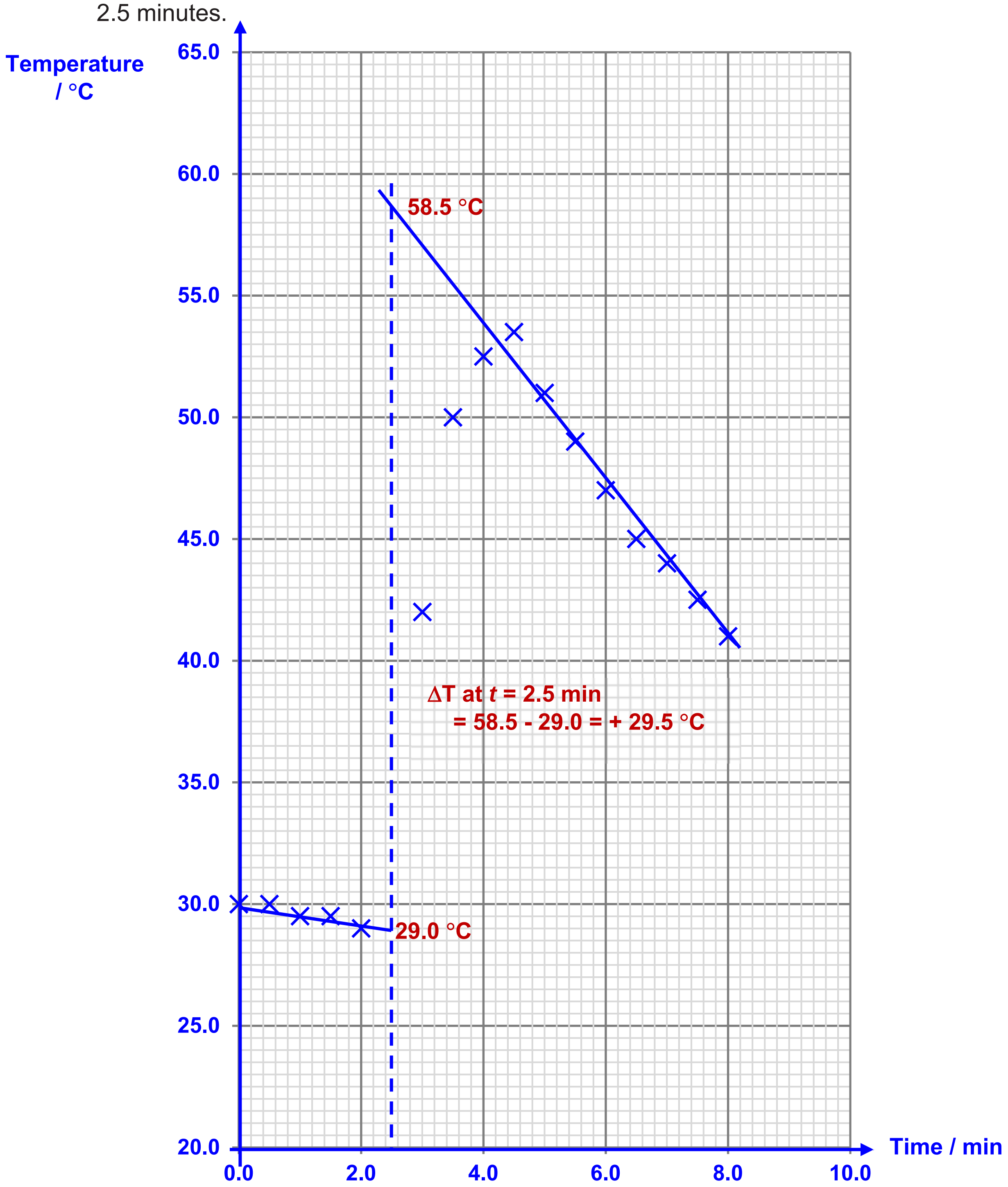
Mass of magnesium strip = **0.162 g**

Time / min	**Temperature / °C**	**Time / min**	**Temperature / °C**
0.0	30.0	5.5	49.0
0.5	30.0	6.0	47.0
1.0	29.5	6.5	45.0
1.5	29.5	7.0	44.0
2.0	29.0	7.5	42.5
2.5	–	8.0	41.0
3.0	42.0		
3.5	50.0		
4.0	52.5		
4.5	53.5		
5.0	51.0		

[4]

M1	M2	M3	M4

(b) Plot a graph of temperature on the y–axis against time on the x–axis on the grid below. The scale for the temperature axis should extend 10 °C greater than the maximum temperature you recorded. You will use the graph to determine the theoretical maximum temperature rise at 2.5 minutes.



Draw two lines of best fit through the points on your graph, the first for the temperature before adding FA 6 and the second for the cooling of the mixture once the reaction is complete.

Extrapolate the two lines to 2.5 minutes, draw a vertical line between the two and determine the theoretical rise in temperature at this time.

theoretical rise in temperature at 2.5 minutes = ... **[4]**

M5	M6	M7	M8

(c) Magnesium reacts with hydrochloric acid according to the equation shown.

$$Mg\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$$

(i) Use your answer to **(b)** to calculate the heat energy, in joules, given out when **FA 6** is added to the acid.
[Assume 4.2 J of heat energy raises the temperature of 1.0 cm^3 of the mixture by 1.0 °C.]
[1]

Energy evolved $= 25.0 \times 4.2 \times \Delta T$
$= 25.0 \times 4.2 \times (58.5 - 29.0)$
$= 3098$ J

heat energy evolved = ...

M9	

(ii) Calculate the enthalpy change when 1 mole of **FA 6**, Mg, reacts with hydrochloric acid.
[A_r: Mg, 24.3]
[1]

$$\Delta H = -\frac{Q}{n_{limiting}} = -\frac{3098}{\frac{0.158}{24.3}} = -476.3 \text{ kJ mol}^{-1}$$

enthalpy change, ΔH = ...

M10	

(d) **(i)** Calculate the percentage error in the measurement of ΔT in the experiment.
[1]

$$\text{Percentage error} = \left(\frac{\pm 0.5 \times 2}{29.5}\right) \times 100\% = \pm 3.39\ \%$$

M11	

(ii) A student suggested that the experiment carried out in **(a)** could be improved by using a catalyst.

Would the use of a catalyst improve the accuracy of the results in this experiment? Give a reason for your answer.
[1]

YES because the reaction is faster so less heat is lost. Hence, Δ*T will be more accurately determined.*

OR NO because a catalyst does not alter Δ*H or* Δ*T*

M12	

(ii) Another student could not find the hydrochloric acid, **FA 5**, and used sulfuric acid, H_2SO_4, instead. He used the same volume and the same concentration as the hydrochloric acid in **FA 5**.

What effect would this change have on the temperature rise in the experiment? Give a reason for your answer.

[1]

No effect because the acid is in excess / magnesium is the limiting reagent /

all the Mg has reacted.

OR

ΔT would be larger because the reaction is faster as acid is diprotic / dibasic so less

heat is lost to surroundings

M13	

(e) **Experiment 2**

FA 7 is 1.0 mol dm^{-3} ethanoic acid, CH_3COOH
FA 8 contains one strip of magnesium, Mg of a mass of 0.087 g

Read the whole **Experiment 2** before starting any practical work.

1. Support the Sytrofoam cup in the 250 cm^3 beaker.
2. Coil the magnesium strip loosely so that it fits into the bottom of the Sytrofoam cup and then remove the strip.
3. Use the measuring cylinder to transfer 25 cm^3 of the acid, **FA 7**, into the Sytrofoam cup.
4. Place the thermometer in the acid and measure and record the initial temperature of the acid.
5. Add the piece of magnesium, **FA 8**, into the acid in the cup.
6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. This could take several minutes. Record this temperature, T_{max}.
7. Calculate and record the change in temperature, ΔT.
8. Complete **Table 2.1** by recording all measurements of temperature.

Table 2.1

Initial temperature / °C	31.0
Maximum temperature, T_{max} / °C	45.0
Change in temperature, ΔT / °C	+14.0

[1]

M14	

Magnesium reacts with ethanoic acid according to the equation shown.

$$Mg\,(s) + 2CH_3COOH\,(aq) \longrightarrow Mg(CH_3COO)_2\,(aq) + H_2\,(g) \qquad \Delta H_1$$

Use your results in Table 2.1 to calculate the enthalpy change, ΔH_1, when 1 mole of Mg, FA 8, reacts with excess ethanoic acid. Assume 4.2 J of heat energy changes the temperature of 1.0 cm^3 of the mixture by 1.0 °C. [A_r: Mg, 24.3]

[1]

Amount of heat energy evolved, Q = $mC\Delta T$ = 25.0 x 4.2 x 14.0 = **<u>1470 J</u>**

$$\Delta H_1 = -\frac{Q}{n_{limiting}} = -\frac{1470}{\frac{0.087}{24.3}} = \mathbf{-410.6\ kJ\ mol^{-1}}$$

ΔH_1 = ...

M15	

(f) Hydrochloric acid is a strong acid; it is fully ionised in aqueous solution. When the same experiment in **(e)** was repeated with hydrochloric acid, **FA 5**, instead of ethanoic acid, the enthalpy change, ΔH_2, when 1 mole of Mg reacts with excess hydrochloric acid was determined to be – 461.1 kJ mol^{-1}.

Ethanoic acid is a weak acid. It is partially ionised in aqueous solution.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$$

You are to determine the energy needed for one mole of ethanoic acid to ionise completely.

$$CH_3COOH\,(aq) \longrightarrow CH_3COO^-\,(aq) + H^+\,(aq) \qquad \Delta H_3$$

Use the values for the enthalpy changes, ΔH_1 you obtained in **(e)** and the ΔH_2 provided to calculate the energy change for the ionisation of ethanoic acid, ΔH_3.

Show clearly how you obtained your answer.

[2]

$Mg(s) + 2CH_3COOH(aq) \longrightarrow Mg(CH_3COO)_2(aq) + H_2(g)$ $\quad \Delta H_1 = \mathbf{-410.6\ kJ\ mol^{-1}}$

$Mg(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2(g)$ $\quad \Delta H_2 = \mathbf{-461.1\ kJ\ mol^{-1}}$

$CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H^+(aq)$ $\quad \Delta H_3$

$$\Delta H_3 = \frac{1}{2}(\Delta H_1 - \Delta H_2) = \frac{1}{2}(-410.6 - (-461.1))$$

= **<u>+ 25.3 kJ mol^{-1}</u>**

ΔH_3 = ...

M16	M17

(g) The experiment in **(e)** was repeated using trichloroethanoic acid instead of ethanoic acid.

$$Mg(s) + 2\,CCl_3COOH\,(aq) \longrightarrow Mg(CCl_3COO)_2\,(aq) + H_2\,(g) \qquad \textbf{\textit{reaction 3}}$$

Trichloroethanoic acid, CCl_3COOH, is a weak acid that is however stronger than ethanoic acid. The enthalpy change for ***reaction 3*** is between the two values given in **Table 2.2**.

Table 2.2

reaction	equation	ΔH / kJ mol^{-1}
1	$Mg\,(s) + 2CH_3COOH\,(aq) \longrightarrow Mg(CH_3COO)_2\,(aq) + H_2\,(g)$	–460.3
2	$Mg\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$	–464.1

(i) Explain why the enthalpy change for reaction 3 is more exothermic than the enthalpy change for reaction 1.

[1]

CCl_3COOH is a stronger acid than ethanoic acid.

Increased electronegativity of C*l* / *electron withdrawing Cl group* increases the strength of (trichloroethanoic) acid / makes it easier to release H^+ / deprotonate/ dissociate / ionise. (compared to ethanoic acid). Hence, less energy is required to dissociate H^+ from CCl_3COOH compared to CH_3COOH and reaction 3 is more exothermic.

M18	

(ii) Explain why the enthalpy change for reaction 3 is less exothermic than the enthalpy change for reaction 2.

[1]

Cl_3COOH is a weaker acid than HC*l*.

Hence, some energy released during neutralisation is used to dissociate Cl_3COOH completely.

M19	

[Total: 19]

3 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where reagents are selected for use in a test, the **name** or **correct formula** of the element or compound must be given.

Where gases are released they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

(a) **(i)** **FA 9**, **FA 10** and **FA 11** each contain one anion and one cation.

Carry out the following tests and record your observations.

Test	***observations***		
	FA 9	**FA 10**	**FA 11**
To a 1 cm depth of solution in a test–tube, add a few drops of aqueous silver nitrate, then	• White ppt formed.	• No ppt formed.	• No ppt formed.
add aqueous ammonia.	• White ppt is soluble in excess NH_3(aq) to form a colourless solution.	• No ppt formed.	• No ppt formed.
To a 1 cm depth of solution in a test–tube, add a few drops of aqueous barium nitrate, then	• No ppt formed.	• White ppt formed.	• No ppt formed.
add dilute nitric acid.	• No ppt formed.	• White ppt is insoluble in excess HNO_3(aq).	• No ppt formed.
To a 1 cm depth of solution in a test–tube, add a spatula of solid sodium carbonate.	• Effervescence seen. • Gas evolved formed a white ppt with limewater.	• Effervescence seen. • Gas evolved formed a white ppt with limewater.	• Effervescence seen. • Gas evolved formed a white ppt with limewater.

M1	M2	M3	M4

(ii) What cation is present in **FA 9**, **FA 10** and **FA 11**?

H^+ / hydrogen ions

(iii) Suggest another chemical test that you could carry out to confirm the presence of the cation you identified in **(ii)**.

Carry out this test on one of **FA 9**, **FA 10** and **FA 11** and record your observations.

Test: Add some Mg turnings to 2 cm depth of **FA 9** / **FA10** / **FA 11**.

Observations: Effervescence seen. Gas extinguishes a lighted splint with a 'pop' sound

(iv) Complete the table to identify, as far as possible, the anions present in **FA 9**, **FA 10** and **FA 11**. If you are not able to identify the anion from the tests you carried out in **(i),** write 'unknown'.

	FA 9	**FA 10**	**FA 11**
ion present	Cl^-	SO_4^{2-}	unknown

M5	M6	M7	M8

(v) For any one anion that you were unable to identify in **(iv)** you are to devise a test or tests that will enable you to identify it. You can assume that it is one of the anions listed in the Qualitative Analysis Notes.

Carry out the test(s), record the observation(s) you obtained and identify the unknown anion. In the space below, draw a single table to record details of the test(s) performed and observations made.

No.	***Test***	***Observation***
1	Add 1 cm depth of FA 11 into the test–tube. Add 1 cm depth of NaOH(aq). Then add aluminium foil to the mixture and warm gently.	Effervescence observed upon heating with Al. Gas evolved turns moist red litmus blue.
2	Place 1 cm depth of FA 11 in a test–tube.Add 1 cm depth of hydrochloric acid solution to FA 11. Warm. *	No brown fumes evolved

Identify the anion and state the evidences for your identification.

Anion: NO_3^-

Evidence: In test (1), NH_3 (g) was evolved on heating with aq NaOH and A*l*, which turns moist red litmus paper blue. No brown NO_2 gas was evolved with aq HC*l* in test (2).

[10]

M9	M10

(b) **FA 12** is an aqueous solution of a mixture containing two anions.
Carry out the following tests and record your observations.

Test	*Observations*
To a 1 cm depth of **FA 12** in a test–tube, add a 1 cm depth of dilute hydrochloric acid, then	- **Effervescence** seen. - **Gas evolved** formed **a white ppt with limewater**.
add a few drops of hydrogen peroxide, then	- **Brown / yellow / red- brown / yellow–brown solution** formed
add a few drops of starch.	- **Blue–black / black / dark blue solution** formed.
To a 1 cm depth of **FA 12** in a test–tube, add a 3 cm depth of aqueous copper(II) sulfate, then	- **Blue / green / brown ppt observed**
add a 1 cm depth of dilute hydrochloric acid, then	- **Brown solution** formed
add aqueous sodium thiosulfate.	- **White / cream / off–white / pale grey and** - **solid / residue / ppt**

From these observations, identify two ions present in **FA 12**.

ions present in **FA 12** CO_3^{2-} and I^-

[5]

M11	M12	M13	M14	M15

[Total: 15]

Meridian Junior College
JC2 Prelim Exam 2018

Reagent List

S/N	Label	Reagent	Amount per student
1	**FA 1**	0.0200 mol dm^{-3} aqueous potassium manganate(VII), $KMnO_4$	200 cm^3
2	**FA 2**	0.0780 mol dm^{-3} aqueous $Na_2C_2O_4$	75 cm^3
3	**FA 3**	0.0980 mol dm^{-3} ammonium iron(II) sulfate, $(NH_4)_2Fe(SO_4)_2.6H_2O$	120 cm^3
4	**FA 4**	1.00 mol dm^{-3} aqueous sulfuric acid, H_2SO_4	250 cm^3
5	**FA 5**	1.00 mol dm^{-3} aqueous hydrochloric acid, HCl	60 cm^3
6	**FA 6**	Magnesium ribbon	1 piece of 10 ± 0.1 cm length
7	**FA 7**	0.950 mol dm^{-3} ethanoic acid CH_3COOH	60 cm^3
8	**FA 8**	Magnesium ribbon	1 piece of 5 ± 0.1 cm length
9	**FA 9**	0.50 mol dm^{-3} hydrochloric acid, HCl	20 cm^3
10	**FA 10**	0.50 mol dm^{-3} sulfuric acid, H_2SO_4	20 cm^3
11	**FA 11**	0.5 mol dm^{-3} nitric acid, HNO_3	20 cm^3
12	**FA 12**	Aqueous solution mixture of 0.20 mol dm^{-3} potassium iodide, KI and 0.20 mol dm^{-3} sodium carbonate, Na_2CO_3	20 cm^3
13	**hydrogen peroxide**	10 ‘vol’ OR 0.891 mol dm^{-3} hydrogen peroxide, H_2O_2	2 cm^3
14	**copper(II) sulfate**	0.2 mol dm^{-3} aqueous copper(II) sulfate, $CuSO_4.5H_2O$	5 cm^3
15	**sodium thiosulfate**	0.20 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3.5H_2O$	5 cm^3
16	**starch solution**	2% starch solution	2 cm^3
17	**sodium carbonate**	Solid sodium carbonate	1 g
18	**Magnesium turnings**	Solid Mg turnings	1 g

Apparatus List

S/N	Apparatus	Quantity per student
1	100 cm^3 beaker	1
2	250 cm^3 beaker	1
3	25 cm^3 measuring cylinder	1

S/N	Apparatus	Quantity per student
4	50 cm^3 measuring cylinder	1
5	10.0 cm^3 pipette	1
6	25.0 cm^3 pipette	1
7	Pipette filler	1
8	50.0 cm3 burette (with tap valve)	1
9	250 cm^3 conical flasks	2
10	Filter funnel	1
11	Bunsen Burner	1
12	Tripod Stand with Wire Gauze	1
13	Lighter	1
14	Thermometer (–10 °C to +110 °C at 1 °C)	1
15	Foam strip (for handling hot glassware)	1
16	White tile	1
17	Retort stand with clamp	1
18	Stopwatch	1
19	Styrofoam cup	1
20	Deionised water bottle	1
21	Glass rod	1
22	Delivery tube	1
23	Safety Goggles	1
24	Weighing Balance	Communal
25	Test-tube rack	1
26	Test-tube holder	1
27	Test-tubes	8
28	Droppers	6
29	Spatula (small)	1
34	Marker for writing on apparatus	1

<u>Common Bench Reagent</u>

1. aqueous sodium hydroxide (approximately 2.0 mol dm^{-3})
2. aqueous ammonia (approximately 2.0 mol dm^{-3})
3. hydrochloric acid (approximately 2.0 mol dm^{-3})
4. nitric acid (approximately 2.0 mol dm^{-3})
5. sulfuric acid (approximately 1.0 mol dm^{-3})
6. aqueous silver nitrate (approximately 0.05 mol dm^{-3})
7. aqueous barium nitrate (approximately 0.2 mol dm^{-3})
8. limewater (a saturated solution of calcium hydroxide)
9. aqueous potassium manganate(VII) (approximately 0.02 mol dm^{-3})
10. aqueous potassium iodide (approximately 0.1 mol dm^{-3})
11. red and blue litmus paper
12. aluminium foil strip
13. filter paper strip
14. wooden splint

Class	Reg Number
17S	

Name ______________________________

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9729/04

Paper 4

11 September 2018

2 hours 30 minutes

READ THESE INSTRUCTIONS FIRST

Write your name, register number and class in the space provided above.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.
Do not use correction fluid.

Answer **all** questions in the space provided on the Question Paper.

The use of approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are provided on Pages **23** and **24**.
At the end of the examination, fasten all your work accurately together.

The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

Examiner's Use	
Q1	**/ 21**
Q2	**/ 19**
Q3	**/ 15**
Total	**/ 55**

This document consists of **24** printed pages (including this cover page).

1 In this experiment, you are to determine the number of water of crystallisation (value of x) in an iron(II) salt, $(NH_4)_2Fe(SO_4)_2.\ x\ H_2O$ by titration with potassium manganate(VII).

You are provided with the following reagents.

FA 1 is potassium manganate(VII), $KMnO_4$ solution, of an approximate concentration 0.02 mol dm^{-3}
FA 2 is 0.0780 mol dm^{-3} ethanedioate ions $C_2O_4^{2-}$
FA 3 is a solution of the iron(II) salt containing 38.4 g dm^{-3} of $(NH_4)_2Fe(SO_4)_2.\ x\ H_2O$.
FA 4 is dilute sulfuric acid

Before using the provided solution of manganate(VII) ions, it is important to accurately determine its concentration. The exact concentration of **FA 1** can be determined with the given **FA 2** solution.

In an acidic medium, ethanedioate ions $C_2O_4^{2-}$ reacts with manganate(VII) ions MnO_4^- to form Mn^{2+} and CO_2 gas.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

As this reaction is very slow initially, MnO_4^- should only be added to a pre–heated $C_2O_4^{2-}$ solution in the presence of excess dilute acid. Subsequently, as the reaction proceeds, the rate of reaction will speed up and hence eliminating the need to continue heating.

Method

(a) (i) Standardisation of FA 1 solution

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 10.0 cm^3 of **FA 2** into the conical flask.
3. Using an appropriate measuring cylinder, transfer 20 cm^3 of **FA 4** to the same conical flask.
4. Heat this solution to about 65 °C using the Bunsen burner.
5. **Turn off your Bunsen burner.**

Caution: Use the heat–resistant foam to handle the neck of the heated flask.

6. Run **FA 1** from the burette into this flask until a **permanent** pale pink colour is obtained.

Initially, the colour of the **FA 1** will take some time to disappear. Subsequently, as the reaction proceeds, the rate of reaction will speed up

7. Record your titration results in the space provided on page **3**. Make certain that your recorded results show the precision of your working.
8. Repeat steps **1** to **7** as necessary until consistent results are obtained.

Results

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

[2]

volume of **FA 1** = ……………………………….

(iii) Determine the concentration of MnO_4^- in **FA 1**.

[1]

Concentration of MnO_4^- in **FA 1** = ……………………………….

M1	M2	M3

(iv) For the titration in **(a)(i)** between ethanedioate ions $C_2O_4^{2-}$ and manganate(VII) ions MnO_4^-, the ethanedioate solution needs to be at about 60 °C at the start.

However, during the titration, as **FA 1** is added, the temperature of the mixture decreases. This decrease in temperature did not cause the rate of reaction between $C_2O_4^{2-}$ and MnO_4^- added from the burette to decrease.

Suggest an explanation for this.

[1]

M4	

(v) Calculate the maximum total percentage uncertainty for your titration in **(a)(i)** if the associated uncertainty associated with each reading using a 10.0 cm^3 pipette and a burette are ±0.03 cm^3 and ±0.05 cm^3 respectively.

Percentage uncertainty = …………………...……. **[1]**

M5	

(b) **(i)** **Titration**

1. Fill the burette with **FA 1**.
2. Pipette 25.0 cm^3 of **FA3** into a conical flask and add 20 cm^3 of **FA 4** using a measuring cylinder.
3. Titrate **FA 3** with **FA 1** until the end–point is reached.
4. Carry out as many accurate titrations as you think necessary to obtain consistent results. Record your titration results in the space provided below.

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

[3]

volume of **FA 1** = ………………………………

M6	M7	M8

(c) Calculations

(i) The two half–equations for the reaction between the iron(II) salt and manganate(VII) ions are shown below.

$MnO_4^- + 8\ H^+ + 5\ e \longrightarrow Mn^{2+} + 4\ H_2O$

$Fe^{2+} \longrightarrow Fe^{3+} + e$

Calculate the amount of iron(II) ion present in 1.00 dm^3 of **FA 3**.

[1]

Amount of iron(II) ions in 1.00 dm^3 of **FA 3** = ………………………………

M9	

(ii) Using your answer in **(c)(i)**, determine the value of x, the number of water of crystallisation in the iron(II) salt, $(NH_4)_2Fe(SO_4)_2.\ x\ H_2O$.

[A_r: Fe, 55.8; H, 1.0; N, 14.0; O, 16.0; S, 32.1]

[3]

x = ………………………………

M10	M11	M12

(d) In the titration of the iron(II) salt and manganate(VII) ion in **(b)(i)**, it was observed that the colour of the mixture in the conical flask gradually changes before an excess drop of manganate(VII) turns the mixture pale pink at the end point.

State and explain the colour changes you observed in the titration, in terms of the complex ions involved.

[2]

M13	M14

(e) Planning

A saturated aqueous solution of magnesium methanoate, $Mg(HCOO)_2$, has a solubility of approximately **150 g dm^{-3}** at room temperature. Its exact solubility can be determined by titrating magnesium methanoate against aqueous potassium manganate(VII).

During the titration, methanoate ion, $HCOO^-$ reacts with manganate(VII) ion, MnO_4^- in an acidic medium as shown in the equation below.

$$2MnO_4^- + 5HCOO^- + 11H^+ \longrightarrow 2Mn^{2+} + 5CO_2 + 8H_2O$$

You may assume that you are provided with:

- 100 g of solid magnesium methanoate, $Mg(HCOO)_2$
- 0.0200 mol dm^{-3}aqueous potassium manganate(VII), $KMnO_4$
- 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
- the apparatus and equipment normally found in a school or college laboratory.

In order to obtain a reliable and feasible titre value, the saturated solution of magnesium methanoate needs to be diluted accurately (**~50 times** dilution) before titration.

(i) Plan an investigation to determine the effect of temperature on the solubility of magnesium methanoate, $Mg(HCOO)_2$. Your plan must enable you to plot a graph that includes data from the experiment.

Your plan should include details of:

- the preparation of 50 cm^3 of **saturated** aqueous solutions of $Mg(HCOO)_2$ at different temperatures
- the preparation of diluted solutions of $Mg(HCOO)_2$ for titration
- an outline of how the titration could be carried out
- a sketch of the graph you would expect to obtain
- an outline how the results can be used to determine the effect of temperature on the solubility of $Mg(HCOO)_2$

[6]

YOU ARE NOT REQUIRED TO PERFORM THIS EXPERIMENT.

....

....

....

....

....

....

....

M15 to M20

(ii) A student used the same titration method, this time to measure the concentration of a saturated solution of barium methanoate. Explain why the acidification of the solution with dilute sulfuric acid might make the titration difficult to do.

[1]

M21	

[Total: 21]

2 Strong acids, such as hydrochloric acid, HC*l*, are completely ionised in aqueous solution. Weak acids, such as ethanoic acid, CH_3COOH, are partially ionised in aqueous solution.

You will investigate the enthalpy change for the reaction of an excess of each of these acids with magnesium and hence determine the energy needed to cause the weak acid to ionise completely.

(a) **Experiment 1**

FA 5 is 1.0 mol dm^{-3} hydrochloric acid, HC*l*.
FA 6 is magnesium, Mg.

1. Weigh the magnesium strip, **FA 6**, and record the mass reading.
2. Support the Sytrofoam cup in the 250 cm^3 beaker.
3. Coil the magnesium strip loosely so that it fits into the bottom of the Sytrofoam cup and then remove the strip.
4. Use the measuring cylinder to transfer 25 cm^3 of the acid, **FA 5**, into the Sytrofoam cup.
5. Place the thermometer in the acid and read the initial temperature. This is the temperature at time zero (t = 0).
6. Start timing and do not stop the stop watch until the whole experiment has been completed.
7. Read the temperature of the acid every half minute for two minutes.
8. At time t = 2.5 minutes drop the magnesium strip, **FA 6**, into the acid and stir the mixture. **Do not try to read the temperature at this time**.
9. Measure and record, the temperature of the mixture at t = 3.0 minutes and then every half minute until t = 8.0 minutes. Stir the mixture continuously between thermometer readings.
10. Rinse the Sytrofoam cup for use in **Experiment 2**. Shake to remove excess water.

In the space provided below, record all measurements of mass. Record all your results of temperature and time in a table.

Results

[4]

M1	M2	M3	M4

(b) Plot a graph of temperature on the y–axis against time on the x–axis on the grid below. The scale for the temperature axis should extend 10 °C greater than the maximum temperature you recorded. You will use the graph to determine the theoretical maximum temperature rise at 2.5 minutes.

Draw two lines of best fit through the points on your graph, the first for the temperature before adding **FA 6** and the second for the cooling of the mixture once the reaction is complete.

Extrapolate the two lines to 2.5 minutes, draw a vertical line between the two and determine the theoretical rise in temperature at this time.

theoretical rise in temperature at 2.5 minutes = ... **[4]**

M5	M6	M7	M8

(c) Magnesium reacts with hydrochloric acid according to the equation shown.

$$Mg\ (s)\ +\ 2HCl\ (aq) \longrightarrow MgCl_2\ (aq) + H_2\ (g)$$

(i) Use your answer to **(b)** to calculate the heat energy, in joules, given out when **FA 6** is added to the acid.
[Assume 4.2 J of heat energy raises the temperature of 1.0 cm^3 of the mixture by 1.0 °C.]
[1]

heat energy evolved = ...

M9	

(ii) Calculate the enthalpy change when 1 mole of **FA 6**, Mg, reacts with hydrochloric acid. [A_r: Mg, 24.3]
[1]

enthalpy change, ΔH = ...

M10	

(d) **(i)** Calculate the percentage error in the measurement of ΔT in the experiment.
[1]

M11	

(ii) A student suggested that the experiment carried out in **(a)** could be improved by using a catalyst.

Would the use of a catalyst improve the accuracy of the results in this experiment? Give a reason for your answer.

[1]

M12	

(iii) Another student could not find the hydrochloric acid, **FA 5**, and used sulfuric acid, H_2SO_4, instead. He used the same volume and the same concentration as the hydrochloric acid in **FA 5**.

What effect would this change have on the temperature rise in the experiment? Give a reason for your answer.

[1]

M13	

(e) **Experiment 2**

FA 7 is 1.0 mol dm^{-3} ethanoic acid, CH_3COOH
FA 8 contains one strip of magnesium, Mg of a mass of 0.087 g

Read the whole **Experiment 2** before starting any practical work.

1. Support the Sytrofoam cup in the 250 cm^3 beaker.
2. Coil the magnesium strip loosely so that it fits into the bottom of the Sytrofoam cup and then remove the strip.
3. Use the measuring cylinder to transfer 25 cm^3 of the acid, **FA 7**, into the Sytrofoam cup.
4. Place the thermometer in the acid and measure and record the initial temperature of the acid.
5. Add the piece of magnesium, **FA 8**, into the acid in the cup.
6. Using the thermometer, stir the mixture continuously until it reaches its maximum temperature. This could take several minutes. Record this temperature, T_{max}.
7. Calculate and record the change in temperature, ΔT.
8. Complete **Table 2.1** by recording all measurements of temperature.

Table 2.1

Initial temperature / °C	
Maximum temperature, T_{max} / °C	
Change in temperature, ΔT / °C	

[1]

M14	

Magnesium reacts with ethanoic acid according to the equation shown.

$$Mg\ (s)\ +\ 2CH_3COOH\ (aq) \longrightarrow Mg(CH_3COO)_2\ (aq) + H_2\ (g) \qquad \Delta H_1$$

Use your results in **Table 2.1** to calculate the enthalpy change, ΔH_1, when 1 mole of Mg, **FA 8**, reacts with excess ethanoic acid. Assume 4.2 J of heat energy changes the temperature of 1.0 cm^3 of the mixture by 1.0 °C. [A_r: Mg, 24.3]

[1]

ΔH_1 = ...

M15	

(f) Hydrochloric acid is a strong acid; it is fully ionised in aqueous solution. When the same experiment in **(e)** was repeated with hydrochloric acid, **FA 5**, instead of ethanoic acid, the enthalpy change, ΔH_2, when 1 mole of Mg reacts with excess hydrochloric acid was determined to be – 461.1 kJ mol^{-1}.

Ethanoic acid is a weak acid. It is partially ionised in aqueous solution.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-\,(aq) + H^+\,(aq)$$

You are to determine the energy needed for one mole of ethanoic acid to ionise completely.

$$CH_3COOH\,(aq) \longrightarrow CH_3COO^-\,(aq) + H^+\,(aq) \qquad \Delta H_3$$

Use the values for the enthalpy changes, ΔH_1 you obtained in **(e)** and the ΔH_2 provided to calculate the energy change for the ionisation of ethanoic acid, ΔH_3.

Show clearly how you obtained your answer.

[2]

ΔH_3 = ...

M16	M17

(g) The experiment in **(e)** was repeated using trichloroethanoic acid instead of ethanoic acid.

$$Mg(s) + 2\,CCl_3COOH\,(aq) \longrightarrow Mg(CCl_3COO)_2\,(aq) + H_2\,(g)$$ ***reaction 3***

Trichloroethanoic acid, CCl_3COOH, is a weak acid that is however stronger than ethanoic acid. The enthalpy change for ***reaction 3*** is between the two values given in **Table 2.2**.

Table 2.2

reaction	equation	ΔH / kJ mol^{-1}
1	$Mg\,(s) + 2CH_3COOH\,(aq) \longrightarrow Mg(CH_3COO)_2\,(aq) + H_2\,(g)$	−460.3
2	$Mg\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + H_2\,(g)$	−464.1

(i) Explain why the enthalpy change for reaction 3 is more exothermic than the enthalpy change for reaction 1.

[1]

M18	

(ii) Explain why the enthalpy change for reaction 3 is less exothermic than the enthalpy change for reaction 2.

[1]

M19	

[Total: 19]

3 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where reagents are selected for use in a test, the **name** or **correct formula** of the element or compound must be given.

Where gases are released they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

(a) **(i)** **FA 9**, **FA 10** and **FA 11** each contain one anion and one cation.

Carry out the following tests and record your observations.

Test	***observations***		
	FA 9	**FA 10**	**FA 11**
To a 1 cm depth of solution in a test–tube, add a few drops of aqueous silver nitrate, then			
add aqueous ammonia.			
To a 1 cm depth of solution in a test–tube, add a few drops of aqueous barium nitrate, then			
add dilute nitric acid.			

Test	***observations***		
	FA 9	**FA 10**	**FA 11**
To a 1 cm depth of solution in a test–tube, add a spatula of solid sodium carbonate.			

M1	M2	M3	M4

(ii) What cation is present in **FA 9**, **FA 10** and **FA 11**?

…………………………………………………………………………………………

(iii) Suggest another chemical test that you could carry out to confirm the presence of the cation you identified in **(ii)**.

Carry out this test on one of **FA 9**, **FA 10** and **FA 11** and record your observations.

Test: …………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

Observations: …………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

(iv) Complete the table to identify, as far as possible, the anions present in **FA 9**, **FA 10** and **FA 11**. If you are not able to identify the anion from the tests you carried out in **(i),** write 'unknown'.

	FA 9	**FA 10**	**FA 11**
ion present			

M5	M6	M7	M8

(v) For any one anion that you were unable to identify in **(iv)** you are to devise a test or tests that will enable you to identify it. You can assume that it is one of the anions listed in the Qualitative Analysis Notes.

Carry out the test(s), record the observation(s) you obtained and identify the unknown anion.

In the space below, draw a single table to record details of the test(s) performed and observations made.

Identify the anion and state the evidences for your identification.

Anion: ....

Evidence: ....

....

....

....

[10]

M9	M10

(b) **FA 12** is an aqueous solution of a mixture containing two anions.
Carry out the following tests and record your observations.

Test	*Observations*
To a 1 cm depth of **FA 12** in a test–tube, add a 1 cm depth of dilute hydrochloric acid, then	
add a few drops of hydrogen peroxide, then	
add a few drops of starch.	
To a 1 cm depth of **FA 12** in a test–tube, add a 3 cm depth of aqueous copper(II) sulfate, then	
add a 1 cm depth of dilute hydrochloric acid, then	
add aqueous sodium thiosulfate.	

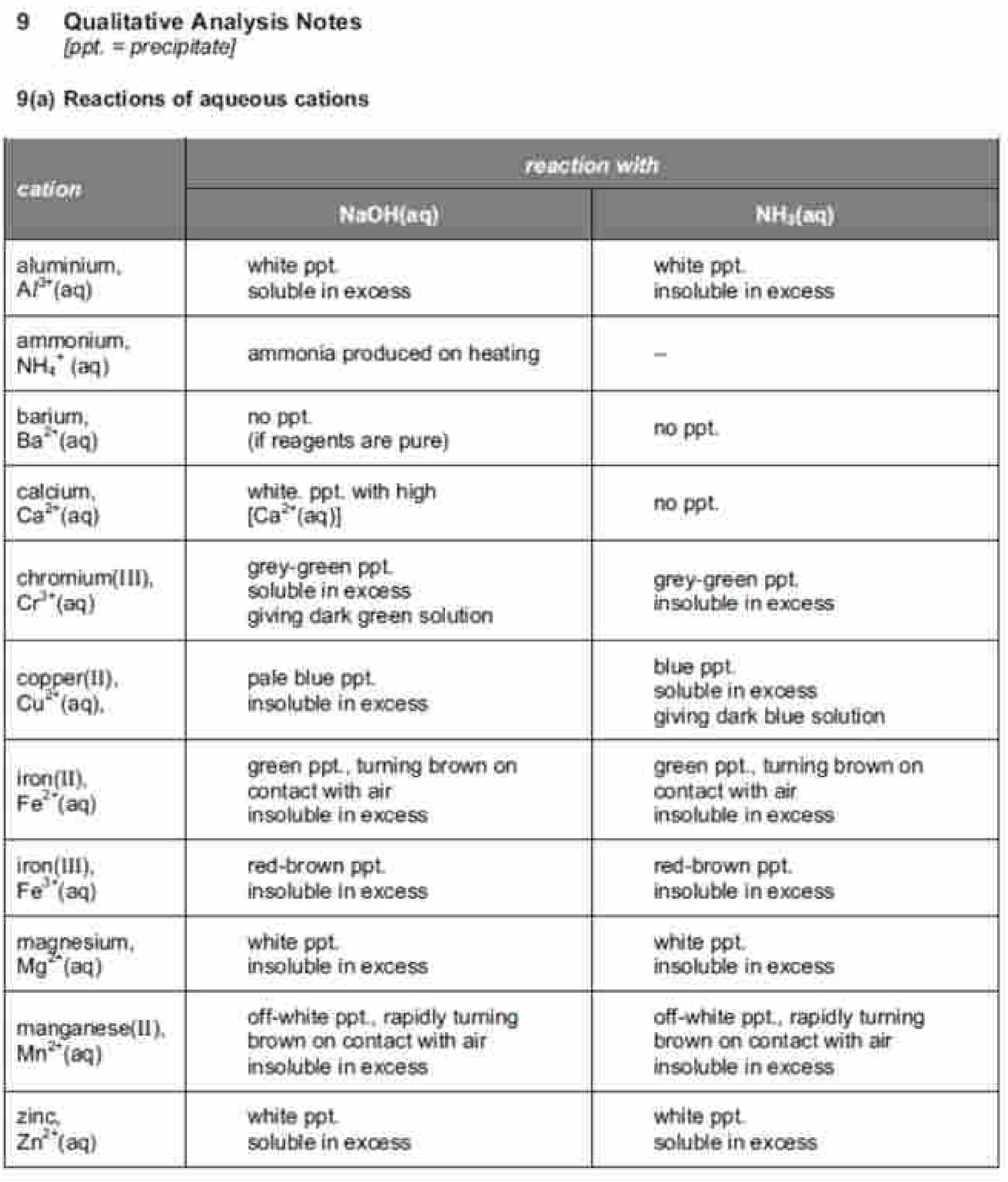
From these observations, identify the two anions present in **FA 12**.

Anions present in **FA 12** .... and ....

[5]

M11	M12	M13	M14	M15

[Total: 15]



9 Qualitative Analysis Notes

[ppt. = precipitate]

9(a) Reactions of aqueous cations

cation	*reaction with*	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+ (aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

9(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, NO_3^- (aq)	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-} (aq)	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-} (aq)	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

9(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

9(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

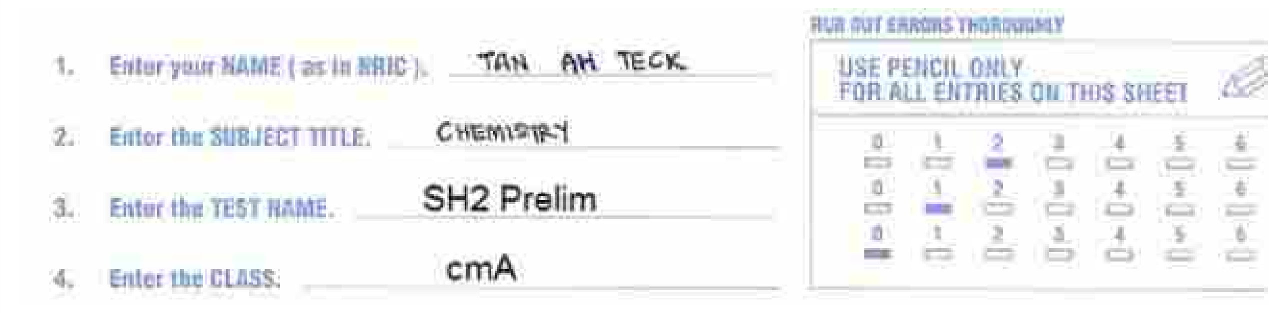
CHEMISTRY
Paper 1 Multiple Choice
Additional Materials: Optical Answer Sheet
Data Booklet

9729/01
Thur 13 September 2018
1 hour

READ THESE INSTRUCTIONS FIRST
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.
There are **30** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.
Read the instructions on the Answer Sheet very carefully.
Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This paper consists of **17** printed pages

Instructions on how to fill in the Optical Mark Sheet



1. Enter your NAME (as in NRIC). TAN AH TECK
2. Enter the SUBJECT TITLE. CHEMISTRY
3. Enter the TEST NAME. SH2 Prelim
4. Enter the CLASS. cmA

RUB OUT ERRORS THOROUGHLY

USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET

0 ☐	1 ☐	2 ■	3 ☐	4 ☐	5 ☐	6 ☐
0 ☐	1 ■	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐
0 ■	1 ☐	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐

Student	Examples of Registration No.	Shade:
	1705648	75648

Example:

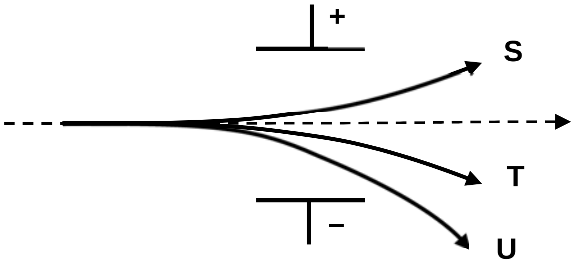
Shade the index number in a 5 digit format on the optical mark sheet:

2nd digit and the last 4 digits of the Registration Number.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

1 *Use of the Data Booklet is relevant to this question.*

The following are flight paths of charged particles when accelerated in an electric field.



Which correctly identifies **S**, **T** and **U**?

	S	**T**	**U**
A	$^{15}O^{+}$	$^{14}C^{+}$	$^{14}N^{+}$
B	$^{15}O^{-}$	$^{15}O^{+}$	$^{28}Si^{+}$
C	$^{14}N^{-}$	$^{28}Si^{2+}$	$^{14}C^{2+}$
D	$^{14}N^{-}$	$^{14}C^{+}$	$^{28}Si^{2+}$

2 In which sequence is the molecules listed in the order of increasing dipole moment?

A SO_3, CO_2, $AlCl_3$

B H_2O, H_2S, HBr

C CF_4, CO, HF

D NH_3, HF, $BeCl_2$

3 In which row are the molecules arranged in order of increasing bond angle?

1 CH_4, $AlCl_3$, XeF_2

2 H_2S, PH_3, NH_3,

3 NF_3 , NCl_3, SO_3

A 1, 2 and 3

B 1 and 2

C 2 and 3

D 1 only

4 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$\underset{\text{propadiene}}{H_2C{=}C{=}CH_2} \rightleftharpoons \underset{\text{propyne}}{CH_3C{\equiv}CH}$$

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by s – sp overlap

B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap

5 *Use of the Data Booklet is relevant to this question.*

A reaction scheme regarding manganese compounds is shown below.

$$\begin{tikzcd}
KMnO_4(aq) \arrow[r, "Fe(OH)_2"] \arrow[d, "\text{reagent } \mathbf{Q}"'] & \text{brown solid } \mathbf{P} \\
{[Mn(H_2O)_6]^{2+}(aq)} \arrow[r, "NaOH(aq)"] \arrow[d, "NH_3(aq)"'] & \text{off-white solid } \mathbf{S} \\
\text{off-white solid } \mathbf{S} &
\end{tikzcd}$$

Which statements are true?

1 Off-white solid **S** is able to dissolve in excess of $NH_3(aq)$.

2 Manganese in brown solid **P** has an oxidation state of +4.

3 Reagent **Q** can be acidified $[V(H_2O)_6]^{3+}(aq)$.

4 Off white solid **S** turns brown upon standing.

A 1, 2 and 4

B 2, 3 and 4

C 2 and 3

D All correct

6 In which chemical reaction does the transition metal compound or element behave as the described catalyst?

	Reaction	Catalyst
1	Formation of ethanal from ethanol, using acidified potassium dichromate	Homogeneous
2	Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide	Heterogeneous
3	Chlorination of benzene, using chlorine and iron(III) chloride	Homogeneous
4	Removal of air pollutants in exhaust systems of cars, using nickel	Heterogeneous

A 1, 2 and 4

B 2 and 3

C 3 and 4

D 2, 3 and 4

7 *Use of the Data Booklet is relevant to this question.*

Given the following standard enthalpy changes,

	ΔH /kJ mol^{-1}
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	−75

What is the standard enthalpy change of atomisation of graphite?

A +693 kJ mol^{-1}

B +1129 kJ mol^{-1}

C −2151 kJ mol^{-1}

D −2587 kJ mol^{-1}

8 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta H^{\ominus} = -176 \text{ kJ mol}^{-1}$$

The magnitude of standard entropy change of this reaction is 284 J K^{-1} mol^{-1}.

Which statements are correct?

1 $\Delta G^{\ominus} = -261$ kJ mol^{-1}.

2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

3 There is an increase in order as strong hydrogen bonding between NH_3 and HCl hold the particles in NH_4Cl in fixed positions and close to each other.

A 1 only

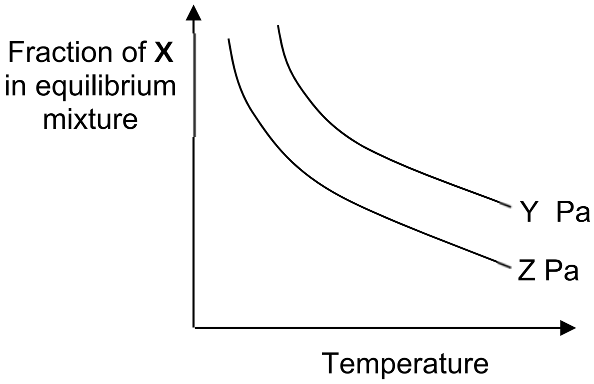
B 1 and 2

C 2 only

D 2 and 3

9 The graph below shows how the fraction of **X**, which represents one of the following compounds in the given equilibrium mixture, varies with temperature at pressures of Y Pa and Z Pa.

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \quad \Delta H = -1267 \text{ kJ mol}^{-1}$$



Identify **X** and the correct relative magnitudes of Y and Z.

	X	**Pressure**
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

10 One of the key production stages in the Contact Process is the production of sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

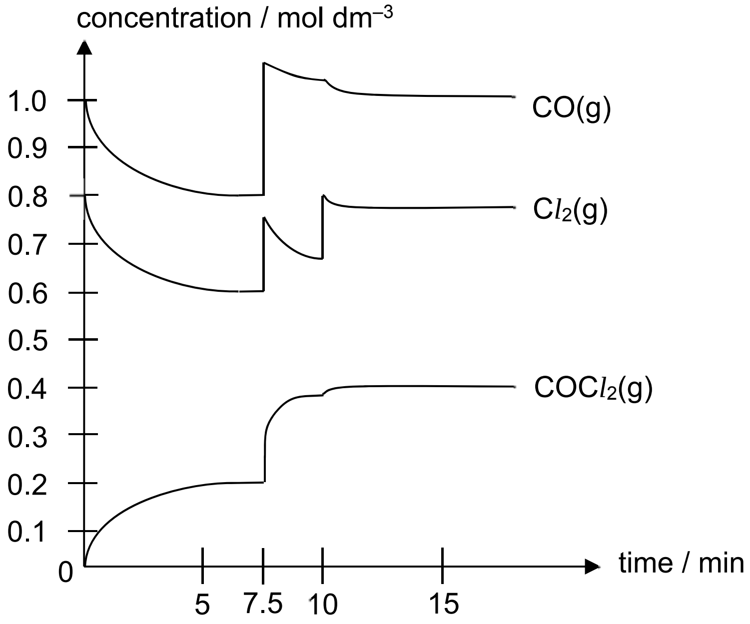
The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to k_1, k_{-1} and K_c if the temperature of the reaction is increased?

	k_1	k_{-1}	K_c
A	increase	increase	increase
B	increase	decrease	increase
C	decrease	increase	decrease
D	increase	increase	decrease

11 The reaction between carbon monoxide and chlorine was studied in an experiment by mixing the two gases and changing the reaction conditions inside the reaction vessel at different times during the experiment. The concentrations of the gases in the vessel were followed with time, and the following graph is obtained.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H^\ominus = -113.4\ \text{kJ mol}^{-1}$$



Which conclusion deduced from the graph is **incorrect**?

A The rate of forward reaction equals the rate of backward reaction at 7 min.

B The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.

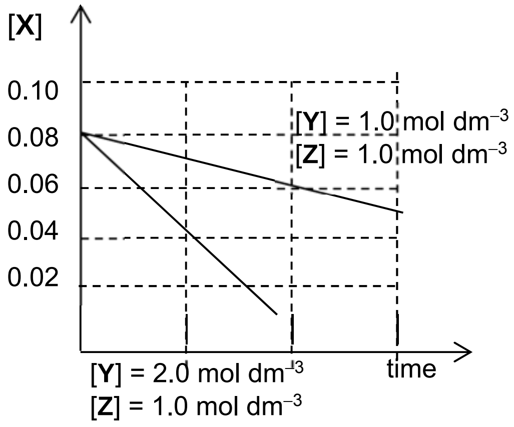
C The equilibrium constant, K_c, for the system when determined at 7 min is 0.417 mol^{-1} dm^3.

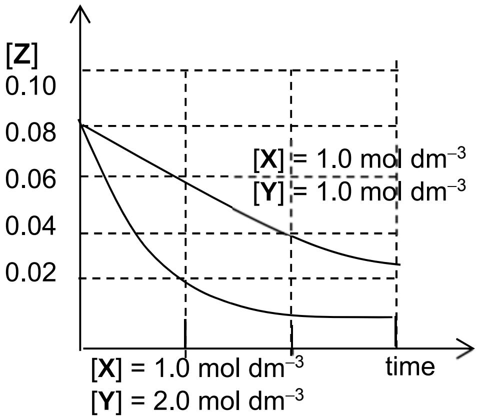
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

12 Substances **X**, **Y** and **Z** react according to the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) + \mathbf{Z}(aq) \rightarrow 2\mathbf{W}(aq) + \mathbf{U}(aq)$$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied while the other two were kept constant. The results are shown below.





Which rate equations represent the experimental results?

A rate = $k[\mathbf{Y}]^2$

B rate = $k[\mathbf{Y}][\mathbf{Z}]$

C rate = $k[\mathbf{Y}]^2[\mathbf{Z}]$

D rate = $k[\mathbf{X}][\mathbf{Y}][\mathbf{Z}]$

13 *Use of the Data Booklet is relevant to this question.*

The reaction of acidified aqueous potassium iodide with hydrogen peroxide is represented by the following equation.

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Which statements about the reaction are true?

1 E^θ_{cell} = +1.23 V.

2 E_{cell} becomes more negative when Br_2(aq) is added to the anode.

3 E_{cell} becomes more positive when a few drops of $AgNO_3$(aq) is added to the anode.

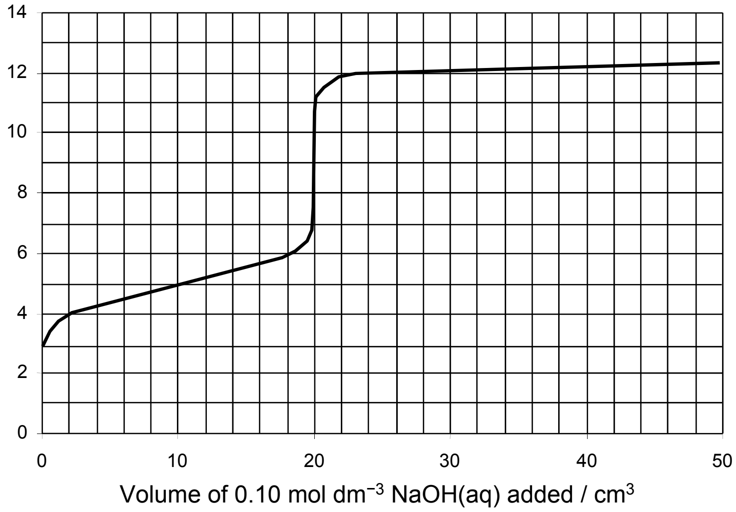
A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

14 The titration curve below shows the reaction between a monoprotic acid, **HX**, and aqueous sodium hydroxide.



Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Methyl red	red to yellow	4.2 – 6.3
Bromothylmol blue	yellow to blue	6.0 – 7.6
Thymolpthalein	colourless to blue	8.3 – 10.5

What statements are correct?

1 Methyl red will indicate an endpoint at a value lower than 20.0 cm^3.

2 K_a value of HX is 1.0×10^{-5}

3 Buffer at maximum buffer capacity is formed at 25.0 cm^3 since the pH change in that region is relatively constant.

4 Alkaline hydrolysis of salt takes place after the equivalence point accounting for the alkaline pH value of the reaction mixture.

A 1,2 and 3 **B** 2,3 and 4 **C** 1 and 2 **D** 3 and 4

15 Given the following data,

K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Reaction mixture **X**:
25.0 cm^3 of 2.0×10^{-5} mol dm^{-3} CH_3COOH and 25.0 cm^3 water

Reaction mixture **Y**:
25.0 cm^3 of 0.02 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.01 mol dm^{-3} NaOH

Reaction mixture **Z**:
25.0 cm^3 of 0.01 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.02 mol dm^{-3} NaOH

Which is the correct order of pH values of the above reaction mixture?

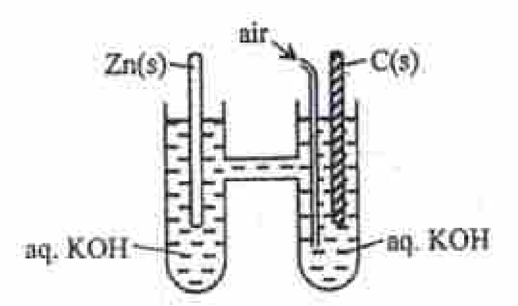
A **Z** > **Y** > **X**

B **Z** > **X** > **Y**

C **Y** > **X** > **Z**

D **X** > **Y** > **Z**

16 A cell is constructed with zinc and carbon electrodes, each weighing 50 g, partly immersed in aqueous KOH.



When connected in a circuit, some zinc passes into solution as zincate(II) ions, $ZnO_2^{2-}(aq)$. The cell delivers a current of 1.68×10^{-2} A. The zinc electrode is replaced once 60% of it is used up.

What is the time taken, in seconds, before replacement of zinc electrode becomes necessary?

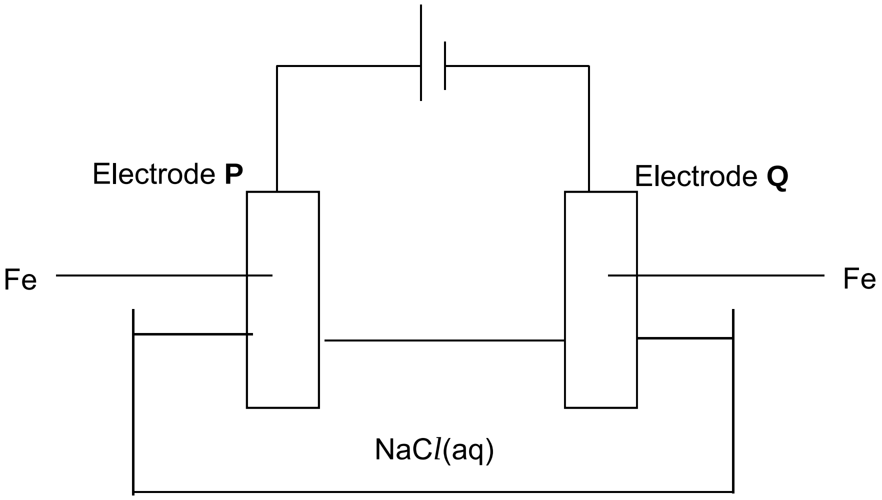
A 2.63×10^6

B 4.39×10^6

C 5.27×10^6

D 8.78×10^6

17 An experiment is set up as shown below to study the corrosion of iron.



What will occur at electrodes **P** and **Q**?

	Electrode **P**	Electrode **Q**
A	No corrosion of Fe	Corrosion of Fe ; H_2 gas evolved
B	No corrosion of Fe	Corrosion of Fe ; O_2 gas evolved
C	Corrosion of Fe	No corrosion of Fe ; Na deposited
D	Corrosion of Fe	No corrosion of Fe ; H_2 gas evolved

18 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been replaced by safer options such as the standard hydrogen electrode (S.H.E.).

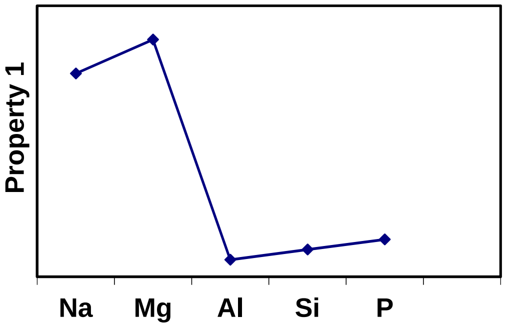
Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

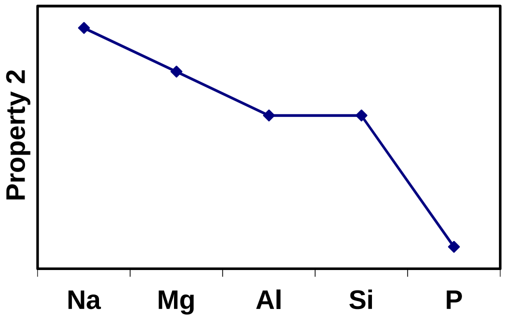
When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V **B** +1.30 V **C** –1.79 V **D** –2.82 V

19 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.





Which correctly describes properties 1 and 2?

	Property 1	**Property 2**
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the chlorides at the highest oxidation states	pH of the oxides when added to water
C	melting point of the oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the chlorides at the highest oxidation states when added to water

20 What mass of sodium ethanedioate, $Na_2C_2O_4$, should be added to 250 cm^3 of a 2.2×10^{-3} mol dm^{-3} solution of calcium nitrate before a precipitate is formed?
[K_{sp} of CaC_2O_4 = 2.27×10^{-9} mol^2 dm^{-6}]

A 3.5×10^{-5} g
B 1.0×10^{-6} g
C 2.5×10^{-7} g
D 2.3×10^{-9} g

21 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

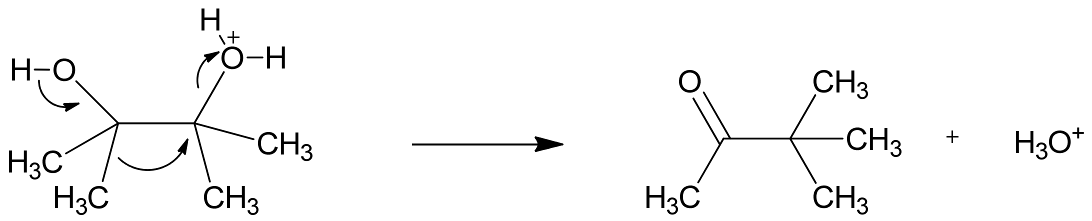
A It can be formed by the reduction of $C_6H_5CH_2CN$.

B It reacts with CH_3CO_2H to form $C_6H_5CH_2NHCOCH_3$.

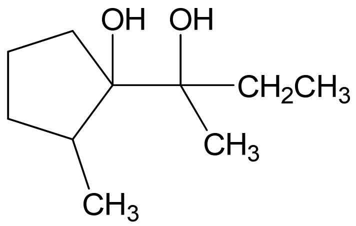
C It is formed by the reaction between $C_6H_5NO_2$ and tin in concentrated HCl, followed by NaOH.

D It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

22 When a 1,2–diol is treated with a dilute acid, the protonated diol undergoes the following pinacol rearrangement.

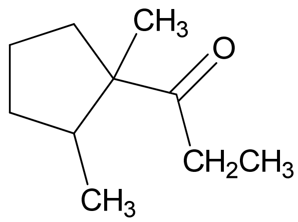


Which structure is **not** formed when diol **Z** undergoes pinacol rearrangement?

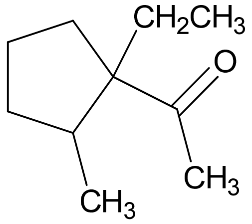


diol **Z**

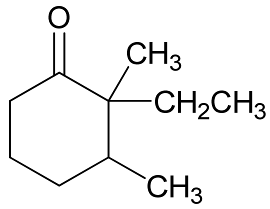
A



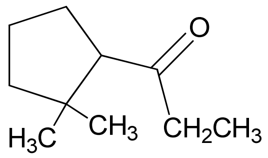
B



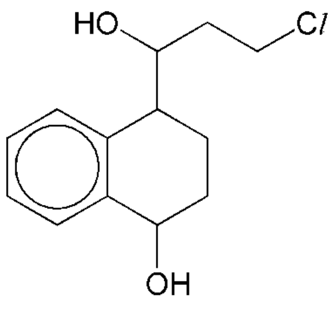
C



D



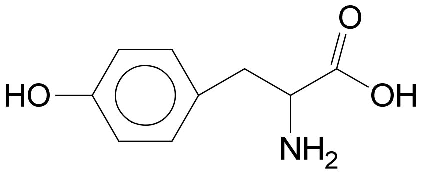
23 What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H_2SO_4?



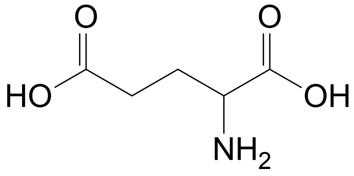
A 2 **B** 4 **C** 6 **D** 8

24 Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species move towards the anode.

With a buffer at pH 4, which statement is true?



Tyrosine (pI = 5.7)



Glutamic acid (pI = 3.2)

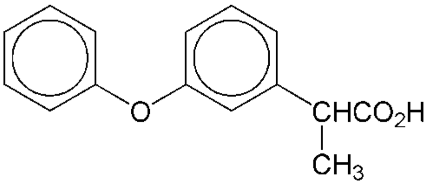
A Both species move towards the anode

B Both species move towards the cathode.

C Tyrosine moves towards the anode, glutamic acid moves towards the cathode.

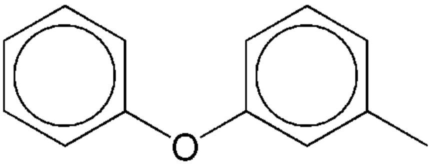
D Tyrosine moves towards the cathode, glutamic acid moves towards the anode.

25 *Fenoprofen* is an anti-arthritic agent.



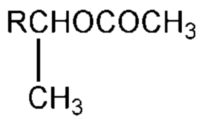
Which of the following could be part of a reaction sequence for synthesising *Fenoprofen*?

In the sequences below, R =



A $RCHBrCH_3 \xrightarrow[\text{heat}]{\text{NaCN(ethanolic)}} \text{Intermediate} \xrightarrow[\text{heat}]{H^+(aq)}$ *Fenoprofen*

B $RCH(CH_3)_2 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

C 

$\underset{\displaystyle CH_3}{RCHOCOCH_3} \xrightarrow[\text{warm}]{I_2,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

D $RCH(OH)CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

26 Chlorofluorocarbons (CFCs) are commonly used as aerosols, propellants and refrigerants. However in the stratosphere, CFCs can damage the ozone layer through a radical chain reaction.

In which sequence are the following compounds listed in increasing order of their ability to destroy ozone?

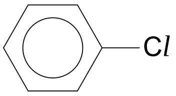
A $CHClFCClF_2 < CCl_2FCCl_2F < CHClF_2$

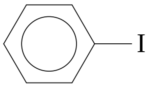
B $CCl_2FCCl_2F < CHClF_2 < CHClFCClF_2$

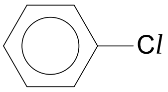
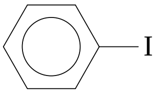
C $CHClF_2 < CCl_2FCCl_2F < CHClFCClF_2$

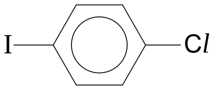
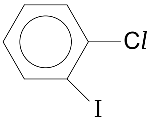
D $CHClF_2 < CHClFCClF_2 < CCl_2FCCl_2F$

27 Which is the product formed when benzene reacts with iodine chloride, ICl in the presence of a suitable catalyst?

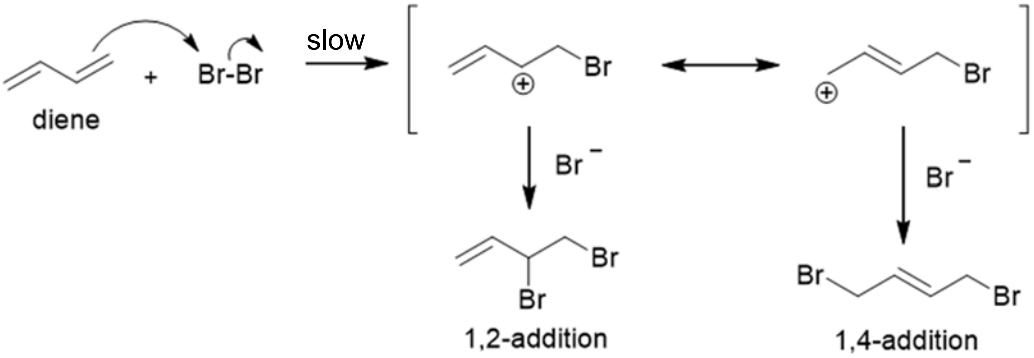
A 

B 

C a mixture of  and 

D a mixture of  and 

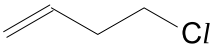
28 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.

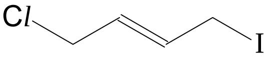


Which statement is **not** correct?

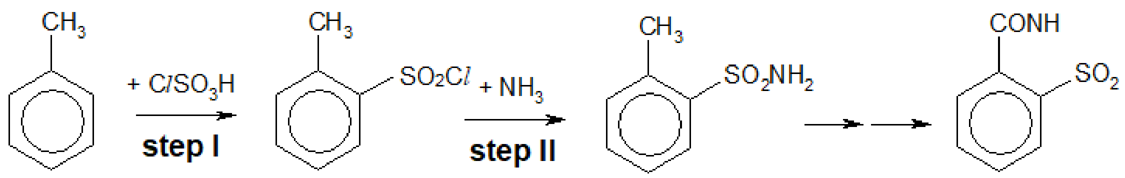
A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HCl is used is .

D The 1,4–addition product formed when ICl is used is .

29 Saccharin is an artificial sweetening agent used in some soft drinks and is manufactured from methylbenzene through a four-step synthesis. Part of the reaction scheme is shown below.



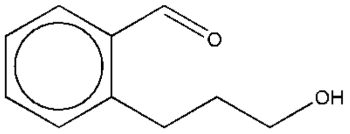
What type of reaction do steps **I** and **II** illustrate?

	Step I	**Step II**
A	Electrophilic addition	Nucleophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

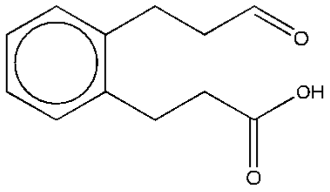
30 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 respectively but a negative result when treated with alkaline Cu(II) complex.

What could **X** be?

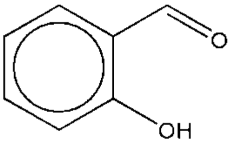
A



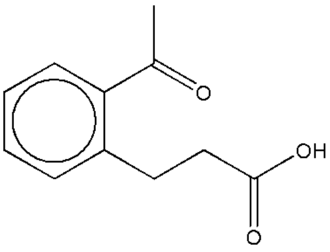
B



C



D

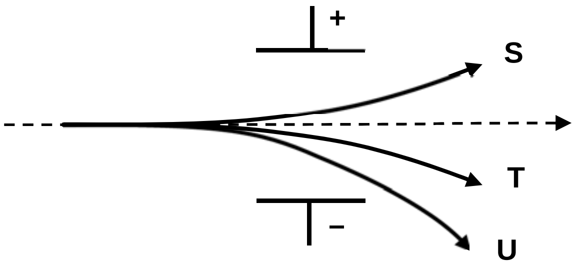


END of PAPER

NJC 2018 SH2 H2 Chemistry Paper 1 Solutions:

1 *Use of the Data Booklet is relevant to this question.*

The following are flight paths of charged particles when accelerated in an electric field.



Which correctly identifies **S**, **T** and **U**?

	S	T	U
A	$^{15}O^{+}$	$^{14}C^{+}$	$^{14}N^{+}$
B	$^{15}O^{-}$	$^{15}O^{+}$	$^{28}Si^{+}$
C	$^{14}N^{-}$	$^{28}Si^{2+}$	$^{14}C^{2+}$
D	$^{14}N^{-}$	$^{14}C^{+}$	$^{28}Si^{2+}$

C: Negatively charged ions attracted to positive plate, positive ions to negative plate.

particles	$^{14}N^{-}$	$^{14}C^{2+}$	$^{14}C^{+}$	$^{28}Si^{2+}$
Charge /mass	1/14	2/14 = 1/7	1/14	2/28 = 1/14

Since angle of deflection is charge/mass ratio, **S** and **T** have roughly the same angle of deflection but different polarity, while **U** has almost double the angle of deflection as **T**.

2 In which sequence is the molecules listed in the order of increasing dipole m

A SO_3, CO_2, $AlCl_3$

All non-polar. Dipole moments cancel out due to shape of molecule.

B H_2O, H_2S, HBr

H_2O and H_2S have bent shape. **H_2O is more polar than H_2S** as O is more electronegative than S.

C CF_4, CO, HF

CF_4 is non-polar, dipole moments cancel out due to tetrahedral shape of molecule.
CO and HF are linear. HF is more polar than CO, as electronegativity difference is greater between H and F than between C and O.

D NH_3, HF, $BeCl_2$

NH_3 and HF are polar but $BeCl_2$ is non-polar, dipole moments cancel out due to linear shape of molecule.

3 In which row are the molecules arranged in order of increasing bond angle?

1 CH_4, $AlCl_3$, XeF_2

CH_4 (tetrahedral, 109 degrees)
$AlCl_3$ (trigonal planar, 120 degrees)
XeF_2 (linear, 180 degrees)

2 H_2S, PH_3, NH_3,

H_2S (tetrahedral, 109 degrees)
PH_3 and NH_3 (trigonal pyramidal, around 107 degrees)
NH_3 has a larger bond angle than PH_3 as

1) N is more electronegative than P, N pulls electron density of bond pairs more towards itself, leading to greater bond-pair bond-pair repulsion.
2) N has a smaller lone pair region than P (N is above P in group 15). Lone-pair bond-pair repulsion is smaller, leading to a larger bond angle.

3 NF_3 , NCl_3, SO_3

NF_3 , NCl_3 (trigonal pyramidal, around 107 degrees)

NF_3 has a smaller bond angle than NCl_3. F is more electronegative than N and N is more electronegative than Cl). F pulls electron density of bond pairs more towards itself/ away from central N atom, leading to smaller bond-pair bond-pair repulsion.

SO_3 (trigonal planar, 120 degrees)

A 1, 2 and 3
B 1 and 2
C 2 and 3
D 1 only

4 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$\underset{\text{propadiene}}{H_2C{=}C{=}CH_2} \rightleftharpoons \underset{\text{propyne}}{CH_3C{\equiv}CH}$$

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by s – sp overlap

B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap

propadiene hybridisation: $H_2C{=}C{=}CH_2$
sp^2 sp sp^2

propyne hybridisation: $CH_3C{\equiv}CH$
sp^3 sp sp

A a σ bond formed by s – sp overlap: in propyne **$CH_3C\equiv C–H$**, not in propadiene

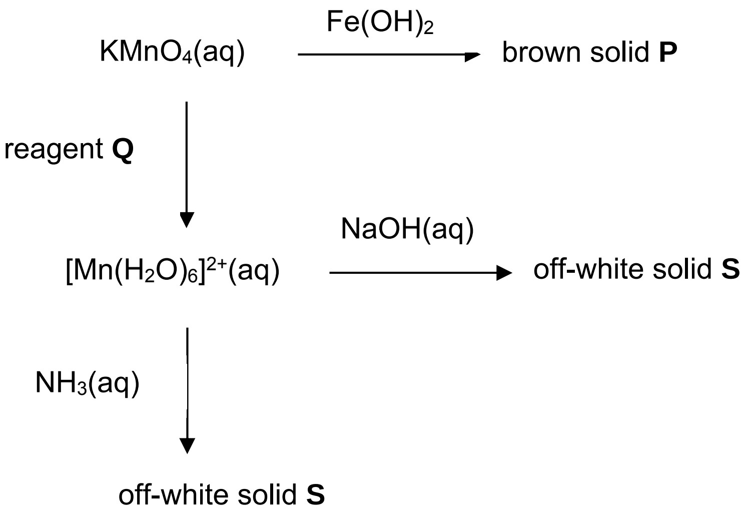
B a π bond formed by p – p overlap: present in both molecules

C a σ bond formed by sp – sp^2 overlap: in propadiene H_2**C=C**$=CH_2$, not in propyne

D a σ bond formed by sp^2 – sp^2 overlap :absent in both

5 *Use of the Data Booklet is relevant to this question.*

A reaction scheme regarding manganese compounds is shown below.



Which statements are true?

1 Off-white solid **S** is able to dissolve in excess of NH_3(aq).

2 Manganese in brown solid **P** has an oxidation state of +4.

3 Reagent **Q** can be acidified $[V(H_2O)_6]^{3+}$(aq).

4 Off white solid **S** turns brown upon standing.

A	1, 2 and 4	**B**	2, 3 and 4
C	2 and 3	**D**	All correct

1 off-white solid S is $Mn(OH)_2$. It is insoluble in excess of NH_3(aq). *Check Data Booklet.*

2 Brown solid P is MnO_2. Oxidation state of Mn in MnO_2 is +4. $KMnO_4$(aq) oxidises $Fe(OH)_2$, itself is reduced to MnO_2.
3 Reagent Q can be acidified $[V(H_2O)_6]^{3+}$ as the $E_{cell} > 0$.

(E_{cell} = (+1.52) + (- 0.34) = +1.18V)

4 off-white solid S turns brown upon standing. *Check Data Booklet.* $Mn(OH)_2$ is further oxidised by air.

6 In which chemical reaction does the transition metal compound or element behave as the described catalyst?

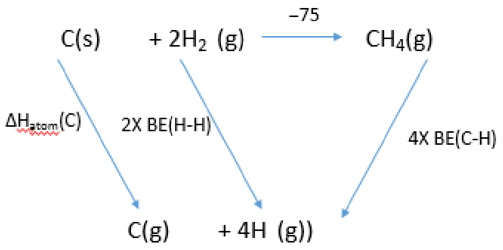
	Reaction	Catalyst
1	Formation of ethanal from ethanol, using acidified potassium dichromate $K_2Cr_2O_7$ is an oxidising agent, not a catalyst.	Homogeneous
2	Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide $Fe(OH)_3$ is a solid catalyst used in the decomposition of hydrogen peroxide, due to the slow rate of reaction.	Heterogeneous
3	Chlorination of benzene, using chlorine and iron(III) chloride $FeCl_3$ is a catalyst as well as a halogen carrier, is regenerated in the last step of the electrophilic substitution.	Homogeneous
4	Removal of air pollutants in exhaust systems of cars, using nickel Nickel is a catalyst in the catalytic converter and is in solid phase, a different phase from the gaseous reactant	Heterogeneous

A 1, 2 and 4
B 2 and 3
C 3 and 4
D 2, 3 and 4

7 *Use of the Data Booklet is relevant to this question.*

Given the following standard enthalpy changes,

	ΔH /kJ mol^{-1}
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	−75



$a + (2 \times 436) - (4 \times 410) = -75$

$a = +693$ kJ mol^{-1}

What is the standard enthalpy change of atomisation of graphite?

A +693 kJ mol^{-1}
B +1129 kJ mol^{-1}
C −2151 kJ mol^{-1}
D −2587 kJ mol^{-1}

8 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta H^{\ominus} = -176 \text{ kJ mol}^{-1}$$

The magnitude of standard entropy change of this reaction is 284 J K^{-1} mol^{-1}.

Which statements are correct?

1 $\Delta G^{\ominus} = -261$ kJ mol^{-1}.

No of mol of gas decreases => $\Delta S^{\ominus} = -284$ J K^{-1} mol^{-1}
$\Delta G^{\ominus} = -176 - 298(-0.284) = -91.4$ kJ mol^{-1}.

2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

Crossover temperature occurs when $\Delta G^{\ominus} = 0$
$\Delta H^{\ominus} = T\Delta S^{\ominus}$
T = -176000/ -284 = 620K

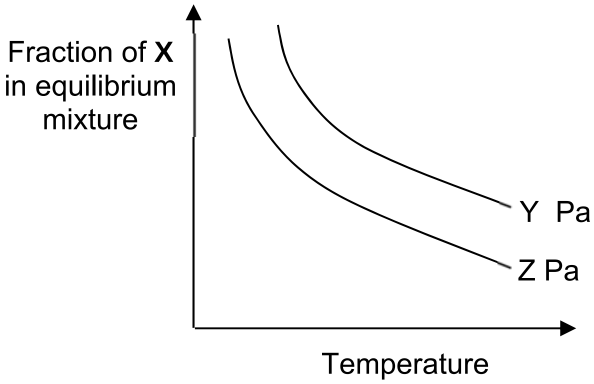
3 There is an increase in order as strong hydrogen bonding between NH_3 and HCl hold the particles in NH_4Cl in fixed positions and close to each other.

NH_4Cl is ionic lattice with strong ionic bonds between NH_4^+ and Cl^-, not strong H bonding between the NH_3 and HCl molecules.

A 1 only **B** 1 and 2 **C** 2 only **D** 2 and 3

9 The graph below shows how the fraction of X, which represents one of the following compounds in the given equilibrium mixture, varies with temperature at pressures of Y Pa and Z Pa.

$$4NH3(g) + 3O2(g) \rightleftharpoons 2N2(g) + 6H2O(g) \qquad \Delta H = -1267 \text{ kJ mol}-1$$



Identify X and the correct relative magnitudes of Y and Z.

	X	Pressure
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

Shape of graph:

(i) As temperature increase, fraction of X decrease.

(ii) As temperature increase, as forward reaction is exothermic, fraction of product should decrease.

Matching (i) and (ii): X should be the product of the reaction => either N_2 or H_2O.

Comparison of the two graphs:

(i) 7 mol of gaseous reactants vs 8 mol of gaseous products => decrease pressure will favour the forward reaction, to partially increase pressure.

(ii) Decrease pressure increase the fraction of X (since X is the product)

Matching (i) and (ii): Fraction of X is higher for Y Pa than Z Pa (Y Pa < Z Pa)

10 One of the key production stages in the Contact Process is the production of sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to k_1, k_{-1} and K_c if the temperature of the reaction is increased?

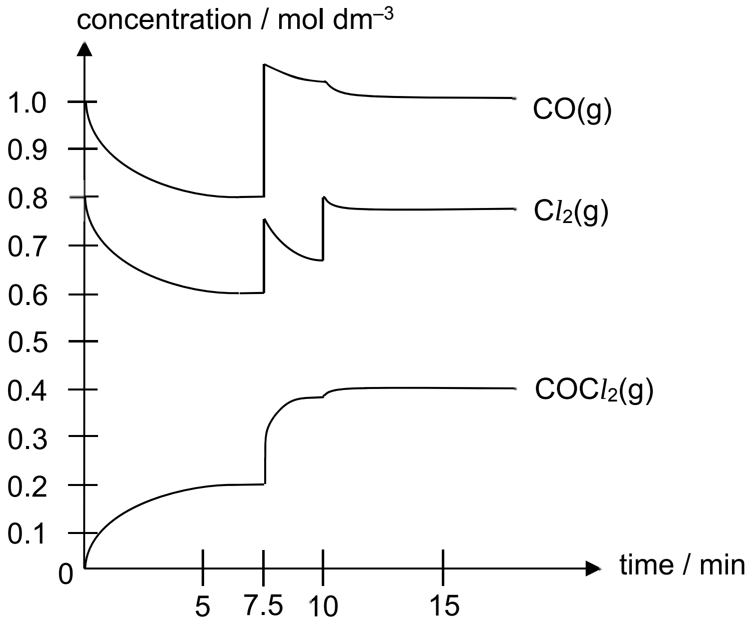
	k_1	k_{-1}	K_c
A	increase	increase	increase
B	increase	decrease	increase
C	decrease	increase	decrease
D	increase	increase	decrease

When temperature increased, no of molecules with energy greater than activation energy increases, frequency of effective collision increased, rate of reaction increases as rate constant increased. k_1 and k_{-1} increase.

As reaction is exothermic, as temperature increase, equilibrium shift backward to partially absorb the excess heat. Hence, K_c decrease as [product]/[reactant] decrease.

11 The reaction between carbon monoxide and chlorine was studied in an experiment by mixing the two gases and changing the reaction conditions inside the reaction vessel at different times during the experiment. The concentrations of the gases in the vessel were followed with time, and the following graph is obtained.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H^\ominus = -113.4\ \text{kJ mol}^{-1}$$



Which conclusion deduced from the graph is **incorrect**?

A The rate of forward reaction equals the rate of backward reaction at 7 min.

Correct: At 7 min, the system is in dynamic equilibrium and hence the rate of forward reaction is equal to the rate of backward reaction.

B The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.

Incorrect: Increase in volume at constant temperature will cause the concentration to decrease.

C The equilibrium constant, K_c, for the system when determined at 7 min is 0.417 mol^{-1} dm^3.

Correct: Using $K_c = \frac{[COCl_2]}{[CO][Cl_2]}$ and calculate

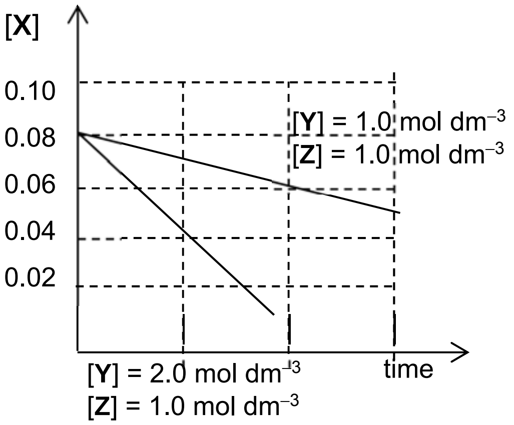
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

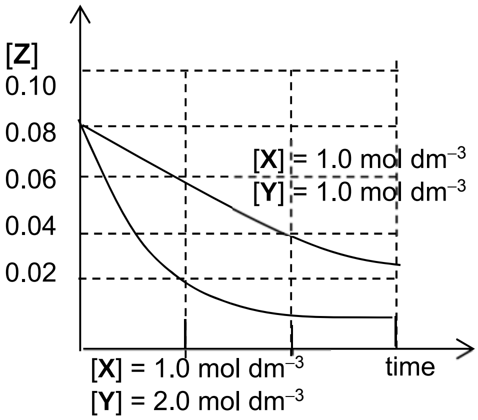
Correct: When chlorine is added, the concentration of chlorine will increase instantaneously as shown in the graph.

12 Substances **X**, **Y** and **Z** react according to the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) + \mathbf{Z}(aq) \rightarrow 2\mathbf{W}(aq) + \mathbf{U}(aq)$$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied while the other two were kept constant. The results are shown below.





Which rate equations represent the experimental results?

A rate = $k[\mathbf{Y}]^2$

B rate = $k[\mathbf{Y}][\mathbf{Z}]$

C rate = $k[\mathbf{Y}]^2[\mathbf{Z}]$

D rate = $k[\mathbf{X}][\mathbf{Y}][\mathbf{Z}]$

From the [X] versus time graph, a straight line indicates that the rate is constant with respect to any changes in [X]. Therefore order of reaction with respect to X is zero.

From the [Z] versus time graph, a constant half-time is obtained which indicates that the reaction is first order with respect to Z.

From the [Z] versus time graph, the time taken when [Y] is 2.0 mol dm^{-3} is $\frac{1}{4}$ of the time taken when [Y] is 1.0 mol dm^{-3} for [Z] to drop from 0.08 mol dm^{-3} to 0.04 mol dm^{-3} . Therefore order of reaction with respect to Y is 2.

13 *Use of the Data Booklet is relevant to this question.*

The reaction of acidified aqueous potassium iodide with hydrogen peroxide is represented by the following equation.

$$2I^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Which statements about the reaction are true?

1 E^{θ}_{cell} = +1.23 V.

True: E^{θ}_{cell} = (-0.54) + (+1.77) = +1.23 V

2 E^{θ}_{cell} becomes more negative when $Br_2(aq)$ is added to the anode.

True: $Br_2(aq)$ added will remove I^- causing $E^{\theta}_{oxidation}$ of I^- to be more negative when will cause E^{θ}_{cell} becomes more negative

3 E^{θ}_{cell} becomes more positive when a few drops of $AgNO_3(aq)$ is added to the anode.

False: $AgNO_3(aq)$ added with remove I^- causing $E^{\theta}_{oxidation}$ of I^- to be more negative when will cause E^{θ}_{cell} becomes more negative

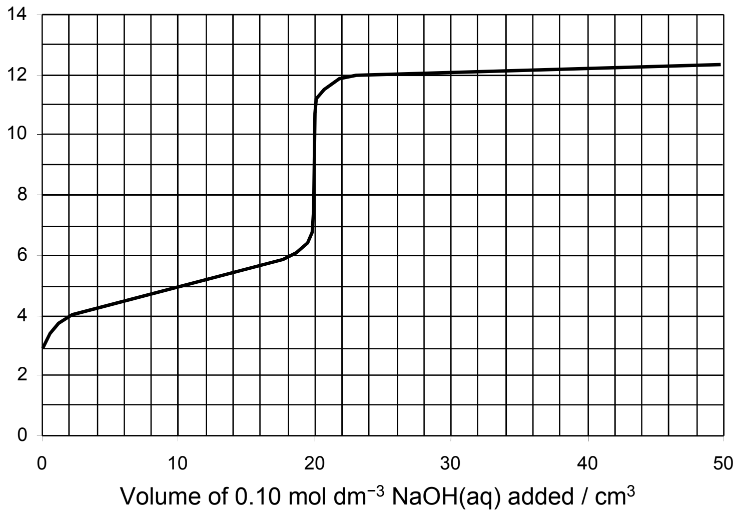
A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

14 The titration curve below shows the reaction between a monoprotic acid, **HX**, and aqueous sodium hydroxide.



Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Methyl red	red to yellow	4.2 – 6.3
Bromothylmol blue	yellow to blue	6.0 – 7.6
Thymolpthalein	colourless to blue	8.3 – 10.5

What statements are correct?

1 Methyl red will indicate an endpoint at a value lower than 20.0 cm^3.

Correct: At a value lower than 20.0 cm^3, the pH is less than 6.5 which coincide with the working range of methyl red.

2 K_a value of HX is 1.0×10^{-5}

Correct: At max buffer capacity, pH= $pK_a = 5$

$K_a = 1.0 \times 10^{-5}$

3 Buffer at maximum buffer capacity is formed at 25.0 cm^3 since the pH change in that region is relatively constant.

Incorrect: Maximium buffer capacity is formed at 10.0 cm^3 where [HX] = [NaX]

4 Alkaline hydrolysis of salt takes place after the equivalence point accounting for the alkaline pH value of the reaction mixture.

Incorrect: Alkaline hydrolysis of salt takes place **AT** equivalence point accounting for the alkaline pH value of the reaction mixture.

A 1,2 and 3 **B** 2,3 and 4 **C** 1 and 2 **D** 3 and 4

15 Given the following data,

K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Reaction mixture **X**:
25.0 cm^3 of 2.0×10^{-5} mol dm^{-3} CH_3COOH and 25.0 cm^3 water

Reaction mixture **Y**:
25.0 cm^3 of 0.02 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.01 mol dm^{-3} NaOH

Reaction mixture **Z**:
25.0 cm^3 of 0.01 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.02 mol dm^{-3} NaOH

Which is the correct order of pH values of the above reaction mixture?

A **Z** > **Y** > **X**

B **Z** > **X** > **Y**

C **Y** > **X** > **Z**

D **X > Y > Z**

For reaction mixture X, $[CH_3COOH]_{new} = 0.5 \times 2.0 \times 10^{-5} = 1.0 \times 10^{-5}$ mol dm^{-3}

$[H^+] = \sqrt{(1.0 \times 10^{-5} \times 1.8 \times 10^{-5})} = 1.3416 \times 10^{-5}$ mol dm^{-3}

$pH = -\lg(1.3416 \times 10^{-5}) = 4.87$

For reaction mixture Y,

	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.0005		0.00025		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0.00025		0		0.00025		-

An acidic buffer is formed.

$pH = pK_a$ since $[CH_3COOH]_{new} = [CH_3COONa]_{new}$

$pH = -\lg(1.8 \times 10^{-5}) = 4.74$

For reaction mixture Z,

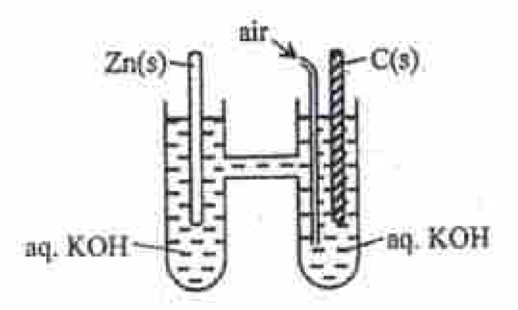
	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.00025		0.0005		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0		0.00025		0.00025		-

Salt hydrolysis is not considered as presence of strong base will suppress the salt's dissociation

$pH = 14 - pOH = 14 + \lg(0.00025 / \frac{25.0+25.0}{1000}) = 11.70$

Answer is B

16 A cell is constructed with zinc and carbon electrodes, each weighing 50 g, partly immersed in aqueous KOH.



When connected in a circuit, some zinc passes into solution as zincate(II) ions, ZnO_2^{2-}(aq). The cell delivers a current of 1.68×10^{-2} A. The zinc electrode is replaced once 60% of it is used up.

What is the time taken, in seconds, before replacement of zinc electrode becomes necessary?

A	2.63×10^6	**B**	4.39×10^6
C	5.27×10^6	**D**	8.78×10^6

Oxidation state of Zn in ZnO_2^{2-} is +2, hence 2 moles of electrons are transferred per mole of Zn.

Amount of Zn used up = $\frac{60}{100} \times \frac{50}{65.4}$ = 0.4587 mol

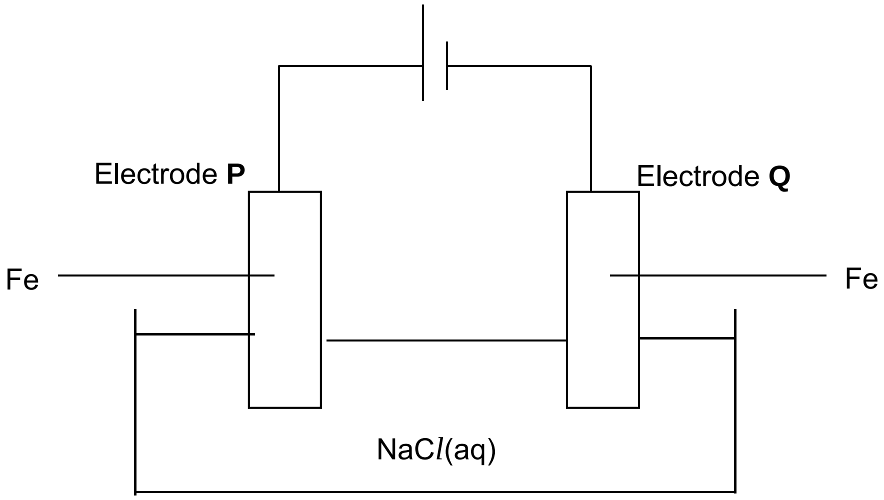
$n_e = 0.4587 \times 2 = 0.9174$ mol and since $Q = It = n_eF$

$(1.68 \times 10^{-2})t = 0.9174 \times 96500$

$= 5.27 \times 10^6$ s

Answer is C

17 An experiment is set up as shown below to study the corrosion of iron.



What will occur at electrodes **P** and **Q**?

	Electrode **P**	Electrode **Q**
A	No corrosion of Fe	Corrosion of Fe ; H_2 gas evolved
B	No corrosion of Fe	Corrosion of Fe ; O_2 gas evolved
C	Corrosion of Fe	No corrosion of Fe ; Na deposited
D	Corrosion of Fe	No corrosion of Fe ; H_2 gas evolved

Electrode P is the positive anode, while electrode Q is the negative cathode

Since oxidation occurs at the anode, while reduction occurs at the cathode,

At the anode:

$Fe \rightleftharpoons Fe^{2+} + 2e^-$	$E^\theta_{ox} = +0.44$ V
$Cl^- \rightleftharpoons Cl_2 + 2e^-$	$E^\theta_{ox} = -1.36$ V
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$	$E^\theta_{ox} = -1.23$ V

Corrosion of Fe will occur at electrode P since first E^θ_{ox} is the most positive

At the cathode:

$Na^+ + e^- \rightleftharpoons Na$	$E^\theta = -2.71$ V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	$E^\theta = -0.83$ V

No corrosion of Fe will occur, since Fe cannot be reduced. H_2 gas will be evolved since second E^θ is the most positive

Answer is D

18 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been replaced by safer options such as the standard hydrogen electrode (S.H.E.).

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A	+0.27 V	**B**	+1.30 V	**C**	–1.79 V	**D**	–2.82 V

A change in Gibbs' free energy of +199 kJ per mole of Zn^{2+} being reduced is equivalent to a change in Gibbs' free energy of –199 kJ per mole of Zn being oxidised

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$

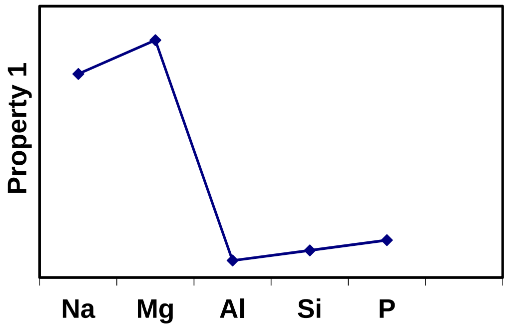
$-199 \times 1000 = -(2)(96500)E^{\theta}_{cell}$

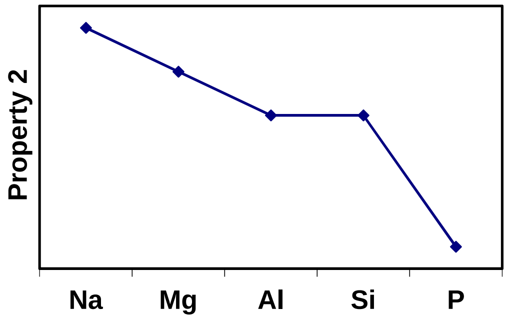
$E^{\theta}_{cell} = +1.03\text{ V} = E^{\theta} + E^{\theta}_{ox\ (Zn\,/\,Zn2+)} = E^{\theta} + 0.76\text{ V}$

$E^{\theta} = +0.27\text{ V}$

Answer is A

19 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.





Which correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the highest oxidation state chlorides	pH of the oxides when added to water
C	melting point of oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the highest oxidation state chlorides when added to water

For option A Property 1 cannot be atomic radii as it should be a continuous decrease across the period due to increase in nuclear attraction for the outermost electron. This is because of increase in nuclear charge but constant shielding caused by the same number of inner electrons.	Property 2: Electrical conductivity should increase from Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.
For option B Boiling point of chloride compounds decreases from NaCl to $AlCl_3$ as $AlCl_3$ is a simple covalent molecule therefore easier to overcome the intermolecular temporary dipole induced dipole than ionic bonds in giant ionic lattice of NaCl and $MgCl_2$. From $AlCl_3$ to PCl_5, they have the structure of simple covalent molecules with Mr of $AlCl_3$ (133.5) < $SiCl_4$ (170.1) < PCl_5 (208.5). B.pt increases with increasing ease of distortion of the electron cloud of the chloride compound. Hence property1 shows the correct trend in the b.pt of chlorides across period 3 element.	Property 2: **acid base property of oxide** depends on the **nature of bonds present in the oxide** compound. While ionic oxide tends to be basic and covalent oxide is acidic; ionic oxides with significant covalent character will be amphoteric, this is usually observed when cation has high charge/size ratio. **pH of oxides in aqueous medium** not only depends on the nature of the bonds, **solubility** also matters. Na_2O is **basic and fully soluble** in water, therefore pH very high (highly alkaline). Solubility of MgO less than Na_2O but more than Al_2O_3, hence pH of MgO > Al_2O_3. **pH of Al_2O_3 and SiO_2 are both equal to 7 because both are insoluble in water** but Al_2O_3 is an amphoteric oxide while SiO_2 is an acidic oxide. Oxides of P dissolves in water to give phosphoric acid therefore pH is very low. Hence property 2 shows the correct trend for pH of aqueous oxides across period 3.
For option C Melting points of oxides across the period should peak at SiO_2 since it has a very strong giant covalent lattice. Phosphoric oxide is a simple covalent molecule, therefore there should be a drastic drop of m.pt from SiO_2 to P_4O_{10}. Hence property 1 cannot be m.pt of oxides across period 3 elements.	First ionisation energy of elements across period should exhibit a general increasing trend due to increasing nuclear attraction for the most loosely held electron. This is due to increase in nuclear charge but constant shielding effect by the same number of inner shell electrons. Hence property 2 cannot be first ionisation energy.
For option D Electrical conductivity should increase from Na to Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero	For chlorides across period 3 element, they are all soluble in aqueous medium. For chlorides that dissociates into ions in aq medium, cation hydrolysis gives rise to acidic solution. Extent of cation hydrolysis increases with charge/size ratio of the cation. Hence $AlCl_3$ (aq) more acidic than $MgCl_2$(aq) while NaCl is neutral (pH =7)

electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.	On the other hand, covalent chlorides react with water to form HCl therefore the pH value should be low for both $SiCl_4$ and PCl_5. Hence graph of property 2 do not agree with the pH trend of aqueous chlorides across the period.

20 What mass of sodium ethanedioate, $Na_2C_2O_4$, should be added to 250 cm^3 of a 2.2×10^{-3} mol dm^{-3} solution of calcium nitrate before a precipitate is formed?
[K_{sp} of CaC_2O_4 = 2.27×10^{-9} mol^2 dm^{-6}]

In order for precipitate to take place, ionic product > Ksp.
Expression for ionic product and K_{sp} is the same.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

Magnitude of Ionic product = K_{sp} when solution is saturated with $Na_2C_2O_4$.

$$\left(\frac{mass}{(23.0 \times 2 + 24.0 + 64.0)} \times \frac{1000}{250}\right)(2.2 \times 10^{-3}) = 2.27 \times 10^{-9}$$

Min mass of $Na_2C_2O_4$ = 3.46×10^{-5} g

A 3.5×10^{-5} g
B 1.0×10^{-6} g
C 2.5×10^{-7} g
D 2.3×10^{-9} g

21 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

A It can be formed by the reduction of $C_6H_5CH_2CN$.

B It reacts with CH_3CO_2H to form $C_6H_5CH_2NHCOCH_3$.

C It is formed by the reaction between $C_6H_5NO_2$ and tin in concentrated HC*l* followed by NaOH.

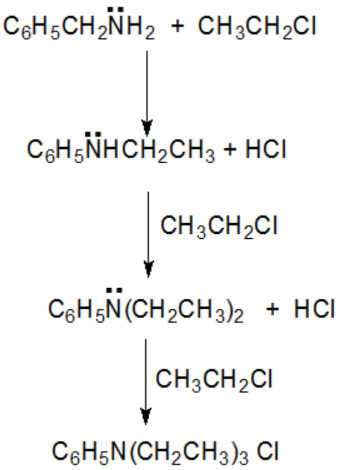
D It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

Option A: reduction of $C_6H_5CH_2CN$ gives $C_6H_5CH_2CH_2NH_2$ with 1 C more than $C_6H_5CH_2NH_2$. Hence it is not the correct answer.

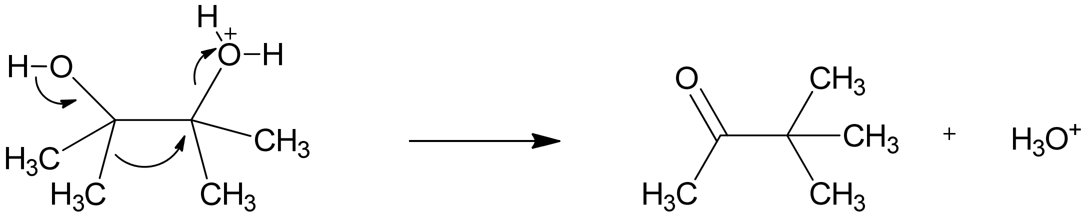
Option B: N in $C_6H_5CH_2NH_2$ uses its lone pair to accept H^+ from CH_3COOH (acid base reaction instead of nucleophilic acyl substitution (condensation)). Hence $(CH_3COO^-)(C_6H_5CH_2NH_3)^+$ is formed instead of $C_6H_5CH_2NHCOCH_3$.

Option C: $C_6H_5NO_2$ will be reduced to $C_6H_5NH_2$ which is isolated as $C_6H_5NH_3Cl$ due to acidic medium. $C_6H_5NO_2$ has 1 less C than $C_6H_5CH_2NH_2$ after reduction, hence not the answer.

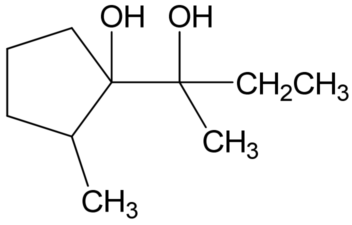
Option D: Correct answer. A quaternary ammonium salt is formed when $C_6H_5CH_2NH_2$ reacts with excess CH_3CH_2Cl.



22 When a 1,2–diol is treated with a dilute acid, the protonated diol undergoes the following pinacol rearrangement.

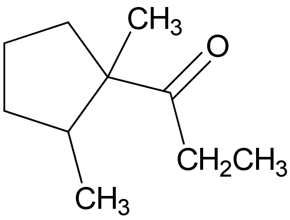


Which structure is **not** formed when diol **Z** undergoes pinacol rearrangement?

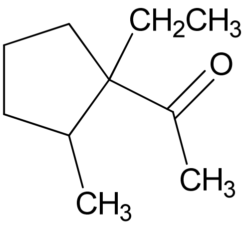


diol **Z**

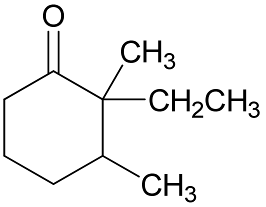
A



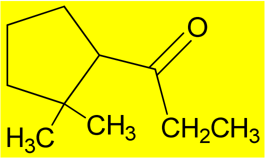
B

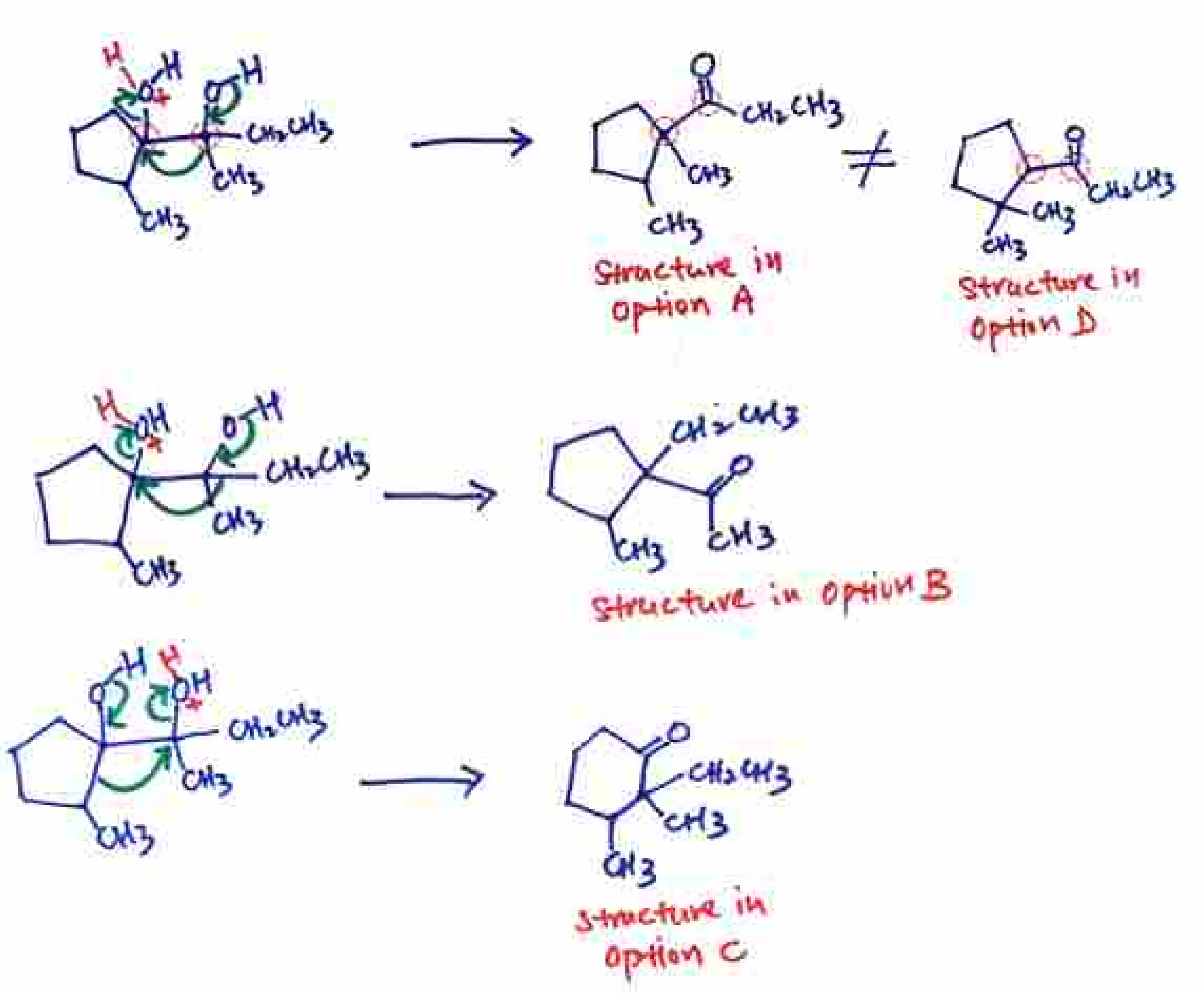


C

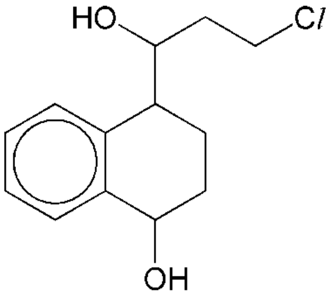


D



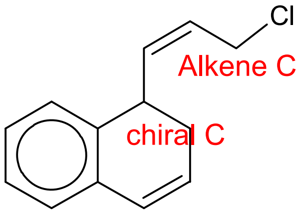


23 What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H_2SO_4?



A 2 **B** 4 **C** 6 **D** 8

The molecule undergoes elimination of H_2O with excess concentrated H_2SO_4 to give alkene. The product is



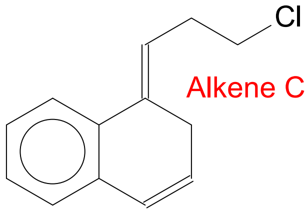
Alkene C that can exhibit cis-trans isomerism

chiral C

Using the formula,

No of stereoisomers = 2^{n+m} where n = no of chiral C and m= no of alkene C that can exhibit cis-trans isomerism, this alkene has $2^{1+1} = 4$ isomers.

Another possible products of elimination:



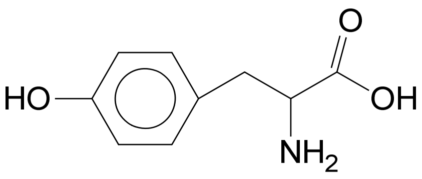
Alkene C that can exhibit cis-trans isomerism

No of stereoisomers: $2^1=2$ isomers

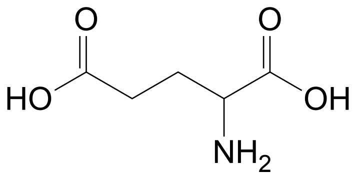
Total no of stereoisomers = $2^2 + 2 = 6$

24 Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species move towards the anode.

With a buffer at pH 4, which statement is true?



Tyrosine (pI = 5.7)



Glutamic acid (pI = 3.2)

A Both species move towards the anode

B Both species move towards the cathode.

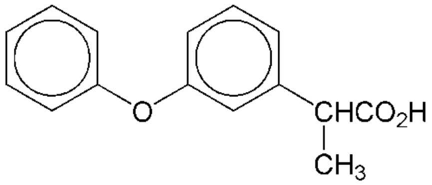
C Tyrosine moves towards the anode, glutamic acid moves towards the cathode.

D Tyrosine moves towards the cathode, glutamic acid moves towards the anode.

Since pH < pI of Tyrosine, the $-NH_2$ grp will get protonated => Overall positively charged, hence move towards cathode.

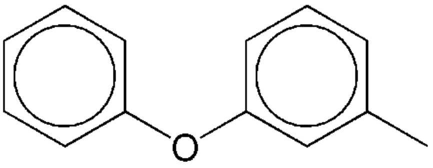
Since pH > pI of Glutamic acid, both the –COOH grps will get deprotonated => Overall negatively charged, hence move towards anode. Answer is (D).

25 *Fenoprofen* is an anti-arthritic agent.



Which of the following could be part of a reaction sequence for synthesising *Fenoprofen*?

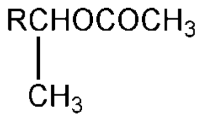
In the sequences below, R =



A $RCHBrCH_3 \xrightarrow[\text{heat}]{\text{NaCN(ethanolic)}} \text{Intermediate} \xrightarrow[\text{heat}]{H^+(aq)}$ *Fenoprofen*

B $RCH(CH_3)_2 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

C



$RCH(CH_3)OCOCH_3 \xrightarrow[\text{warm}]{I_2,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

D $RCH(OH)CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

For option (A), the halogenoalkane $RCHBrCH_3$ undergoes nucleophilic substitution when heated with ethanolic NaCN, forming $RCH(CN)CH_3$ as the intermediate, which then undergoes acidic hydrolysis of the –CN group to form –COOH.

For option (B), $RCH(CH_3)_2$ does not undergo oxidation when heated with alkaline $KMnO_4$.

For option (C), $RCHO(CH_3)COCH_3$ has methyl carbonyl which is part of the ester functional grp, hence does not undergo iodoform reaction when warmed with alkaline iodine.

For option (D), secondary alcohol $RCH(OH)CH_3$ undergoes oxidation to form ketone intermediate, $RCOCH_3$, which does not react with H^+.

26 Chlorofluorocarbons (CFCs) are commonly used as aerosols, propellants and refrigerants. However in the stratosphere, CFCs can damage the ozone layer through a radical chain reaction.

In which sequence are the following compounds listed in increasing order of their ability to destroy ozone?

A $CHClFCClF_2$ < CCl_2FCCl_2F < $CHClF_2$

B CCl_2FCCl_2F < $CHClF_2$ < $CHClFCClF_2$

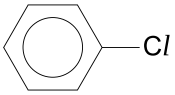
C $CHClF_2$ < CCl_2FCCl_2F < $CHClFCClF_2$

D $CHClF_2$ < $CHClFCClF_2$ < CCl_2FCCl_2F

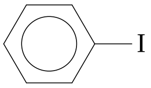
C-F bond is much stronger than C-Cl, it does not break easily to form F radicals => does not damage ozone layer.
All four options (A), (B), (C) and (D) comprise of molecules containing C-F and C-Cl bonds. The molecule with more C-Cl bonds will have higher ability to destroy ozone due to more Cl radicals it is able to produce. Hence, answer is (D).

27 Which is the product formed when benzene reacts with iodine chloride, ICl in the presence of a suitable catalyst?

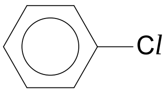
A



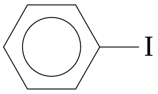
B



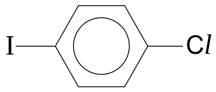
C a mixture of



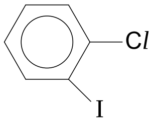
and



D a mixture of



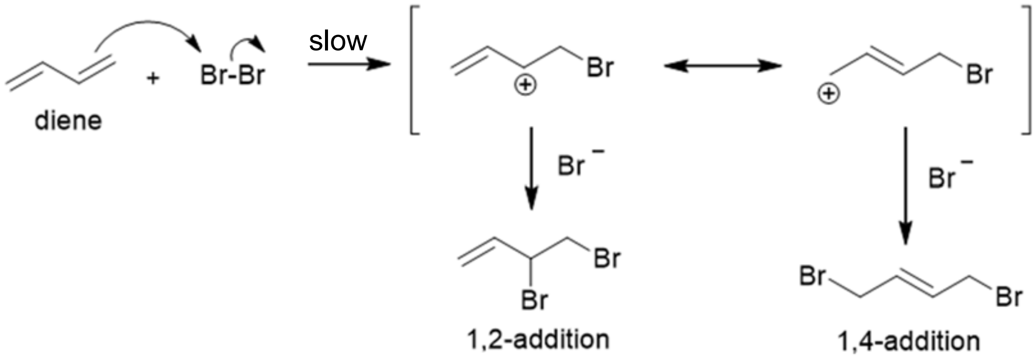
and



Answer:

Cl is more electronegative than I, hence only I^+ electrophile forms for reaction.
$AlCl_3 + ICl \rightarrow AlCl_4^- + I^+$
Hence only 1 electrophilic substitution product is possible.

28 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.

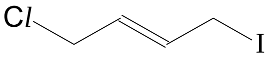


Which statement is **not** correct?

A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HCl is used is  .

D The 1,4–addition product formed when ICl is used is  .

Answer:

A is correct.

Step 1 can be determined to be the slow step as bond breaking occurs. 1 mole of diene and 1 mole of bromine are involved and hence the overall order is 2.

B is correct.

The presence of the pi bond stabilises the positive charge on the cations.

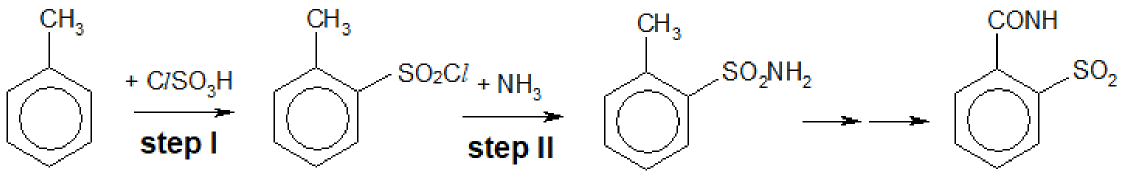
C is incorrect.

For the 1,2-addition product, the positive charge is on the 2nd carbon and hence Cl should be on the 2nd carbon instead.

D is correct.

Cl is more electronegative than I, hence in step 1, the I which is δ+ will function as the electrophile and Cl^- is generated which then attacks the carbocation.

29 Saccharin is an artificial sweetening agent used in some soft drinks and is manufactured from methylbenzene through a four-step synthesis. Part of the reaction scheme is shown below.



What type of reaction do steps **I** and **II** illustrate?

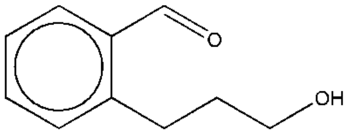
	Step I	**Step II**
A	Electrophilic addition	Nucleophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

Answer:
Step 1: Benzene ring is electron rich: Electrophilic Substitution
Step 2: S is $\delta+$ due to the electronegative atoms attached to it; $-Cl$ replaced by $-NH_2$: Nucleophilic Substitution

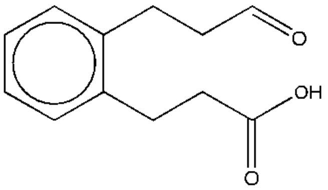
30 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 respectively but a negative result when treated with alkaline Cu(II) complex.

What could **X** be?

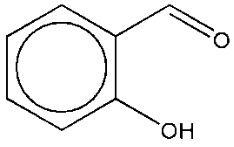
A



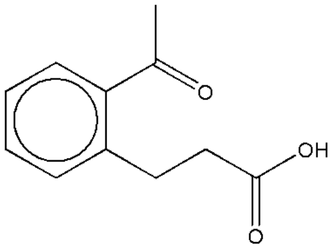
B



C



D



Reacts with $[Ag(NH_3)_2]^+$ (Tollen's)	Aldehyde
Reacts with PCl_5	-OH which can undergo substitution present (not phenol)
No reaction with alkaline Cu(II) complex (Fehlings)	Aromatic aldehyde

END of PAPER

1	C	11	B	21	D
2	C	12	C	22	D
3	A	13	B	23	C
4	C	14	C	24	D
5	B	15	B	25	A
6	D	16	C	26	D
7	A	17	D	27	B
8	C	18	A	28	C
9	A	19	B	29	B
10	D	20	A	30	A

NATIONAL JUNIOR COLLEGE
SH 2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

Tues 21 Aug 2018
2 hours

Candidates answer **all** questions on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

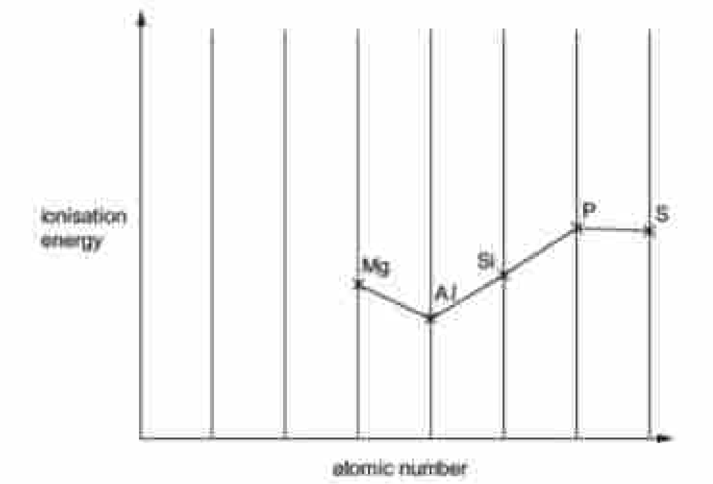
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use			
1	/8		
2	/14		
3	/13		
4	/11		
5	/14		
6	/15		
Penalty units			
Penalty sf			
Paper 2	/75		

Answer ALL questions on the space provided.
This paper consists of **18** printed pages.

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*: ....

....

....

P and S: ....

....

....

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.
L is a chloride of an element in Period 3. A students investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

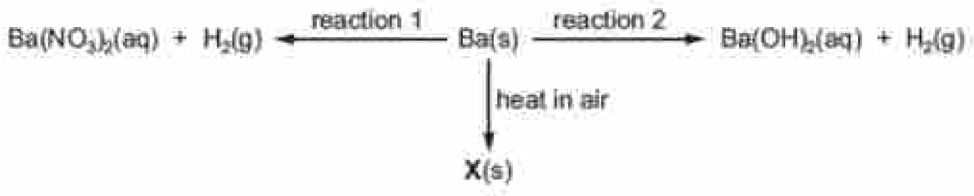
(i) Identify **L** and **M.**

L: .... **M:** ....
[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

.... [1]

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1 ....

Reaction 2 ....
[2]

(ii) Write an equation for the formation of **X**.

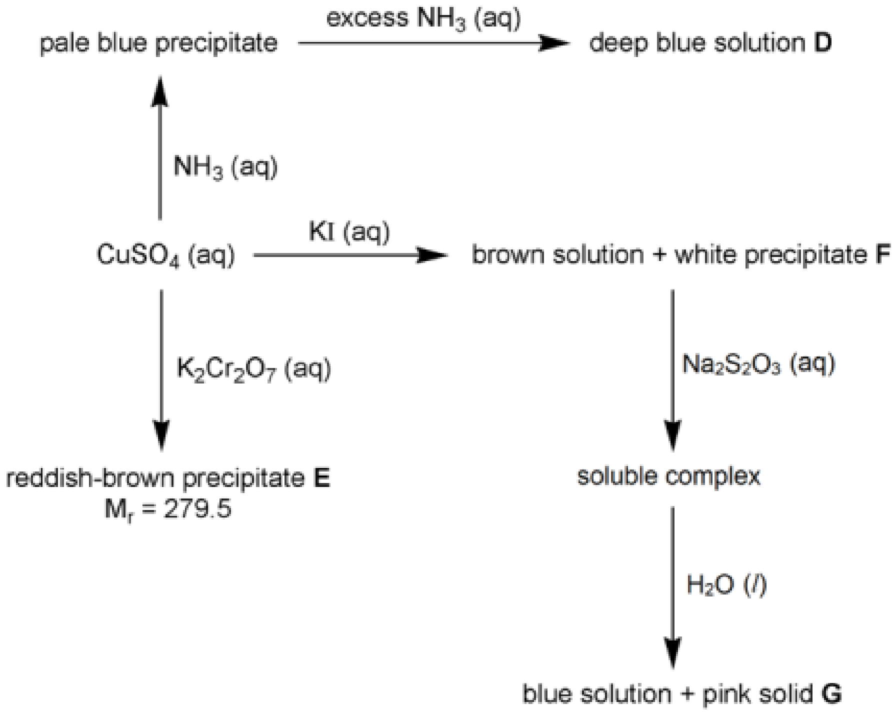
....

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: ……………………………….. **E**: ………………………………..

F: ……………………………….. **G**: ………………………………..

[4]

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

……………………………………………………………………………………………..

……………………………………………………………………………………………...

……………………………………………………………………………………………...

……………………………………………………………………………………………..

[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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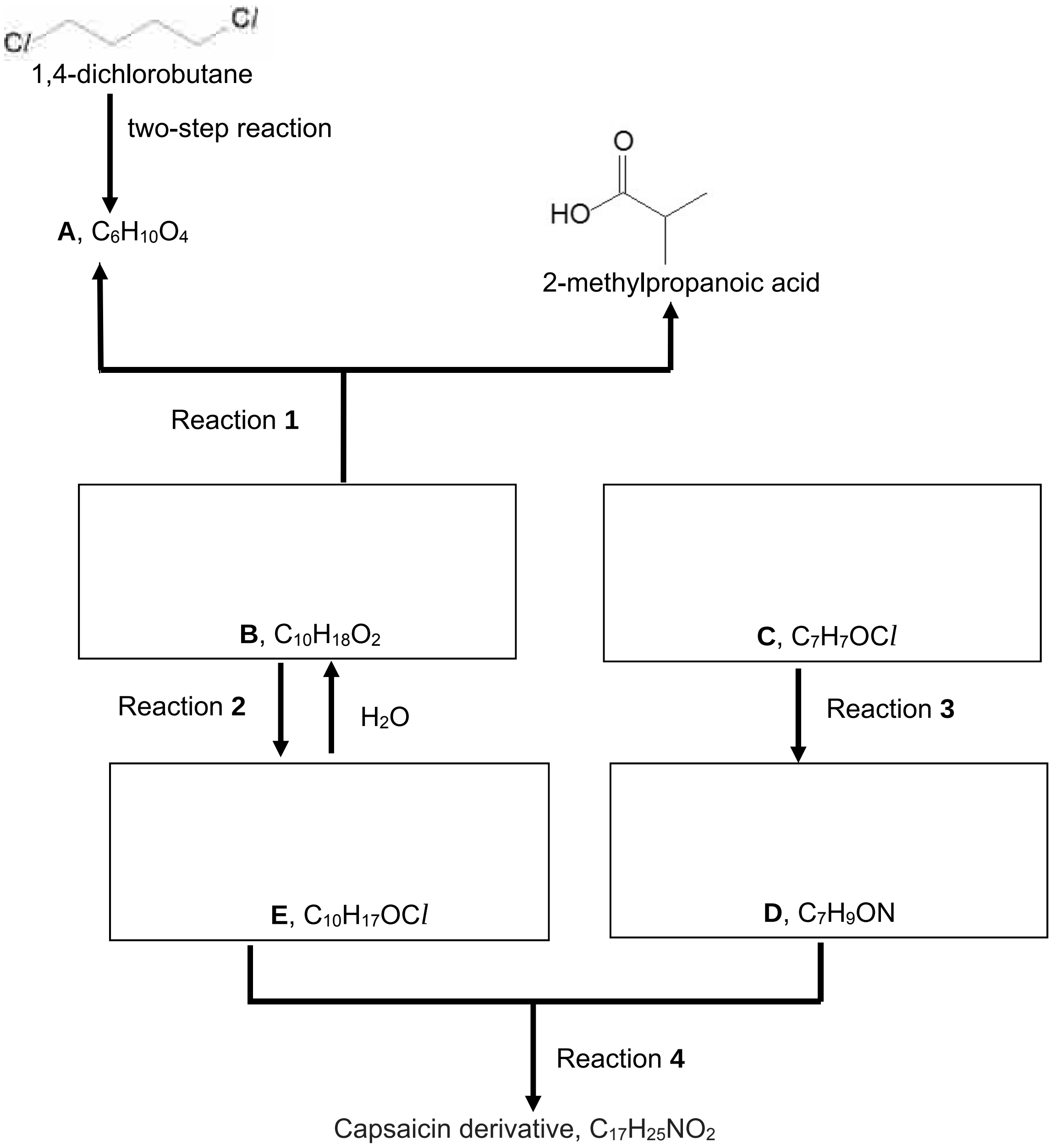
…………………………………………………………………………………………

[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

.... [1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps.
Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: ……………………………………………………..

Step 2: ……………………………………………………..

Intermediate product:

[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: ………………..………………

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: …………………………………………………..

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt.
Draw the structure of Compounds **C** and **D** in the box on pg 6.
Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: ……………………………………………………………

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: …………………………………………………..
[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.

[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	**Volume Percentage**
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	Rapidly increasing
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HCl	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume}$$

However, percentages are only additive for ideal gases.

(a) **(i)** State **two** assumptions of the kinetic theory of gases.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

……………………………………………………………………………………………

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

……………………………………………………………………………………………...

……………………………………………………………………………………………...

……………………………………………………………………………………………...

[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.
Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43^oC and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Volume percentage of carbon dioxide = …………………

……………………………………………………………………………………………...

……………………………………………………………………………………………...

[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + H_2(g)$$

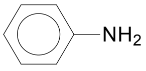
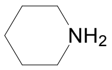
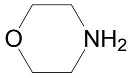
1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960^{o}C and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

Examiners Comments:

Most students are able to identify that O is electronegative and hence able to exert electron withdrawing effect. There are a handful who thought that the lone pair will delocalise into O. This is impossible as the 2 atoms are not adjacent to each other and no orbital overlap exists.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

Examiners Comments:

Most students are able to recognise that the lone pair on N can delocalise into the ring and hence a reduction in availability of lone pair for donation to a proton. Do use the correct key word “delocalisation” as some students will use terms like “dissociate” or “diffuse” into the ring which is not very accurate.

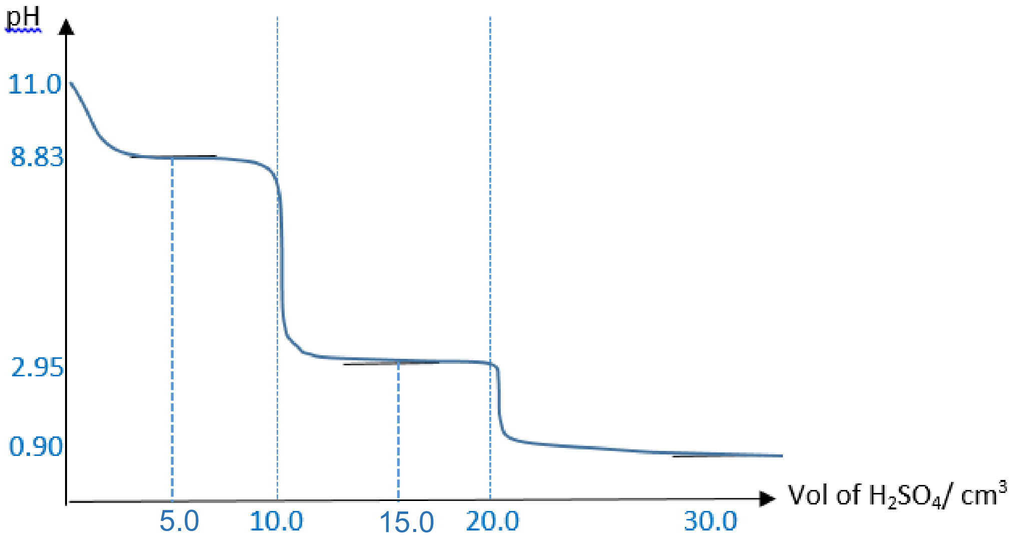
[2]

(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the pH–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- pH of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.
- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
pOH = pK$_b$ at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
[H^+] = 0.005 x 1000/ 40 = 0.125 moldm^{-3}
pH = 0.90

Examiners Comments:
Students did badly for this question.
Most students did not manage to recognise two equivalence point (represented by 2 steep slope).
To identify how many equivalence point(s) there is, students need to **focus on the analyte**. If the analyte is (1) weak **and** (2) multi-protic, then it will have multiple equivalence points.

Most students also could not calculate the volume of H_2SO_4 used correctly. To do so, since both acid and base are diprotic,

$N_2H_4 + H_2A \rightarrow N_2H_6^{2+} + A^{2-}$
Mol ratio is 1:1

Hence **total volume** of acid required is 20 cm^3

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

$$\underset{\textbf{A}}{C_4H_{10}} \xrightarrow{\text{step 1}} \underset{\textbf{B}}{C_4H_9Cl} \xrightarrow{\text{step 2}} C_4H_{11}N$$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

Step 1: limited Cl_2, UV. light

Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

(ii) Outline the mechanism for step 1.

			[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **c(ii).**

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[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

....

[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH⁻, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

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[3]

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Order with respect to $C_6H_5CHClCH_3$ = ……………………

Order with respect to OH^- = ……………………

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ……………………………………………………………… mol dm^{-3} s^{-1}

units of *k* = ………………………………………………………… .

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers.
Explain your answer.

....

....

....

[2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

....

....

....

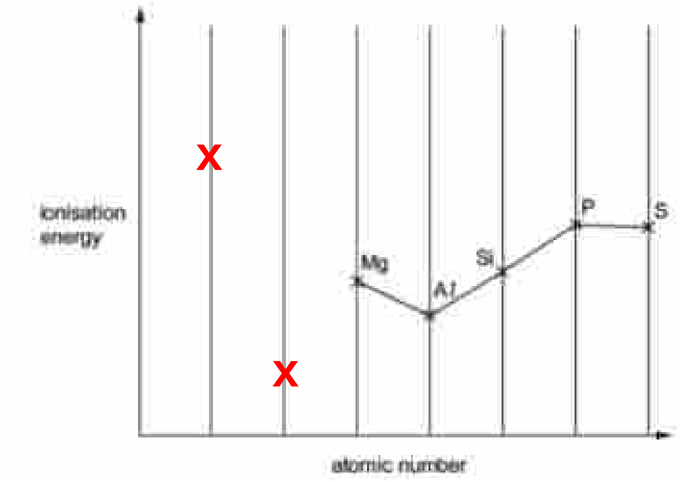
[2]

[Total: 15]

NJC SH2 H2 Chemistry P2 Solutions

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

Cross shown on first vertical line from the y-axis (group 0/Ne) is clearly higher than all shown.
Cross shown on second vertical line from the y-axis (group 1/Na) is clearly lower than all shown.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*:
The most loosely held electron in A*l* is in the **higher energy 3p subshell** while that of Mg is in the **lower energy 3s subshell.**
This **outweighs the effect of the increase in nuclear charge** from Mg to A*l*.
Hence **nuclear attraction for the most loosely held electron in A*l* is weaker**, i.e. A*l* has a lower 1st IE. [1]

P and S:
The most loosely held electron in S is one of the **paired electrons in 3p** orbital while that of P is in the **singly filled 3p** orbital.
Inter-electronic repulsion between the paired electrons in the same p orbital **outweighs the effect of an increase in nuclear charge**.
Hence, **nuclear attraction for the most loosely held electrons is weaker in S**, i.e. S has a lower first IE. [1]

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

L is a chloride of an element in Period 3. A student investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

(i) Identify **L** and **M.**

L: $MgCl_2$ **M:** $Mg(OH)_2$

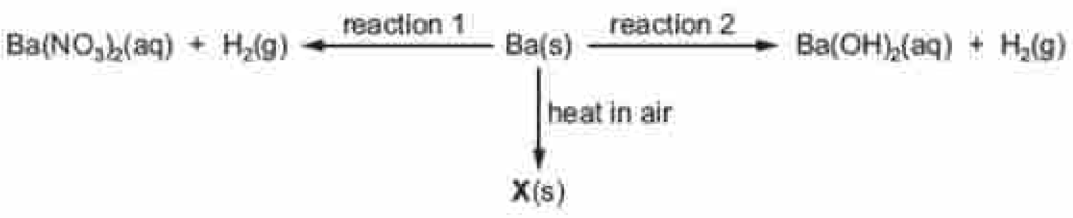
[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$ [1]

(state symbols not necessary)

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1: HNO_3 [1]

Reaction 2: H_2O [1]

(ii) Write an equation for the formation of **X**.

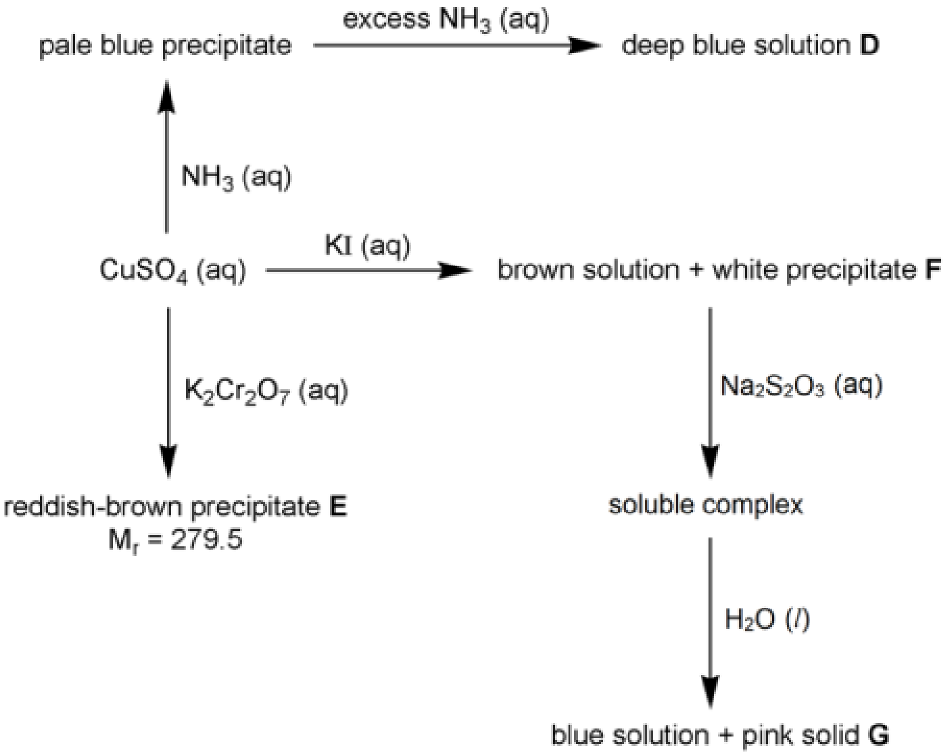
$2Ba + O_2 \rightarrow 2BaO$

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ or $[Cu(NH_3)_4]^{2+}$ E: $CuCr_2O_7$

F: CuI G: Cu

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ ---(1)

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ ---(2)

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. This causes the ionic product of $Cu(OH)_2$ to become less than K_{sp} of $Cu(OH)_2$, and hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

OR

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. By Le Chatelier's Principle, the position of equilibrium (2) shifts to the right to partially increase $[Cu^{2+}]$. Hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

BE(H–C*l*) = 431 kJ mol^{-1} BE(H–Br) = 366 kJ mol^{-1}
BE(H–I) = 299 kJ mol^{-1}

Down the group, less energy is needed to break the weaker H–X bond, resulting in decreasing thermal stability of HX.

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

The transition metal cation is Fe^{2+}.

From Data Booklet	$E^\ominus$ / V
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$ $E^\ominus_{cell} = +0.30 \text{ V} > 0$

Br_2 can oxidise Fe^{2+} to Fe^{3+} since the reaction is spontaneous.

$I_2 + 2Fe^{2+} \rightarrow 2I^- + 2Fe^{3+}$ $E^\ominus_{cell} = -0.23 \text{ V} < 0$

I_2 cannot oxidise Fe^{2+} to Fe^{3+} since the reaction is non-spontaneous.

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

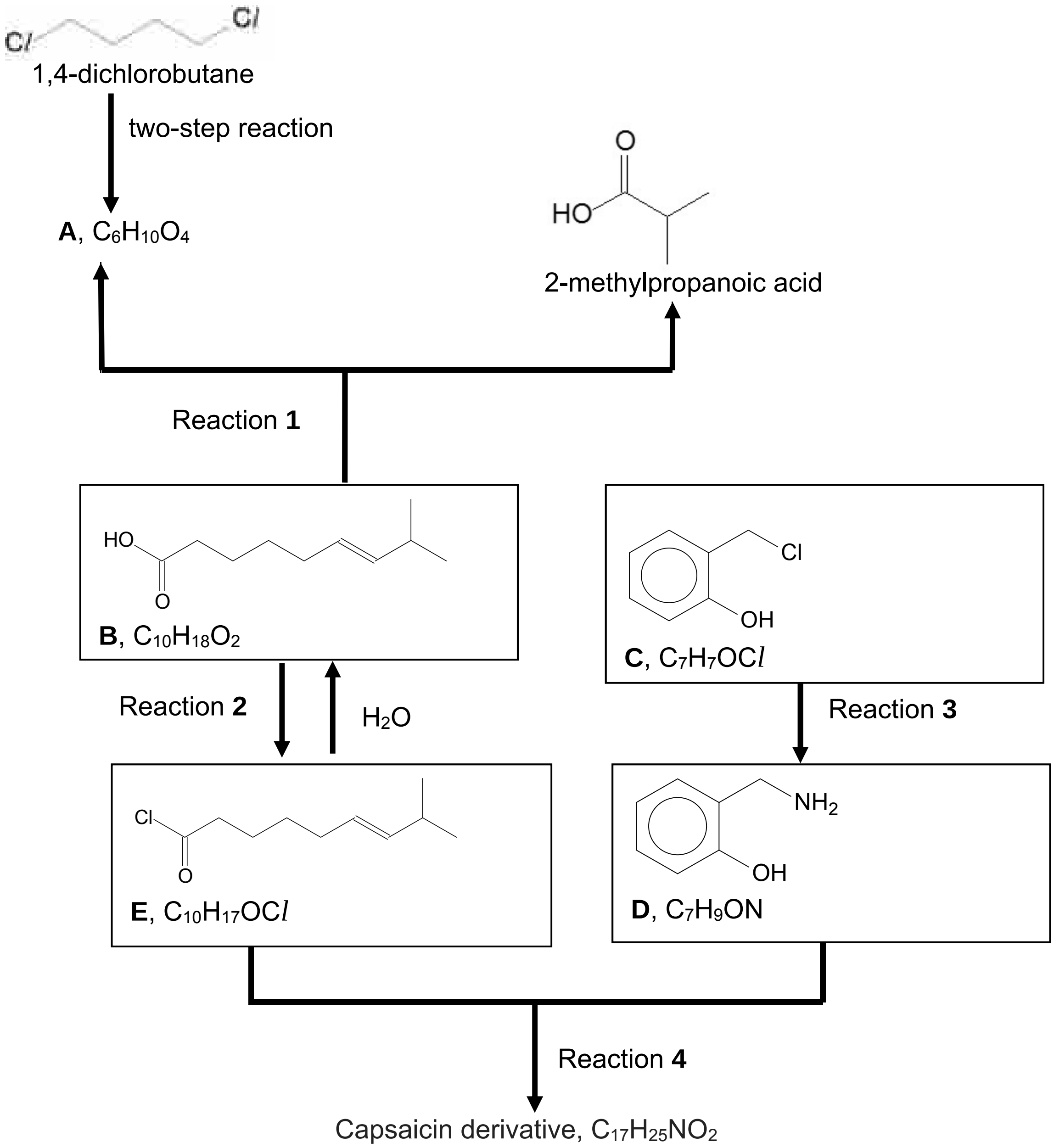
1. Add excess aqueous silver nitrate to the mixture. Yellowish-white precipitate is formed.
2. Next, add excess aqueous ammonia. Some of the precipitate will dissolve and only a yellow precipitate remains.
3. Filter the mixture with filter paper and filter funnel. Yellow residue indicates the presence of iodide ions.
4. To the colourless filtrate, add excess aqueous nitric acid. White precipitate formed indicates the presence of chloride ions.

[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.

Information on compounds **A** to **D** are given on pages 6 and 7.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

Carboxylic acid

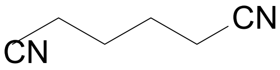
[1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps. Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: ethanolic NaCN, heat

Step 2: dil H_2SO_4, heat

Intermediate product:



[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: alkene

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: $KMnO_4$, dil H_2SO_4, heat

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt.
Draw the structure of Compounds **C** and **D** in the box on pg 6.
Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: nucleophilic substitution

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

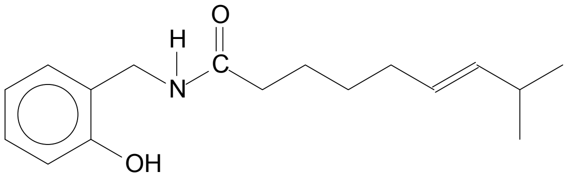
Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: PCl_5 (s), anhydrous

[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.



[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HCl	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume} \times 100\%$$

However, percentages are only additive for ideal gases.

(a) **(i)** State **two** assumptions of the kinetic theory of gases.

1) Negligible attractive or repulsive forces between gas particles
2) Negligible volume of gas particles compared to the volume they are moving in/ volume of the container they are in.

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

Low pressure and high temperature.

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

At low temperatures, there is insufficient energy to overcome the strong temporary dipole induced dipole (tdid) interactions between CO_2 molecules. Hence CO_2 would aggregate together/ more CO_2 molecules in a smaller volume and have a higher density thus sink down.

[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.

Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43 ^oC and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Amt of CO_2 = $\frac{0.30 \times 0.001}{44.0} = 6.818 \times 10^{-6} mol$

pV = nRT

$(11200)(V) = (6.818 \times 10^{-6})(8.31)(273 + 43)$

$V = 1.598 \times 10^{-6}$ m^3

volume percentage of $CO_2 = \frac{1.598 \times 10^{-6}}{10 \times 10^{-6}} \times 100\% = 16.0\%$

Ans: 16.0%   unconsciousness and death can result quickly.

[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + \mathbf{4\,H_2(g)}$$

1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960^oC and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

Q says to reach equilibrium at 960°C and 2 atm, i.e. Total P initially and Total P at eqm is same, 2 atm.

	$CH_4(g)$	$+ 2 H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	$+ 4 H_2(g)$
Initial/ mol	1	2		1	1
Eqm/ mol	1-x	2-2x		1 + x	1 + 4 x

Total mol at eqm = 5 + 2x

partial pressure of CS_2 == $2\left(\frac{1+x}{5+2x}\right) = 0.5\text{ atm}$

solve for x , x = 0.5

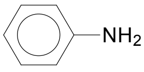
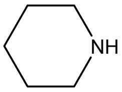
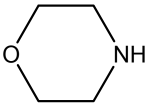
	$CH_4(g)$	$+ 2 H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	$+ 4 H_2(g)$
Eqm/ mol	0.5	1		1.5	3
	Total amt of gas at eqm = 6				
Eqm / atm	$\frac{0.5}{6}\times 2 = \frac{1}{6}$	$\frac{1}{6}\times 2 = \frac{1}{3}$		0.5	$\frac{3}{6}\times 2 = 1$

$$K_p = \frac{(P_{H2})^4 . P_{CS2}}{P_{CH4} . (P_{H2S})^2}$$

$$K_p = \frac{1^4(0.5)}{(1/6).(1/3)^2} = 27.0\text{ atm}^2$$

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

[2]

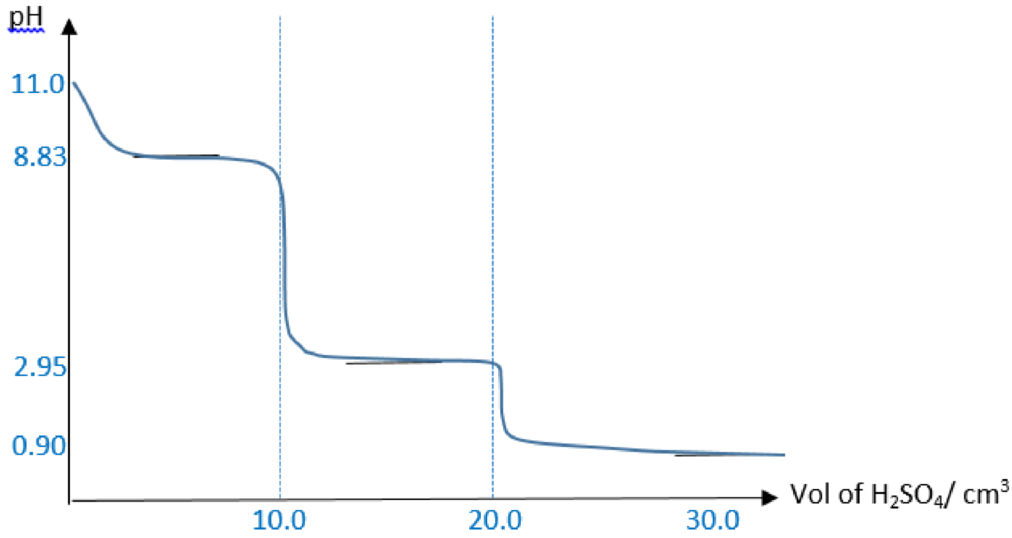
(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the p*H*–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- p*H* of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.

- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
pOH = pK$_b$ at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
$[H^+]$ = 0.005 x 1000/ 40 = 0.125 moldm^{-3} => pH = 0.90

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

$$\underset{\textbf{A}}{C_4H_{10}} \xrightarrow{\text{step 1}} \underset{\textbf{B}}{C_4H_9Cl} \xrightarrow{\text{step 2}} C_4H_{11}N$$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

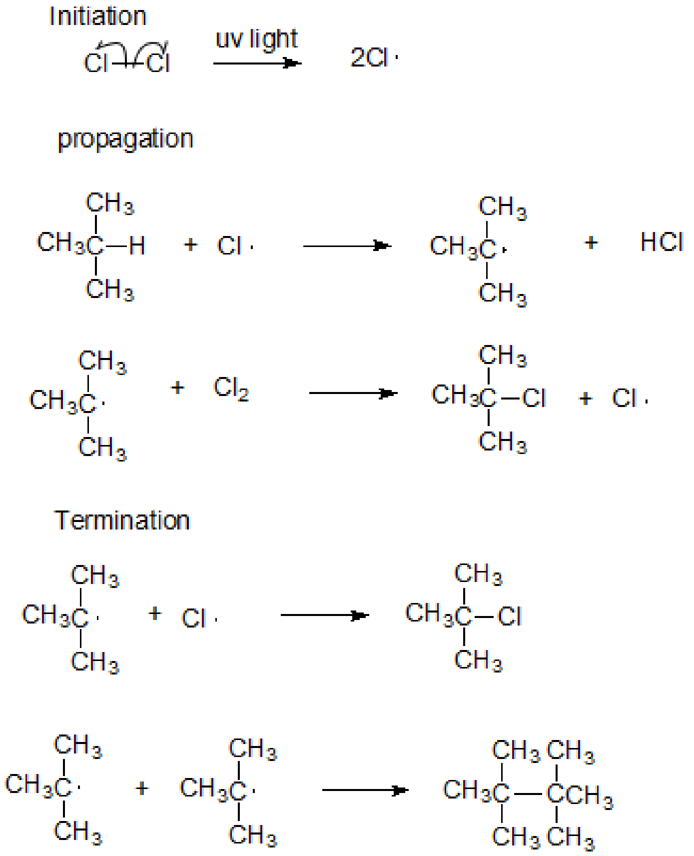
Step 1: limited Cl_2, UV. light

Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

(ii) Outline the mechanism for step 1.

Free radical substitution



[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **(c) (ii).**

Electrophilic addition via alkene can only give two possible products and the tertiary carbocation is formed at a greater rate that forms the major product 2-amino-2-methylpropane, while free radical substitution of alkane gives rise to a variety of reactive intermediates that lead to multiple products being formed.

[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

cold water

[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH^-, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

Continuous Method:

1. Mix Solution **A** & **B**, swirl the beaker and start the stopwatch.
2. At a certain time, withdraw a fixed volume of mixture into a conical flask, add fixed volume of cold water to the mixture to quench the reaction.
3. Titrate against hydrochloric acid, using phenolphthalein as indicator.
4. Titrate until colour of mixture turns from pink to colourless.
5. Repeat steps 2 - 4 at fixed time intervals (eg, 6 min, 9 min, 12 min)
6. Plot graph of volume of HCl against time.
7. If straight-line graph, it means that reaction is 0 order wrt OH^-
   If constant half-life, it means that reaction is 1st order wrt OH^-
   If increasing half-life, it means that reaction is 2nd order wrt OH^-

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Comparing experiment 1 & 3, when [OH^-] is constant, [$C_6H_5CHClCH_3$] is tripled, relative rate is tripled. Hence, reaction is 1st order with respect to $C_6H_5CHClCH_3$. [1]

Comparing experiment 1 & 2, when both [OH^-] and [$C_6H_5CHClCH_3$] are doubled, relative rate is doubled. Since reaction is 1st order with respect to $C_6H_5CHClCH_3$, the doubling of [OH^-] has no effect on rate, so reaction is zero order with respect to OH^-. [1]

* Accept if student write conc / rate <u>increases by</u> 3 times.

Order with respect to $C_6H_5CHClCH_3$ = **first order**

Order with respect to OH^- = **zero order**

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

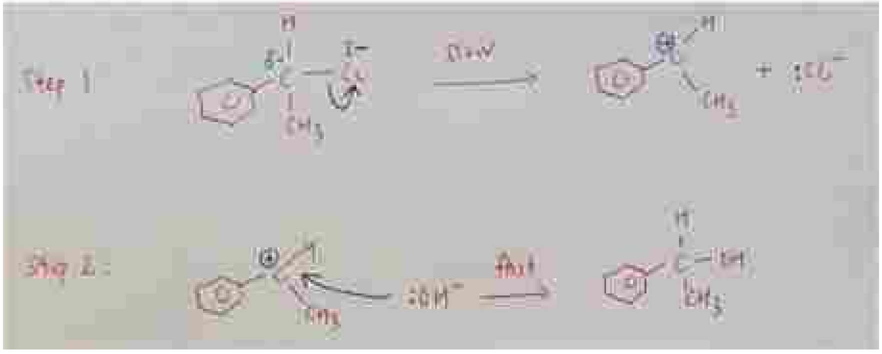
rate = $k[C_6H_5CHClCH_3]$ mol $dm^{-3}s^{-1}$

units of *k* = s^{-1}

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

<u>Nucleophilic substitution (S_N1)</u>



(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers.
Explain your answer.

A mixture of 2 optical isomers (racemic mixture) will be formed because the nucleophile can attack the trigonal planar intermediate from top or bottom of the plane with equal probability.

If S_N2 in c(i),
A single optical isomer will be formed as the nucleophile attack the molecule from the opposite side of the leaving chloride, resulting in an inversion of configuration. [2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

In 1-chloro-2-ethyl benzene, the p-orbital of C*l* overlaps with the π-electron cloud of benzene, resulting in delocalisation of electrons, strengthening the C-C*l* bond, giving it a partial double bond character.

Hence, the C-C*l* bond does not break easily and the ease of hydrolysis will be much lower than that of 1-chloro-1-phenylethane.

[Total: 15]

NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/03

Paper 3 Free Response

Monday 10 Sep 2018
2 hours

Candidates answer on separate paper.
Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid/tape.

Section A
Answers **all** questions.

Section B
Answers **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Section A

Answer **all** the questions in this section.

1 **(a)** The melting points of some compounds are given

Substance	Octan-1-ol	Iodine	Fullerene	Graphite
Formula	$CH_3(CH_2)_7OH$	I_2	C_{60}	C
Melting point/ K	277	286	873	>3000

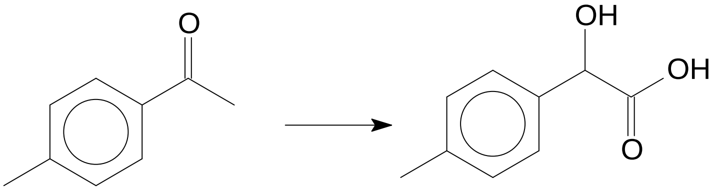
(i) Explain why the melting points of octan-1-ol and iodine are comparable. [2]

(ii) Explain why the melting point of graphite is higher than that of fullerene. [2]

(b) In 1932, Harry Lister Riley and coworkers published their findings on the use of selenium dioxide, SeO_2, in the synthesis of aldehyde and ketone functional groups. One of such reactions is shown below.

$CH_3COCH_3 + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$ reaction **I**

Using the synthetic method above in one of your steps, devise a three–stage synthesis of compound **B** from compound **A**.



Compound **A** Compound **B**

[5]

(c) The most common source of acidity in water is dissolved carbon dioxide.

Carbon dioxide enters the water through equilibrium with the atmosphere.

$CO_2(g) \rightleftharpoons CO_2(aq)$ $K_H = 3.3 \times 10^{-4}$ mol dm^{-3} kPa^{-1}

where K_H is known as the Henry's Law constant given by the equation:

$$[CO_2(aq)] = K_H \times P_{CO2}$$

Carbon dioxide can react with water to form carbonic acid as shown in the following reaction.

$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq)$ $K_c = 1.3 \times 10^{-3}$

(i) Calculate $[CO_2(aq)]$ at a pressure of 101.3 kPa, given that air contains 0.035% by volume of carbon dioxide. [2]

(ii) Using your answer from **(i)**, calculate $[H_2CO_3]$. [1]

Carbonic acid will further dissociate in the following reactions.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \quad K_{a1} = 2.5 \times 10^{-4}$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

(iii) The pH of the carbonic acid is largely contributed by K_{a1}. Explain why. [1]

(iv) Hence, calculate pH of carbonic acid. [1]

(c) Many organic compounds that occur naturally have molecules that can show stereoisomerism, that is cis-trans or optical isomerism.

Draw the structures of all the possible stereoisomers which have the following features.

- They are acyclic.
- They have molecular formula $C_4H_{10}N_2$.
- No nitrogen atom is attached to any carbon atom which is involved in a double bond.
- No carbon atom has more than one nitrogen atom joined to it.

For **each** structure you draw, state the type of stereoisomerism it shows.

[4]

[Total:18]

2 Electric or hybrid vehicles are expected to reach 27 million by 2027. Copper is used as a major component in the windings and copper rotors of electric vehicles.

Crude copper was obtained when a particular copper ore was reduced. Crude copper contains cobalt and silver as minor impurities. It contained no other metal. In order to purify it, crude copper was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

(a) Explain, with reference to relevant $E^\ominus$ values, what happens to the cobalt and silver impurities during this purification process.

[3]

An experiment was carried out to determine the percentage purity of the crude copper obtained from reduction of copper ore. A current of 2.15 A was passed through the cell described in **(a)** for 28.0 minutes, and the electrodes removed and weighed. It was found that the anode has lost 1.25 g.

After filtering it off, the deposit underneath the anode weighed 0.07 g. On adding an excess of dimethylglyoxime to the electrolyte, the highly insoluble red complex with the formula $Co(C_4H_7N_2O_2)_2$ was precipitated. Its mass was 0.55 g.

(b) **(i)** Calculate the *actual mass of copper* removed from the crude copper.

[2]

(ii) Hence determine the percentage purity of the crude copper produced in **(a),** assuming that the crude copper is of uniform mixture.

[1]

(iii) Suggest how the procedure can be improved to increase the reliability of results.

[1]

(iv) Calculate the *expected increase* in mass of the cathode.

[2]

(c) $Co(C_4H_7N_2O_2)_2$ has a solubility of 1.23×10^{-4} mol dm^{-3}.

Calculate its solubility product.

[2]

Lithium is a scavenger for hydrogen, hence it is able to prevent the reaction between hydrogen and copper during pure copper casting. Reaction with hydrogen makes the copper brittle, causing it to fall apart under very light stress.

Table 1

	Enthalpy / kJ mol^{-1}
Enthalpy change of formation of LiH(s)	–90.5
Enthalpy change of formation of $LiAlH_4(l)$	–152.5
Enthalpy change of formation of $Li_3AlH_6(s)$	–454
Enthalpy change of atomisation of Li(s)	+159.5
Electron affinity of hydrogen atoms	–73.0

(d) Heating lithium in a stream of hydrogen gas produces white, crystalline, ionic lithium hydride, LiH.

(i) With the help of a suitable energy level diagram, calculate the lattice energy of LiH using relevant data from **Table 1** and the *Data Booklet*.

[3]

(ii) By quoting relevant data from the *Data Booklet*, suggest and explain how the magnitude of the lattice energy of LiC*l* would compare to LiH.

[2]

(e) When lithium hydride is heated with anhydrous aluminium chloride, lithium aluminium hydride, $LiAlH_4$ and lithium chloride are produced.

$$4\ LiH + AlCl_3 \rightarrow LiAlH_4 + 3\ LiCl$$

When 5 g each of $AlCl_3$ and LiH are reacted in a bomb calorimeter, the temperature rise is 8.4 ^{o}C. Given that the heat capacity of the bomb calorimeter is 1.24 kJ K^{-1}, determine the enthalpy change of this reaction per mole of $LiAlH_4$.

[3]

(f) Just above its melting point, $LiAlH_4$ decomposes according to the following equation.

$$3\ LiAlH_4\ (l) \rightarrow Li_3AlH_6(s) + 2Al(s) + 3H_2(g)$$

(i) Use relevant data in **Table 1**, calculate the standard enthalpy change of this reaction.

[1]

(ii) Given that $\Delta G^{\ominus} = -27.7$ kJ mol^{-1}, calculate $\Delta S^{\ominus}$ for this reaction at 298K, and comment on its sign with respect to the equation for this reaction.

[2]

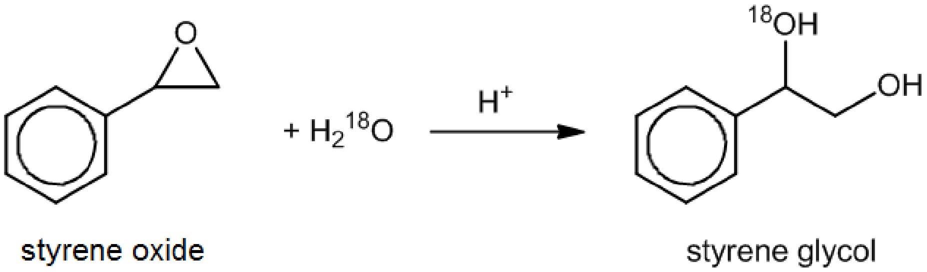
(iii) Hence calculate the melting point of $LiAlH_4$. [1]

[Total: 23]

3 **(a)** Epoxides are a class of organic compounds with a three-membered ring structure. The three-membered ring in epoxides makes them highly reactive and susceptible to "ring-opening reactions" whereby one of the C–O bonds breaks.

(i) An example of an epoxide ring-opening reaction is the hydrolysis of styrene oxide in the presence of a strong acid catalyst to form styrene glycol.

To determine the reaction mechanism, isotopic labelling was used. The hydrolysis was carried out using "heavy-oxygen water", $H_2{}^{18}O$.



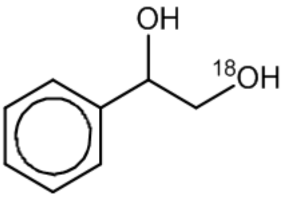
Some details of the mechanism are as given.

1. Protonation of the oxygen atom by a strong acid catalyst
2. Heterolytic fission of the C–O bond to generate a carbocation intermediate, which is a slow step
3. Attack of the carbocation by one molecule of $H_2{}^{18}O$ to form a new C–O bond
4. Loss of a proton to form styrene glycol and regenerate the acid catalyst

Describe steps 1 to 4 of the unimolecular nucleophilic substitution mechanism, showing all relevant charges, lone pairs, dipoles and movement of electrons by curly arrows. You are to label the ^{18}O atom in all necessary species.

[3]

(ii) Trace amounts of an isotopic isomer **A** are also detected upon analysis of the styrene glycol product formed from the hydrolysis.



isotopic isomer **A**

Explain why **A** was formed only in trace amounts.

[2]

(iii) Draw the structure of a side product formed if the same reaction is carried out in the presence of aqueous sodium chloride.

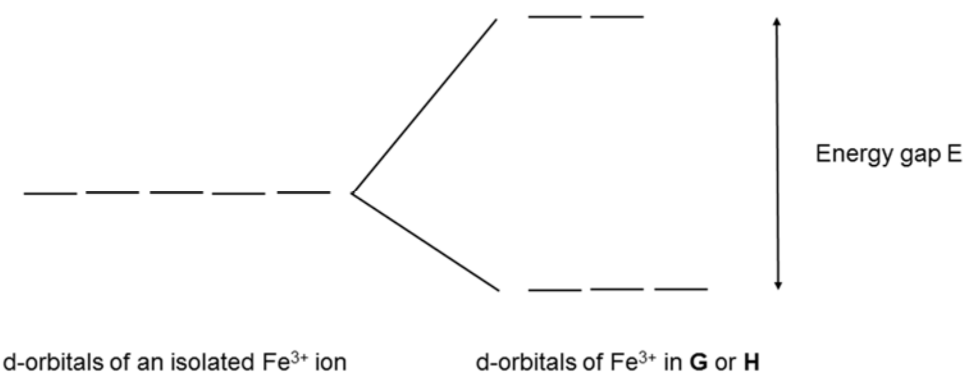
[1]

(b) In 2012, a group of scientists synthesised two ligands, N,N-diethylethylenediamine and N-ethylethylenediamine, and reacted each with Fe^{3+} to form two complexes, **G** and **H**, with different colours respectively.

(i) Explain why iron(III) complexes are usually coloured.

[3]

The following diagram shows how the d-orbitals are split in an octahedral environment.



When the ligand in **H** is substituted with N,N-diethylethylenediamine ligand to form **G**, the Fe^{3+} ion changes its electronic configuration from a ‘high spin’ state to a ‘low spin’ state.

In a ‘high spin’ state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a ‘low spin’ state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

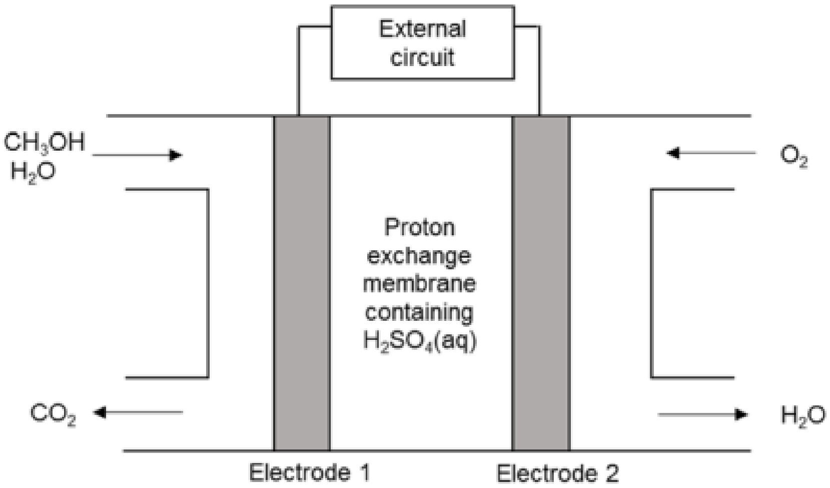
(ii) Use diagrams like the one above to show the electronic distribution of a Fe^{3+} ion in a high spin state, and in a low spin state.

[2]

(iii) By using the information provided thus far and your answer in **(ii)**, state and explain which of the two complexes will contain the larger energy gap, E, between its d-orbitals.

[2]

(c) The following diagram illustrates the parts of a type of fuel cell, Direct methanol fuel cell (DMFC). Methanol is supplied to Electrode 1 where methanol and water react to form carbon dioxide. Oxygen is supplied to Electrode 2 simultaneously and reacts with the protons at the cathode to form water.



(i) Determine the oxidation number of carbon in carbon dioxide and methanol.

[1]

(ii) Write half equations for the reactions which take place at Electrode 1 and Electrode 2. Hence, construct an equation for the overall reaction.

[2]

(iii) The cell is capable of producing an e.m.f. of 1.62 V.

Predict how the voltage of this cell would change if the concentration of methanol was reduced.

[2]

(iv) Suggest a possible advantage of using DMFC as compared to a hydrogen-oxygen fuel cell.

[1]

[Total:19]

Section B

Answer **one** question from this section.

4 **(a)** Proteins are diverse groups of polypeptides required by the human body for growth and maintenance. Human serum albumin, HSA is an important protein that transports hydrophobic molecules in the blood stream.

Four of the most common amino acids in the HSA molecule are listed below.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Glutamic acid	$-CH_2CH_2CO_2H$
Leucine	$-CH_2CH(CH_3)_2$
Lysine	$-CH_2CH_2CH_2CH_2NH_2$
Valine	$-CH(CH_3)_2$

(i) Use the above amino acids to draw the structural formula of a section of the polypeptide chain of HSA, consisting of 3 amino acid residues.

[2]

(ii) The ability of a protein to carry out its function lies in its unique structure that is a result of interactions within the polypeptide chain.

Given that the secondary structure occurs due to interactions between the peptide linkages, state the type of interaction in the secondary structure and illustrate it with a simple diagram.

[2]

(iii) The hydrophobic groups are transported in the inside of the spherical HSA molecule.
Which 2 amino acids from the above table are likely to be responsible for this? Explain your answer.

[2]

(b) **(i)** Amino acids exist as zwitterions. Using leucine as an example, suggest what is meant by the term *zwitterion*.

[1]

(ii) How would you expect the melting point and the solubility in water, of an unionised form of leucine to compare with the actual properties of the zwitterionic form?

[3]

(c) Compound **A**, $C_8H_{10}O_2$, reacts with aqueous bromine to form a white precipitate, compound **B** with molecular formula, $C_8H_7O_2Br_3$.

Compound **A** also reacts with dilute nitric acid to give compound **C**, $C_8H_9NO_4$. Treatment of compound **C** with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound **D**, $C_8H_{10}NO_2Na$.

Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$. 1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.

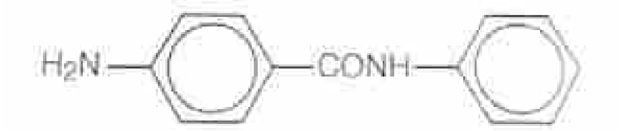
Compound **E** reacts with phosphorus pentachloride to give compound **F**, $C_8H_7NO_2$.

Deduce the structures of compounds **A, B, C, D, E and F** and explain the chemistry of the reactions described.

[10]

[Total:20]

5 **(a)** The structure of 4-amino-N-phenylbenzamide, used in the treatment of epilepsy, is given below. It forms interactions with water but has low solubility in water.



(i) State the type of interaction occurring between water molecules and 4-amino-N-phenylbenamide. Illustrate it with a simple diagram involving a water molecule.

[2]

(ii) Explain the low solubility of 4-amino-N-phenylbenzylamide in water.

[2]

(b) 4-amino-N-phenylbenzylamide is warmed with aqueous sodium hydroxide. Distillation was carried out to separate the products.

(i) Draw the structures of the products formed when 4-amino-N-phenylbenzylamide is warmed with aqueous sodium hydroxide.

[2]

(ii) Suggest and explain the identity of the distillate.

[2]

(iii) When the other product is carefully neutralised, a compound that can be used to maintain the pH of systems at a desired value is obtained.

By means of equations, show how this is achieved when small amounts of

I. dilute HCl,
II. dilute NaOH,

is added to a solution of the compound.

[2]

(c) **G**, $C_6H_9O_2N$, is a neutral compound with the ability to rotate plane polarized light.

On heating **G** with aqueous NaOH, a pungent gas **H** that turned moist red litmus blue was liberated. Upon acidification of the reaction mixture, **J**, $C_5H_8O_4$, was formed.

J reacts with $LiAlH_4$ to form **K**, $C_5H_{12}O_2$. On heating with excess concentrated H_2SO_4, **K** forms **L**, C_5H_8. **L** does not exhibit cis-trans isomerism. When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed.

M reacts with aqueous Na_2CO_3 to produce effervescence that forms a white precipitate in limewater. **M** also forms a yellow precipitate when warmed with alkaline aqueous I_2.

Deduce the structures of compounds **G, H, J, K, L** and **M,** and explain the chemistry of the reactions described.

[10]

[Total:20]

COVER PAGE

NATIONAL JUNIOR COLLEGE SENIOR HIGH 2
PRELIM EXAMINATION

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NATIONAL JUNIOR COLLEGE SENIOR HIGH 2
PRELIM EXAMINATION

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Question Number	Marks Obtained
4	
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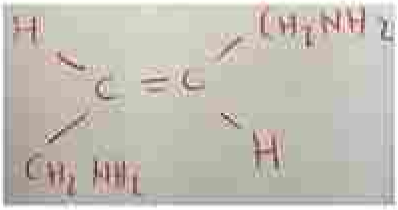
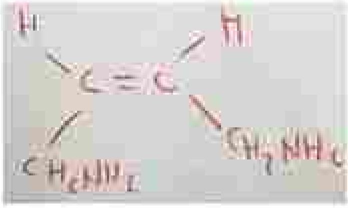
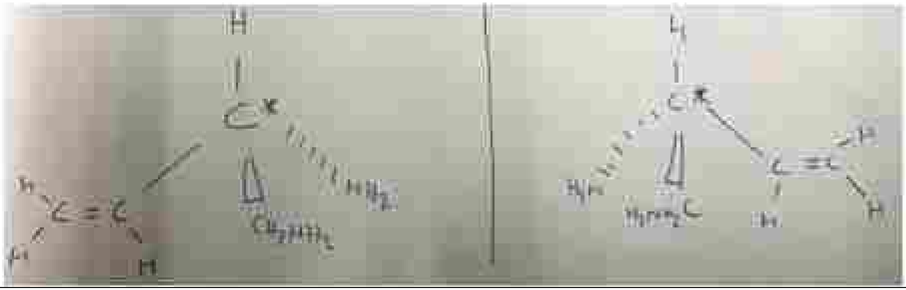
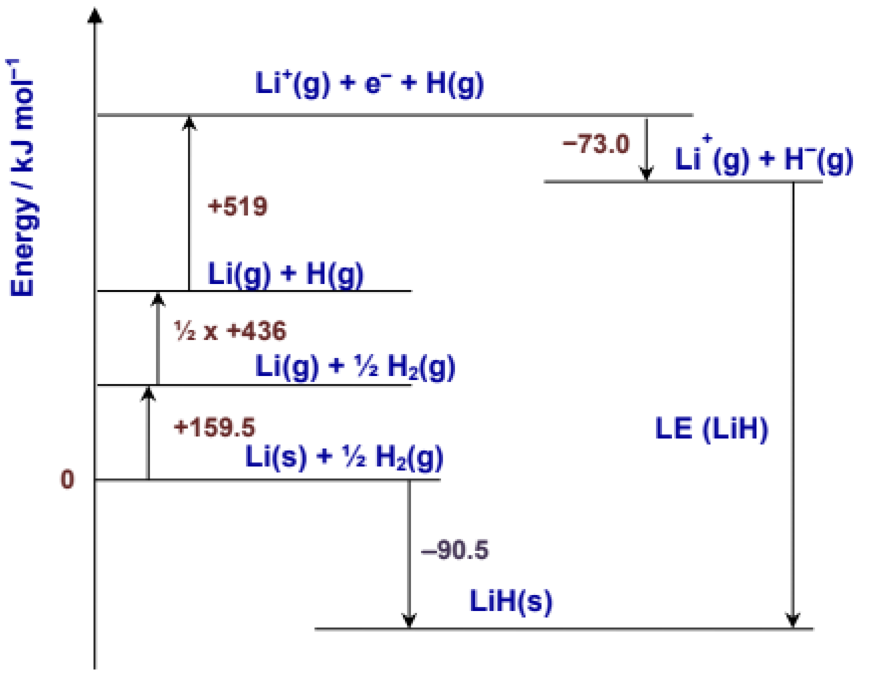
Penalty	
Sf/Units	
Total for **Section B**	

NJC 2018 SH2 H2 Chemistry Prelim Paper 3 Solutions:

Question 1	
(a)(i)	**Suggested solution** Both octan-1-ol and iodine have simple covalent structure Strength of Td-Id in iodine due to its large electron cloud size is comparable to the stronger hydrogen bonding between octan-1-ol molecules.
(ii)	**Suggested solution** Graphite has a giant molecular structure with strong covalent bonds between carbon atoms to be overcome during melting. Fullerene has a simple covalent structure with weaker td-id interactions between fullerene molecules to be overcome during melting. Hence, more energy is required to melt graphite and a higher temperature is required.
(b)	**Suggested solution** Step 1: reaction 1 ;(-COCHO) Step 2: $K_2Cr_2O_7$/$KMnO_4$ with H_2SO_4(aq) and heat; (-COCOOH) Step 3: $NaBH_4$ in ethanol or H_2 with Nickel/Pt ; (compound B)
c(i)	**Suggested solution** $P_{CO2} = \frac{0.035}{100} \times 101.3\text{kPa}$ $= 0.03546\text{kPa}$ $K_H = \frac{[CO_2(aq)]}{P_{CO2}}$ $[CO_2(aq)]= 1.17 \times 10^{-5}$ mol dm^{-3}
c(ii)	**Suggested solution** $K_c = \frac{[H_2CO_2(aq)]}{[CO_2]}$ $[H_2CO_3] = 1.52 \times 10^{-8}$ mol dm^{-3}
(iii)	**Suggested solution** Ka_1 is larger than Ka_2. H_2CO_3 will dissociate accordingly to eqm 1 first and $[H^+]$ from eqm 1 suppresses the dissocation of HCO_3^- in eqm 2. OR HCO_3^- from eqm 1 is low as Ka_1 is small. Hence $[H^+]$ from HCO_3^- is negligible. $[H^+]$ is largely from eqm 2.
c(iv)	**Suggested solution** $K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ $[H^+]=1.915 \times 10^{-6}$ $moldm^{-3}$ pH = 5.71
d	**Suggested solution**

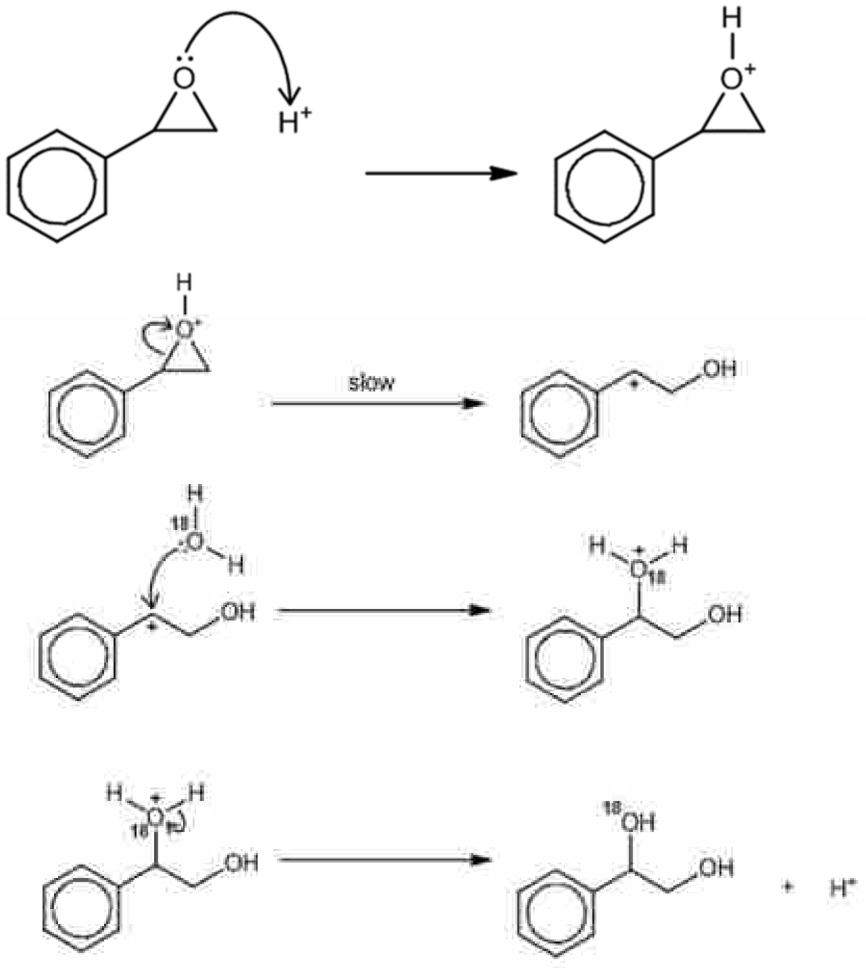
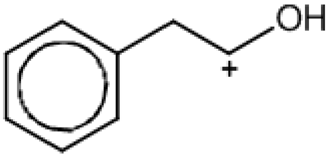
	  

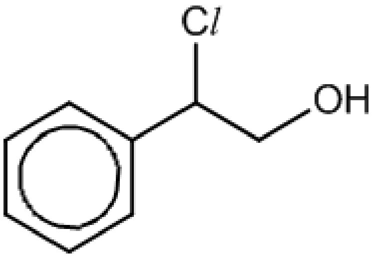
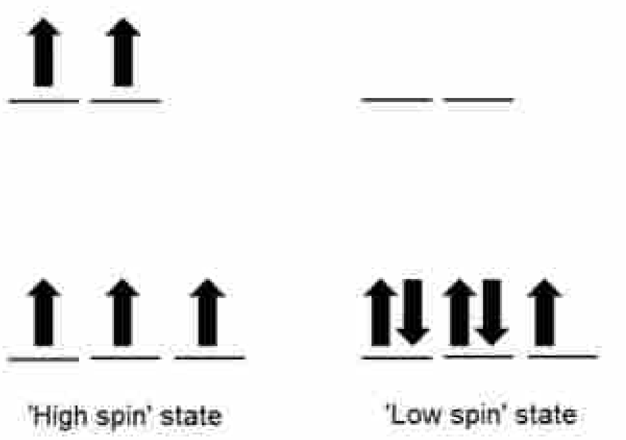
Question 2	
(a)	**Suggested solution:** At anode: Co has $E^{\ominus}_{ox}$ (Co/Co^{2+}) = +0.28V more positive that $E^{\ominus}_{ox}$ (Cu/Cu^{2+}) = –0.34V, hence Co will be oxidised together with Cu and dissolve as Co^{2+}, becoming part of the electrolyte. Ag on the other hand has more negative $E^{\ominus}_{ox}$ (Ag/Ag^{+}) of –0.80V, hence will not be oxidised. It will fall below anode as sludge. At cathode: Co^{2+} has a more negative $E^{\ominus}_{red}$(Co^{2+}/Co) = –0.28 V than $E^{\ominus}_{red}$(Cu^{2+}/Cu) = 0.34 V, hence Co^{2+} is not reduced at the cathode, remain dissolved as electrolyte.
(b) (i)	**Suggested solution** • mass of Ag = 0.07 g • No of moles of Co oxidised at anode = no of moles of Co($C_4H_7N_2O_2$)$_2$ $= \frac{0.55}{58.9+2(4\times12+7+2\times14+2\times16)}$ = 0.0019038 mol Mass of Co in alloy (anode) = 0.0019038 x 58.7 = 0.112 g Mass of Cu = 1.25 – 0.07 – 0.112 = 1.068 g
b(ii)	% purity = 1.068 /1.25 x 100 = 85.4%
b(iii)	**Suggested solution:** **Any one of the suggestion below is acceptable:** (i) Mass of Ag and Co($C_4H_7N_2O_2$)$_2$ should be heated to consistent mass to ensure all water is driven off, so that mass measured is that of dry mass of Ag and Co($C_4H_7N_2O_2$)$_2$. (ii) As mass of Ag (sludge) is rather small, use electronic balance of higher precision in order to reduce % uncertainty in mass measurement. (iii) Repeat the experiment using fresh samples so that an average of the mass measurements can be taken to reduce random error.
b(iv)	**Suggested solution:**

	Total no of moles of e used for electrolysis = 2.15 x 28.0 x 60 ÷ 96500 = 0.03743 No of moles of Cu expected to be discharged = 0.043523 ÷ 2 = 0.018715 Mass expected = 0.018715 x 63.5 = 1.19 g (3sf)
(c)	**Suggested solution:** $Co(C_4H_7N_2O_2)_2$ + aq ⇌ Co^{2+} + 2 $C_4H_7N_2O_2^-$ −1.23 x 10^{-4} +1.23 x 10^{-4} + 2 x 1.23 x 10^{-4} Ksp = $[Co^{2+}][C_4H_7N_2O_2]^2$ = (1.23 x 10^{-4})(1.23 x 10^{-4} x 2)^2 = 7.44 x 10^{-12} mol^3dm^{-9}
(d)(i)	**Suggested solution**  By Hess' law: L.E. = 73.0 – 519 – (½ x 436) – 159.5 – 90.5 = **– 914 kJ mol^{-1}**
d(ii)	**Suggested solution:** $|LE| = \left|\frac{q^+q^-}{r^+ + r^-}\right|$ Ionic radii of Cl^- = 0.181, ionic radii of H^- = 0.208nm They have the same product but LiH has a larger interionic distance than LiC*l*, therefore LE magnitude of LiH is smaller.
(e)	**Suggested solution:** Amt of $AlCl_3$ = $\frac{5}{27+35.5\ x\ 3)}$ = 0.037453 mol

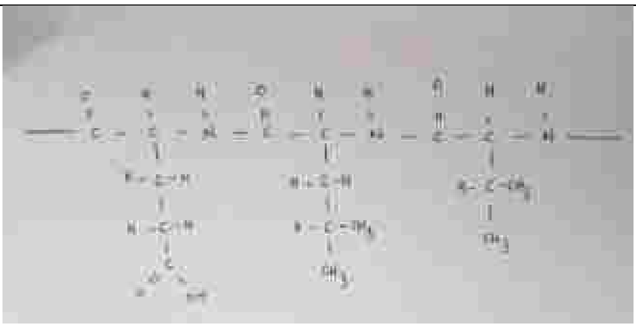
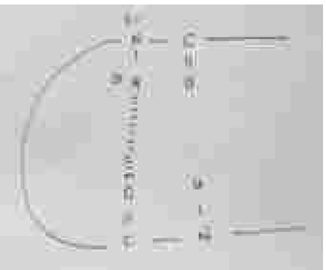
	Amt of LiH = $\frac{5}{7.9}$ = 0.6329 mol $AlCl_3$ is limiting since 0.037453 mol of $AlCl_3$ requires 0.037453 x 4 mol of LiH_4 = 0.14981 mol < 0.6329 mol. No of moles of $LiAlH_4$ formed = 0.037453 mol 0.037453 x $\Delta H_{reaction}$ = – 1.24 x 8.4 $\Delta H_{reaction}$ = – 1.24 x 8.4 ÷ 0.037453 = –278 $kJmol^{-1}$
(f)(i)	**suggested solution** $\Sigma n\Delta Hf(products) - \Sigma n\Delta Hf(reactants) = –454 – 3(–152.5)$ = +3.5 $kJmol^{-1}$
f(ii)	**Suggested solution** $\Delta G^{\ominus} = \Delta H^{\ominus} – T\Delta S^{\ominus}$ $–27.7 = +3.5 – 298 \times \Delta S^{\ominus}$ $\Delta S^{\ominus}$ = +0.105 $kJmol^{-1}K^{-1}$ ΔS is positive as there is an increase of 3 moles of gas molecules after the reaction; there are more ways to distribute the molecules and their energies, increasing entropy level of the system at the end of reaction.
f(iii)	**Suggested solution** Temp at which decomposition becomes spontaneous is the cross over temperature. $\Delta G = 0$ $+3.5 = 0.105 \times T$ T = 33.3 K

Question 3	
(a)(i)	**Suggested solution:**

	
(ii)	**Suggested solution:** A is formed from the primary carbocation as shown.  This primary carbocation is less stable due to the positive charge not being resonance stabilised by the aromatic ring. Hence, the carbocation is formed in trace amounts, leading to trace amounts of A being formed.
(iii)	**Suggested solution:**

	
(b)(i)	**Suggested solution:** In the presence of ligands, d-orbitals of Fe^{3+} are split into two different energy levels with small energy gap. d-d transition, where the electron is promoted from a lower energy d orbital to a higher energy d orbital, is possible. Energy that corresponds to the wavelength of light in the visible region of the electromagnetic spectrum is absorbed. Colour observed is complementary to the wavelength of visible light absorbed.
(ii)	**Suggested solution:** 
(iii)	**Suggested solution:** G has a larger energy gap. Since the electronic configuration of Fe^{3+} in G is in a 'low spin' state, energy required to overcome the energy gap in adding subsequent electrons to higher energy d-orbitals is more than that required to overcome inter-electronic repulsion when electrons paired up in the lower energy d-orbitals.
(c)(i)	**Suggested solution:** Oxidation number of C in carbon dioxide: +4 Oxidation number of C in methanol: -2

(ii)	**Suggested solution:** Electrode 1 : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Electrode 2 : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Overall: $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
(iii)	**Suggested solution:** When $[CH_3OH]$ is decreased, oxidation of methanol becomes less favoured OR by LCP, the position of equilibrium for $CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$ shifts to the left to partially increase $[CH_3OH]$. Thus, $E_{ox(CH3OH/CO2)}$ becomes less positive. A less positive $E_{ox(CH3OH/CO2)}$ will cause E_{cell} to be less positive since $E_{cell} = E + E_{ox}$.
(iv)	**Suggested solution:** CH_3OH is a liquid at room temperature and thus can be easily transported and stored than hydrogen gas OR CH_3OH is less explosive than H_2 gas OR CH_3OH is less expensive to maintain than H_2 gas

Question 4	
(a)(i)	
(ii)	**Suggested solution:**  Hydrogen bonding - lone pair

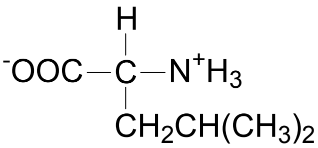
- δ+ / δ-
- dotted lined to show bond

(iii) **Suggested solution:**

Leucine and Valine.

Their side chains consist of hydrocarbon chains which are able to form temporary dipole-induced dipole interactions with hydrophobic groups to transport them in the blood stream.

(b)(i) **Suggested solution:**



$$^{-}OOC-\overset{\displaystyle H}{\underset{\displaystyle CH_2CH(CH_3)_2}{C}}-N^{+}H_3$$

(ii) **Suggested solution:**

Melting point

Unionised form: Hydrogen bonding
Zwitterionic form: Ionic bonding
More energy is required to overcome the stronger ionic bonding compared to the hydrogen bonds. Hence the zwitterionic form will have a higher melting point.

Solubility:

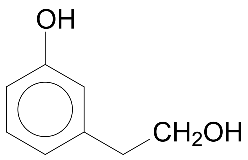
Unionised form: Hydrogen bonds with water
Zwitterionic form: ion-dipole interactions with water
Stronger ion-dipole interactions produce more energy to overcome the hydrogen bonds between water molecules and the interactions between the solute. Hence the zwitterionic form will be more soluble in water.

(c) **Suggested solution:**

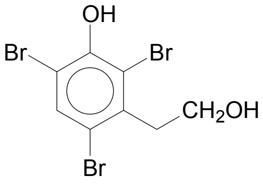
Observation	Deductions
Compound **A**, $C_8H_{10}O_2$, reacts with $Br_2(aq)$ to form a white precipitate compound **B** with molecular formula, $C_8H_7O_2Br_3$	**A** contains phenol (reacts without halogen carrier) **B** is 2,4,6- trisubstituted
Compound **A** also reacts with dilute nitric acid to give compound **C**, $C_8H_9NO_4$	Mononitration of **A** to give **C** Confirm presence of phenol
Compound **C** with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound **D**, $C_8H_{10}NO_2Na$.	NO_2 group in **C** is reduced to $-NH_2$ phenol in **C** is converted to sodium phenoxide in **D**

Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$.	**D** undergoes oxidation to form carboxylic acid primary alcohol present in **D,** phenoxide in **D** is acidified to phenol in **E**
1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.	2 acidic groups present Carboxylic acid and phenol confirmation
Compound **E** reacts with phosphorus pentachloride to give compound **F**, $C_8H_7NO_2$.	$-CO_2H$, in **E** is converted into an acyl chloride, $–COCl$,by PCl_5. Amine undergoes internal nucleophilic substitution),with loss of Cl–, to yield the cyclic amide **F** Carboxymethyl group, $–CH_2CO_2H$, must be adjacent to amine – NH_2 group in **A** to enable ring formation

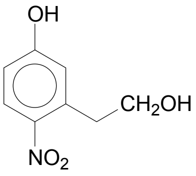
A:



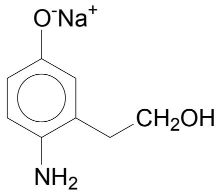
B:



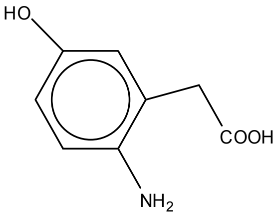
C:



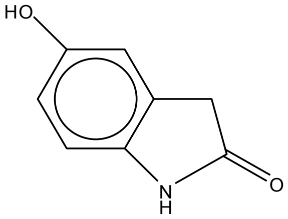
D:



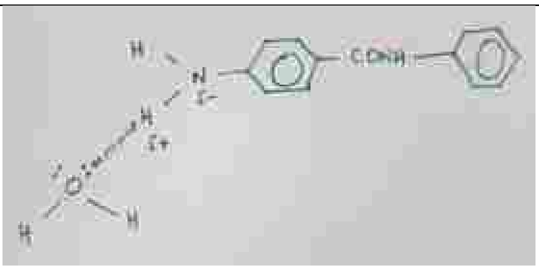
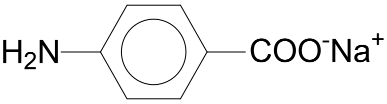
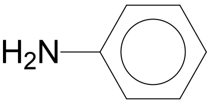
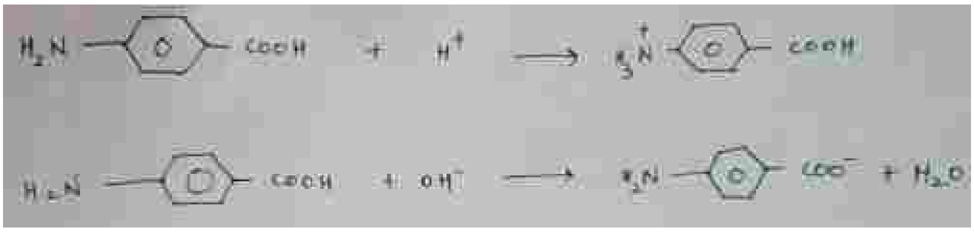
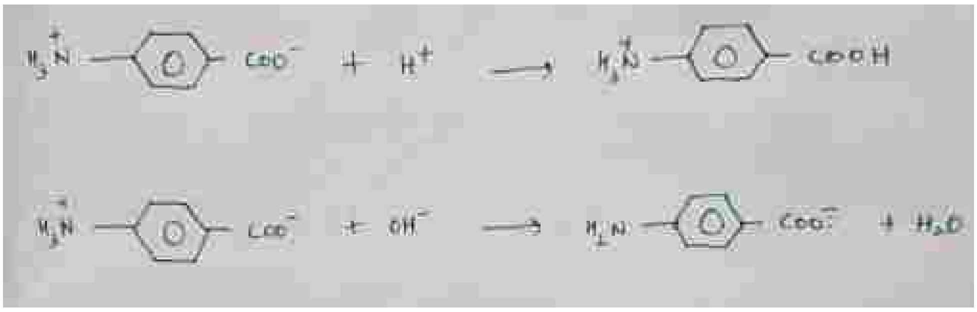
E:



F:

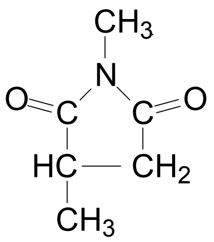
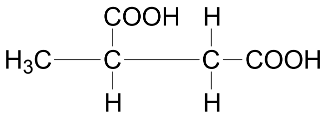


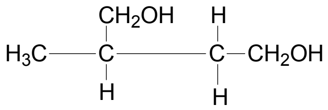
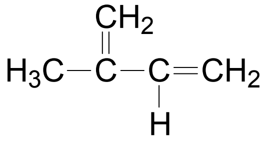
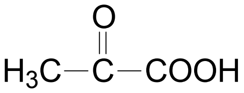
Question 5	
(a)(i)	**Suggested solution:**

	 Hydrogen bond - lone pair - δ+ / δ- - dotted lined to show bond
(ii)	**Suggested solution:** Energy given out when hydrogen bonds are formed between water molecules and 4-amino-N-phenylbenzylamide is insufficient to overcome the extensive temporary dipole-induced dipole interactions between 4-amino-N-phenylbenzylamide molecules. Hence solubility is low.
(b)(i)	**Suggested solution:**  
(ii)	**Suggested solution:** Phenylamine is a simple covalent molecule with weak intermolecular attractions between them whereas the other product is an ionic compound with strong electrostatic forces of attraction between ions. Phenylamine thus has a lower boiling point of the 2 and will distil out first to be the distillate.
(iii)	**Suggested solution:**  OR 

(c) **Suggested solution:**

Information / Type of reaction	**Deductions**
Compound **G**, $C_6H_9O_2N$, is a neutral compound with the ability to rotate plane polarised light.	As **G** contains N and is neutral, **G** is likely to be an amide. **G** contains at least 1 chiral carbon.
G reacts with aqueous sodium hydroxide to form pungent gas **H** that turned moist red litmus blue. Upon acidification with aqueous hydrochloric acid, **J** $C_5H_8O_4$.	Alkaline hydrolysis Alkaline gas **H**: $CH_3NH_2(g)$. (**J** has 1 less carbon than **G**) **J** has 2 carboxylic acid groups. **G** is cyclic amide.
J reacts with LiA/H_4 to form **K**, $C_5H_{12}O_2$.	**K** has 2 is primary alcohol groups.
On heating with excess concentrated H_2SO_4, **K** forms **L**, C_5H_8. **L** does not exhibit cis-trans isomerism.	**K** undergoes elimination of H_2O to form **L**, C_5H_8, with 2 alkene groups. Most likely terminal alkenes as no cis-trans isomerism.
When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed.	**L** undergoes oxidative cleavage to form **M,** $C_3H_4O_3$
M reacts with aqueous Na_2CO_3 to produce effervescence that forms a white precipitate in limewater.	acid-base reaction **M** contains a carboxylic acid**.**
M also forms a yellow precipitate when warmed with alkaline aqueous I_2.	**M** contains CH_3CO- group. (must be ketone as it is a product of oxidative cleavage of a C=C)

G	H	J
	$CH_3NH_2^-$	 $H_3C-CH(COOH)-CH_2-COOH$

K  $H_3C-\overset{\overset{\displaystyle CH_2OH}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-\overset{\overset{\displaystyle H}{\vert}}{\underset{\underset{\displaystyle H}{\vert}}{C}}-CH_2OH$	L  $H_3C-\overset{\overset{\displaystyle CH_2}{\Vert}}{C}-\underset{\underset{\displaystyle H}{\vert}}{C}=CH_2$	M  $H_3C-\overset{\overset{\displaystyle O}{\Vert}}{C}-COOH$

NATIONAL JUNIOR COLLEGE

SH2 Year-End Practical Examination

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/04**

Paper 4 Practical **14 August 2018**

Candidates answer on the Question paper **2 hours 30 minutes**

Additional Materials: As listed in the Confidential Instructions

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READ THESE INSTRUCTIONS FIRST

Write your identification number and name.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 18 and 19.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's use	
1	/ 14
2	/ 6
3	/ 13
4	/ 9
5	/10
Presentation	/3
Total	/ 55

This document consists of **19** printed pages including this cover page.

Answer **all** the questions in the spaces provided.

1 Determination of the average relative formula mass of a mixture of two copper salts

In this experiment, you will determine the average relative formula mass of a mixture of two copper salts by titration.

A solution of the copper salts mixture reacts with excess acidified potassium iodide, producing iodine.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

This iodine is then titrated with aqueous sodium thiosulfate, using starch indicator.

FA 1 is an aqueous solution of the copper salt prepared by dissolving 26.0 g of the salt mixture to make 1.00 dm^3 of solution.
FA 2 is dilute sulfuric acid, H_2SO_4.
FA 3 is aqueous potassium iodide, KI.
FA 4 is 1.50 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
starch indicator

(a) Preparation of diluted FA 4

1. Pipette 25.0 cm^3 of **FA 4** into the 250 cm^3 graduated flask.
2. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
3. Stopper the flask and mix the contents thoroughly to ensure a homogeneous solution.
   This prepared solution is **diluted FA 4**.

Titration

1. Fill the burette with **diluted FA 4**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Use the measuring cylinder to add approximately 10.0 cm^3 of **FA 2** to the same conical flask.
4. Use the measuring cylinder to add approximately 20.0 cm^3 of **FA 3** to the mixture in the conical flask. The mixture will appear brown, due to iodine produced in the reaction.
5. Begin your rough titration by adding **diluted FA 4** from the burette until the intensity of the brown colour decreases.
6. Add 10 drops of starch indicator. The mixture will become darker.
7. Continue titrating until the dark colour is discharged. The mixture should appear off-white. This is the end-point.
8. Add **one** drop of starch indicator to check that no traces of dark colour are produced.
9. If the mixture stays off-white, the titration is completed. If some dark colour is produced, because iodine is still present, continue the titration until mixture appears off-white.
10. Record your burette readings and the rough titre in the space below.
11. Carry out as many accurate titrations as you think necessary to obtain consistent results.

12. Make sure any recorded results show the precision of your practical work.
13. Record in a suitable form below all of your burette readings and the volume of **diluted FA 4** added in each accurate titration.

[7]

I	
II	
III	
IV	
V	
VI	
VII	

From your accurate titration results, obtain a suitable value for the volume of **diluted FA 4** to be used in your calculations.

Show clearly how you obtained this value.

The iodine produced required .... cm^3 of **diluted FA 4**.
[1]

(b) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of sodium thiosulfate, $Na_2S_2O_3$, in the volume of **diluted FA 4** obtained in **(a)**.

moles of $Na_2S_2O_3$ = ... mol
[1]

(ii) Balance the ionic equation for the reaction of iodine with sodium thiosulfate. State symbols are not required.

…..... I_2 + ... $S_2O_3^{2-}$ → .... $S_4O_6^{2-}$ + ……... I^-

Hence calculate the number of moles of iodine that reacted with the number of moles of $Na_2S_2O_3$ calculated in **(i)**.

moles of I_2 = ... mol

[1]

(iii) Using your answer to **(ii)**, calculate the number of moles of copper(II) ions in 25.0 cm^3 of **FA 1**.

moles of Cu^{2+} ions = ... mol

[1]

(iv) Using your answer to **(iii)** and the information on page 2, calculate the average relative formula mass of the copper salts in **FA 1**.

*Average M*r of copper salts = ...

[1]

(v) Write the full electronic configuration of $_{29}Cu$ in CuI.

……………………………………………………………………………..…………[1]

(vi) Hence, explain why solid CuI appears white in colour.

……………………………………………………………………………..…………..…

……………………………………………………………………………..…………..…

……………………………………………………………………………..………..……

[1]

[Total: 14]

2 **Qualitative analysis**

In this question, you will deduce the two anions present in **FA 1.** Perform the tests described in **Table 2** and record your observations in the table. Test and identify any gases evolved.

If any solution is warmed, a boiling tube MUST be used.

Table 2

	Test	Observations
(a)	To a 1 cm depth of **FA 1** in a test-tube, add aqueous silver nitrate.	
(b)	To a 0.5 cm depth of **FA 1** in a boiling tube, add aqueous sodium hydroxide and add one piece of aluminium foil and warm.	
(c)	To a 1 cm depth of **FA 1** in a test-tube, add aqueous barium chloride followed by nitric acid.	
(d)	To a 1 cm depth of **FA 1** in a test-tube, add an equal volume of sulfuric acid followed by $KMnO_4$.	

[3]

(e) From your observations, state the anions present in **FA 1**. Explain your answers.

First anion: ………………………… Second anion:…………………………

……………………………………………………………………………………………..…

……………………………………………………………………………………………..…

……………………………………………………………………………………………..…

……………………………………………………………………………………………..…

……………………………………………………………………………………………..

[3]

[Total: 6]

3 Investigation of thermal decomposition of sodium hydrogencarbonate

Sodium hydrogencarbonate, $NaHCO_3$, is used as baking soda in cooking. Baking soda may also contain small amounts of other chemicals.

When baking soda is heated, carbon dioxide is produced. In this experiment, you will investigate the reaction taking place when the sodium hydrogencarbonate in baking soda is thermally decomposed.

FA 5 is baking soda (impure $NaHCO_3$).

(a) Method

Record all your readings in the space below.

1. Weigh the crucible with its lid.
2. Transfer all the **FA 5** from the container into the crucible.
3. Weigh the crucible, lid and **FA 5**.
4. Calculate and record the mass of **FA 5** used.
5. Place the crucible and contents on a pipe-clay triangle.
6. Heat gently, **with the lid off**, for approximately one minute.
7. Heat strongly, **with the lid off**, for a further three minutes.
8. Replace the lid and leave the crucible to cool for about ten minutes.

While the crucible is cooling, you should work on other questions.

9. When it has cooled down, weigh the crucible with its lid and contents.
10. Heat strongly, **with the lid off**, for a further two minutes.
11. Replace the lid and leave the crucible to cool for ten minutes.
12. When it has cooled down, weigh the crucible with its lid and contents.
13. Calculate and record the mass of residue obtained.
14. This residue is **FA 6**. Keep this for use in **3(d)**.

Results

I	
II	
III	
IV	

[4]

(b) **Calculations**

(i) Given that the percentage purity by mass of **FA 5** is 95.8%, calculate the mass of sodium hydrogencarbonate in the sample of **FA 5** that you weighed out.

mass of $NaHCO_3$ in **FA 5** weighed out = ... g

(ii) Calculate the mass of impurity present in your sample of **FA 5**.

mass of impurity = ... g

[1]

(iii) The impurity in **FA 5** does not decompose when it is heated.

This means that the residue, **FA 6**, contains the mass of impurity calculated in **(ii)** together with the solid decomposition product of sodium hydrogencarbonate.

Calculate the mass of the solid decomposition product.

mass of solid decomposition product = ... g

[1]

(c) Why was the lid put on while the crucible and its contents were cooled?

....

....

[1]

(d) **(i)** Ah Beng carried out the experiment by heating 84.0 g of pure $NaHCO_3$ to constant mass, he obtained 53.0 g of the solid decomposition product.

Ah Hock then suggested the following equation for the thermal decomposition of sodium hydrogencarbonate.

$$NaHCO_3(s) \rightarrow NaOH(s) + CO_2(g)$$

Explain why Ah Hock's suggestion is **incorrect**. Show working in order to explain your answer.

[A_r: C; 12.0; Na; 23.0; H, 1.0; O: 16.0]

....

.... [1]

(ii) Add 1 cm depth of sulfuric acid into a test-tube.
Add some **FA 6** from the crucible to the acid in the test-tube.
Record all your observations.
Use your observations to identify the anion present in **FA 6**.

....

....

.... [2]

(iii) State the assumption you have made in **(ii)**.

....

.... [1]

(iv) Steam is one of **three** products obtained when sodium hydrogencarbonate is thermally decomposed.

Use your answer in **(ii)** to complete and balance the equation for the thermal decomposition of sodium hydrogencarbonate. Include state symbols.

........$NaHCO_3$(   ) $\rightarrow$ ....H_2O(   ) + ...CO_2(   ) + ...

[1]

(v) State whether the balanced equation in **(iv)** agrees with Ah Beng's results.

Show working in order to explain your answer.

....

....

[1]

[Total: 13]

4 Determination of the enthalpy change of a reaction, ΔH_r

FA 7 is 1.00 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$
FA 8 is 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 9 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in Tables 4.1 and 4.2.

Experiment A

Reaction between **FA 7**, $NaHCO_3$, and **FA 8**, NaOH.

Reaction 1 $NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ $\Delta H_{reaction1}$

The molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

1 Using a measuring cylinder, transfer 30.0 cm^3 of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker. Place the lid on the cup.

2 Stir and measure the temperature of this **FA 7**, T_{FA7}.

3 Using another measuring cylinder, measure 20.0 cm^3 of **FA 8.**

4 Stir and measure the temperature of this **FA 8**, T_{FA8}.

5 Add **FA 8** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.

6 Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max}.

7 Calculate the weighted average initial temperature, $T_{average}$, of **FA 7** and **FA 8** using the formula given below:

$$T_{average} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA8} \times T_{FA8})}{(V_{FA7} + V_{FA8})}$$

	Experiment A
T_{FA7} /°C	
T_{FA8} /°C	
$T_{average}$ /°C	
T_{max} /°C	
ΔT_{max} /°C	

Table 4.1

Experiment B

Reaction between **FA 7**, $NaHCO_3$, and **FA 9,** H_2SO_4.

Reaction 2 $NaHCO_3(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l) + CO_2(g)$ $\Delta H_{reaction2}$

The molar enthalpy change for **reaction 2**, $\Delta H_{reaction\,2}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

1 Using a measuring cylinder, transfer 30.0 cm^3 of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker. Place the lid on the cup.

2 Stir and measure the temperature of this **FA 7**, $T_{\mathbf{FA7}}$.

3 Using another measuring cylinder, measure 20.0 cm^3 of **FA 9.**

4 Stir and measure the temperature of this **FA 9**, $T_{\mathbf{FA9}}$.

5 Add **slowly**, the **FA 9** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.

6 Using the thermometer, stir the mixture continuously until a maximum/minimum temperature is reached. Read and record this temperature T_{max}.

7 Calculate the weighted average initial temperature, $T_{average}$, of **FA 7** and **FA 9** using the formula given below:

$$T_{average} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA9} \times T_{FA9})}{(V_{FA7} + V_{FA9})}$$

	Experiment B
$T_{\mathbf{FA7}}$ /°C	
$T_{\mathbf{FA9}}$ /°C	
$T_{average}$ /°C	
T_{max} /°C	
ΔT_{max} /°C	

Table 4.2

[2]

(a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm^{-3} and specific heat capacity, c, of 4.18 J g^{-1} K^{-1}.

(i) Use your results from **Table 4.1** to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$.

$\Delta H_{\text{reaction1}}$ = ...

[2]

(ii) Use your results from **Table 4.2** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$.

$\Delta H_{\text{reaction2}}$ = ...

[2]

(b) Ionic equations for neutralisation, **reaction 1**, and **reaction 2** are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	$\Delta H_{neu} = -57.1$ kJ mol^{-1}
$HCO_3^-(aq) + OH^-(aq) \longrightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{reaction1}$
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$	$\Delta H_{reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \longrightarrow 2HCO_3^-(aq)$ $\Delta H_{reaction3}$

Using your calculated answers in **(a),** together with the given value of enthalpy change of neutralisation, ΔH_{neu}, construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

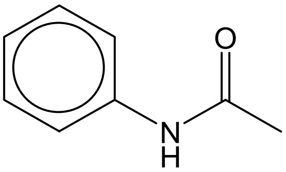
$\Delta H_{reaction3}$ = ……………………

[3]

[Total: 9]

5 **Planning**

The structure of *N*-phenylethanamide is shown below:



N-phenylethanamide, $C_6H_5NHCOCH_3$

The preparation of *N*-phenylethanamide from phenylamine is termed acylation. Ethanoic anhydride, $(CH_3CO)_2O$ is commonly used as an acylating agent as its low reactivity relative to ethanoyl chloride allows the reaction rate to be more easily controlled.

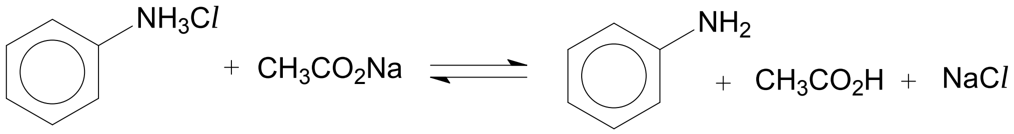
Phenylamine is most conveniently used in the form of the salt phenylammonium chloride, $C_6H_5NH_3Cl$.

The reaction is performed in **two** stages:

Stage **1:**

Phenylamine can be prepared from phenylammonium chloride and sodium ethanoate in an aqueous medium under room temperature.

The reaction is as shown below:



phenylammonium chloride phenylamine

The reaction mixture needs to be continuously stirred for 3 minutes.

Stage **2:**

Phenylamine then reacts with ethanoic anhydride to form solid *N*-phenylethanamide together with ethanoic acid. The addition of ethanoic anhydride to the reaction mixture may be violent.

This mixture is heated under reflux for about 15 minutes, before the crude solid product is removed by filtration and purified by recrystallisation from hot water. The melting point of *N*-phenylethanamide is 114 ^{0}C.

(a) **(i)** State the type of reaction taking place in stage **1**.

……………………………………………………………………………………………. [1]

(ii) Write an equation for the reaction of phenylamine with ethanoic anhydride in stage **2.**

……………………………………………………………………………………………. [1]

(b) The above reaction between phenylamine and ethanoic anhydride in stage **2** gives an 80% yield.

Assuming phenylammonium chloride is completely converted to phenylamine in stage **1**, determine the mass of phenylammonium chloride required to prepare 2 g of *N*-phenylethanamide.
(A_r: C: 12.0, H: 1.0, N: 14.0, O: 16.0, C*l*: 35.5)

[2]

(c) Write a full description of the procedure to carry out stages **1** and **2**.
You do not need to describe the recrystallization process to obtain a pure sample of *N*-phenylethanamide *in stage **2**.*

You may assume that you are provided with :

- 30 cm^3 of water for use as solvent
- 6.0 g of hydrated sodium ethanoate
- 2.0 cm^3 of ethanoic anhydride
- Apparatus normally found in a school or college laboratory

Your plan should include details of:

(i) appropriate quantities of reactants
(ii) appropriate choice of apparatus
(iii) drawing of reflux set-up

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…………………………………………………………………………………………………… [5]

(d) Suggest a method to check the purity of *N*-phenylethanamide obtained.

……………………………………………………………………………………………………

[1]

[Total: 10]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	**NH_3(aq)**
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anions	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated by dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	“pops” with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous potassium manganite(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

2018 SH2 H2 Chemistry P4 Solutions

Answer **all** the questions in the spaces provided.

1 Determination of the average relative formula mass of a mixture of two copper salts

In this experiment, you will determine the average relative formula mass of a mixture of two copper salts by titration.

A solution of the copper salts mixture reacts with excess acidified potassium iodide, producing iodine.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

This iodine is then titrated with aqueous sodium thiosulfate, using starch indicator.

FA 1 is an aqueous solution of the copper salt prepared by dissolving 26.0 g of the salt mixture to make 1.00 dm^3 of solution.

FA 2 is dilute sulfuric acid, H_2SO_4.

FA 3 is aqueous potassium iodide, KI.

FA 4 is 1.50 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$.

starch indicator

(a) Preparation of diluted FA 4

1. Pipette 25.0 cm^3 of **FA 4** into the 250 cm^3 graduated flask.
2. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
3. Stopper the flask and mix the contents thoroughly to ensure a homogeneous solution.
   This prepared solution is **diluted FA 4**.

Titration

1. Fill the burette with **diluted FA 4**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Use the measuring cylinder to add approximately 10.0 cm^3 of **FA 2** to the same conical flask.
4. Use the measuring cylinder to add approximately 20.0 cm^3 of **FA 3** to the mixture in the conical flask. The mixture will appear brown, due to iodine produced in the reaction.
5. Begin your rough titration by adding **diluted FA 4** from the burette until the intensity of the brown colour decreases.
6. Add 10 drops of starch indicator. The mixture will become darker.
7. Continue titrating until the dark colour is discharged. The mixture should appear off-white. This is the end-point.
8. Add **one** drop of starch indicator to check that no traces of dark colour are produced.
9. If the mixture stays off-white, the titration is completed. If some dark colour is produced, because iodine is still present, continue the titration until mixture appears off-white.
10. Record your burette readings and the rough titre in the space below.

11. Carry out as many accurate titrations as you think necessary to obtain consistent results.

12. Make sure any recorded results show the precision of your pra
13. Record in a suitable form below all of your burette readings and
of **diluted FA 4** added in each accurate titration.

I	
II	
III	
IV	
V	
VI	
VII	

I All the following data is recorded
initial and final burette readings for **two** (or more) titrations

II Titre values recorded for accurate titrations, **and**
Appropriate headings and units
- initial / start (burette) reading
- final / end (burette) reading
- titre **or** volume used / added *(not "difference")*

unit: / cm^3 (for each heading) **or** cm^3 unit given for each volume recorded.

III: All burette readings are recorded to the nearest 0.05 cm^3. (2 d.p)
(Rough reading do not need 2 d.p)

including 0.00 cm^3 (if this was the initial reading).

*Do **not** award if: (reverse burette readings)*
- *50(.00) is used as an initial burette reading*
- *more than one final burette reading is 50.(00)*

any burette reading is greater than 50.(00)

IV: at least two titres within 0.10 cm^3

[7]

From your accurate titration results, obtain a suitable value for the volume of **diluted FA 4** to be used in your calculations.

Show clearly how you obtained this value.

Candidate calculates the mean correctly.
- Candidate must take the average of two (or more) titres within 0.10 cm^3.
- Working / explanation ***or*** ticks must be shown
- The mean should be quoted to **2 d.p**, and be rounded to nearest 0.01 cm^3.

(e.g. 26.667 cm^3 must be rounded to 26.67 cm^3)

The iodine produced required .... cm^3 of **diluted FA 4**.
[1]

(b) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of sodium thiosulfate, $Na_2S_2O_3$, in the volume of **diluted FA 4** obtained in **(a)**.

No of moles of thiosulfate used = 1.50 × $\frac{25.0}{250}$ × mean titre / 1000

Or No of moles of thiosulfate used = 0. 150 × mean titre / 1000
(expressed to 3 or 4 sig fig)

moles of $Na_2S_2O_3$ = ... mol
[1]

(ii) Balance the ionic equation for the reaction of iodine with sodium thiosulfate. State symbols are not required.

$$\ldots\ldots\; I_2 \;+\; \ldots\ldots\; S_2O_3^{2-} \;\rightarrow\; \ldots\ldots\; S_4O_6^{2-} \;+\; \ldots\ldots\; I^-$$

Hence calculate the number of moles of iodine that reacted with the number of moles of $Na_2S_2O_3$ calculated in **(i)**.

Equation balanced $I_2 + \mathbf{2}\, S_2O_3^{2-} \rightarrow S_4O_6^{2-} + \mathbf{2}I^-$
no of moles of I_2 = 0.5 × ans. in (i)

moles of I_2 = ... mol
[1]

(iii) Using your answer to **(ii)**, calculate the number of moles of copper(II) ions in 25.0 cm^3 of **FA 1**.

No of moles of copper(II) ions = 2 × answer (ii)
(expressed to 3 or 4 sig fig)

moles of Cu^{2+} ions = ... mol
[1]

(iv) Using your answer to **(iii)** and the information on page 2, calculate the average relative formula mass of the copper salts in **FA 1**.

Average Mr = [26.0 / ans (iii)] × 25 / 1000

Average Mr of copper salts = ...

[1]

(v) Write the full electronic configuration of $_{29}Cu$ in CuI.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(vi) Hence, explain why solid CuI appears white in colour.

- d subshell is fully filled, no vacant / half-filled d orbitals
- electrons cannot be promoted from lower energy d orbitals to higher energy d orbitals / d-d transition not possible
- No wavelength of visible spectrum is absorbed, hence solid appears white

[1]

[Total: 14]

2 Qualitative analysis

In this question, you will deduce the two anions present in **FA 1.** Perform the tests described in **Table 2** and record your observations in the table. Test and identify any gases evolved.

If any solution is warmed, a boiling tube MUST be used.

Table 2

	Test	Observations
(a)	To a 1 cm depth of **FA 1** in a test-tube, add aqueous silver nitrate.	Solution remained blue / no ppt
(b)	To a 0.5 cm depth of **FA 1** in a boiling tube, add aqueous sodium hydroxide and add one piece of aluminium foil and warm.	Blue ppt formed, insoluble in excess sodium hydroxide Black ppt formed upon heating Colourless, pungent gas / **gas evolved turns (damp red) litmus blue**
(c)	To a 1 cm depth of **FA 1** in a test-tube, add aqueous barium chloride followed by nitric acid.	White ppt formed **and** insoluble in excess nitric acid
(d)	To a 1 cm depth of **FA 1** in a test-tube, add an equal volume of sulfuric acid followed by $KMnO_4$.	**FA 1** remained blue. Purple $KMnO_4$ remained/ not decolourised

[3]

(e) From your observations, state the anions present in **FA 1**. Explain your answers.

Nitrate NO_3^- + Sulfate SO_4^{2-}
Explanation for NO_3^-

Both Nitrate or Nitrite is reduced by Al foil in NaOH(aq) to give NH_3 gas +
Since $KMnO_4$ remained purple, **FA 1** does not contain reducing agent NO_2^-.

Or
Since no brown NO_2 gas is evolved with nitric acid, **FA 1** contains Nitrate NO_3^-

Explanation for SO_4^{2-}
Since a white ppt is formed with $BaCl_2$, **and** remained in nitric acid, anion in FA1 cannot be SO_3^{2-}.
Since Since $KMnO_4$ remained purple, **FA 1** does not contain reducing agent SO_3^{2-}.

[3]

[Total: 6]

3 Investigation of thermal decomposition of sodium hydrogencarbonate

Sodium hydrogencarbonate, $NaHCO_3$, is used as baking soda in cooking. Baking soda may also contain small amounts of other chemicals.

When baking soda is heated, carbon dioxide is produced. In this experiment, you will investigate the reaction taking place when the sodium hydrogencarbonate in baking soda is thermally decomposed.

FA 5 is baking soda (impure $NaHCO_3$).

(a) Method

Record all your readings in the space below.

1. Weigh the crucible with its lid.
2. Transfer all the **FA 5** from the container into the crucible.
3. Weigh the crucible, lid and **FA 5**.
4. Calculate and record the mass of **FA 5** used.
5. Place the crucible and contents on a pipe-clay triangle.
6. Heat gently, **with the lid off**, for approximately one minute.
7. Heat strongly, **with the lid off**, for a further three minutes.
8. Replace the lid and leave the crucible to cool for about ten minutes.

While the crucible is cooling, you should work on other questions.

9. When it has cooled down, weigh the crucible with its lid and contents.
10. Heat strongly, **with the lid off**, for a further two minutes.
11. Replace the lid and leave the crucible to cool for ten minutes.
12. When it has cooled down, weigh the crucible with its lid and contents.
13. Calculate and record the mass of residue obtained.
14. This residue is **FA 6**. Keep this for use in **3(d)**.

Results

Four weighings recorded and correct headings given **and**
mass of **FA 5** used **and**
mass of residue recorded

Mass	/g
Crucible + lid	a
Crucible + lid + **FA 5** before heating	b
Crucible + lid + content after 1st heating	c
Crucible + lid + content after 2nd heating	d
FA 5 used	b-a = e
Residue OR **FA 6**	d-a = f

I	
II	
III	
IV	

If 'mass' not written then 'g' must be with each entry.

Use of lid must be consistent

II

- All weighings recorded to 3 decimal places
- Mass of **FA 5** and **FA 6** / residue must be correctly subtracted

[4]

(b) **Calculations**

(i) Given that the percentage purity by mass of **FA 5** is 95.8%, calculate the mass of sodium hydrogencarbonate in the sample of **FA 5** that you weighed out.

Mass $NaHCO_3$ = (95.8 / 100) × mass of **FA 5** used

mass of $NaHCO_3$ in **FA 5** weighed out = ... g

(ii) Calculate the mass of impurity present in your sample of **FA 5**.

Mass impurity = mass of **FA 5** – answer **(i)**
or mass impurity = 4.2/ 100 x mass **FA 5**

mass of impurity = ... g
[1]

(iii) The impurity in **FA 5** does not decompose when it is heated.

This means that the residue, **FA 6**, contains the mass of impurity calculated in **(ii)** together with the solid decomposition product of sodium hydrogencarbonate.

Calculate the mass of the solid decomposition product.

Mass of decomposition solid
= mass of residue (**FA 6)** from table – mass of impurity **(ii) and**
expressed to 3 d.p / 3 s.f

or mass of decomposition solid = mass of $NaHCO_3$ – mass **lost** on heating
[**(i)** – (mass **FA 5** – mass **FA 6**)]

mass of solid decomposition product = ... g
[1]

(c) Why was the lid put on while the crucible and its contents were cooled?

Lid reduces / stops absorption of water (vapour) by solid / residue / **FA 5** while cooling/ prevents reaction with carbon dioxide.

Do not accept: falling impurities/ loss of solid due to wind/oxidation in the air. [1]

(d) **(i)** Ah Beng carried out the experiment by heating 84.0 g of pure $NaHCO_3$ to constant mass, he obtained 53.0 g of the solid decomposition product.

Ah Hock then suggested the following equation for the thermal decomposition of sodium hydrogencarbonate.

$$NaHCO_3(s) \rightarrow NaOH(s) + CO_2(g)$$

Explain why Ah Hock's suggestion is **incorrect**. Show working in order to explain your answer.

[A_r: C; 12.0; Na; 23.0; H, 1.0; O: 16.0]

If Ah Hock is **correct**., (84 g) $NaHCO_3$ would give **40** g residue / NaOH
or
mole ratio of $NaHCO_3$: NaOH is 1:**1.3** (so not 1:1)
or
Answers could refer to mass lost / moles of CO_2

(ii) Add 1 cm depth of sulfuric acid into a test-tube.
Add some **FA 6** from the crucible to the acid in the test-tube.
Record all your observations.
Use your observations to identify the anion present in **FA 6**.

Any observation below + gas forms white ppt in limewater

Do NOT accept milky / chalky / cloudy

- fizzing / effervescence / bubbling
- solid dissolves / colourless solution **formed**

FA 6 contains carbonate ion / CO_3^{2-}

[2]

(iii) State the assumption you have made in **(ii)**.

Complete decomposition of $NaHCO_3$.
OR
There is no leftover $NaHCO_3$.

[1]

(iv) Steam is one of **three** products obtained when sodium hydrogencarbonate is thermally decomposed.

Use your answer in **(ii)** to complete and balance the equation for the thermal decomposition of sodium hydrogencarbonate. Include state symbols.

2$NaHCO_3(s) \rightarrow H_2O(g) + CO_2(g) + $ **$Na_2CO_3(s)$**

[1]

(v) State whether the balanced equation in **(iv)** agrees with Ah Beng's results.

Show working in order to explain your answer.

(From equation) 84.0 g $NaHCO_3$ should give 0.5 × 106 g residue (= 53.0 g)
And this agrees with Ah Beng's 53.0 g

[1]

[Total: 13]

4 Determination of the enthalpy change of a reaction, ΔH_r

FA 7 is 1.00 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$
FA 8 is 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 9 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in Tables 4.1 and 4.2.

Experiment A

Reaction between **FA 7**, $NaHCO_3$, and **FA 8**, NaOH.

Reaction 1 $NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ $\Delta H_{reaction1}$

The molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

1 Using a measuring cylinder, transfer 30.0 cm^3 of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker. Place the lid on the cup.

2 Stir and measure the temperature of this **FA 7**, T_{FA7}.

3 Using another measuring cylinder, measure 20.0 cm^3 of **FA 8.**

4 Stir and measure the temperature of this **FA 8**, T_{FA8}.

5 Add **FA 8** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.

6 Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max}.

7 Calculate the weighted average initial temperature, $T_{average}$, of **FA 7** and **FA 8** using the formula given below:

$$T_{average} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA8} \times T_{FA8})}{(V_{FA7} + V_{FA8})}$$

	Experiment A
T_{FA7} /°C	
T_{FA8} /°C	
$T_{average}$ /°C	
T_{max} /°C	
ΔT_{max} /°C	

Table 4.1

Experiment B

Reaction between **FA 7**, $NaHCO_3$, and **FA 9,** H_2SO_4.

Reaction 2 $NaHCO_3(aq) + \frac{1}{2}H_2SO_4(aq) \rightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l) + CO_2\,(g)$ $\Delta H_{reaction2}$

The molar enthalpy change for **reaction 2**, $\Delta H_{reaction\ 2}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

1 Using a measuring cylinder, transfer 30.0 cm^3 of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker. Place the lid on the cup.

2 Stir and measure the temperature of this **FA 7**, T_{FA7}.

3 Using another measuring cylinder, measure 20.0 cm^3 of **FA 9.**

4 Stir and measure the temperature of this **FA 9**, T_{FA9}.

5 Add **slowly**, the **FA 9** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.

6 Using the thermometer, stir the mixture continuously until a maximum/minimum temperature is reached. Read and record this temperature T_{max}.

7 Calculate the weighted average initial temperature, $T_{average}$, of **FA 7** and **FA 9** using the formula given below:

$$T_{average} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA9} \times T_{FA9})}{(V_{FA7} + V_{FA9})}$$

	Experiment B
T_{FA7} /°C	
T_{FA9} /°C	
$T_{average}$ /°C	
T_{max} /°C	
ΔT_{max} /°C	

Table 4.2

[2]

All temperature readings are recorded to the nearest 0.1 °C.
(for both Tables 4.1 & 4.2)
$\Delta T_{max/min}$ must be correctly calculated i.e. T_{max} – average initial temperature.
(for both Tables 4.1 & 4.2)

(a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm^{-3} and specific heat capacity, c, of 4.18 J g^{-1} K^{-1}.

(i) Use your results from **Table 4.1** to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{reaction1}$.

q = (20.0 + 30.0)(1.00) x 4.18 x ΔT_{max}

n($NaHCO_3$) = 1.00 x 30.0/1000 = 0.03 mol

$\Delta H_{reaction1}$ = – q / n($NaHCO_3$) (this reaction is exothermic)

$\Delta H_{reaction1}$ = ...

[2]

(ii) Use your results from **Table 4.2** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{reaction2}$.

q = (20.0 + 30.0)(1.00) x 4.18 x ΔT_{min}

n($NaHCO_3$) = 1.00 x 30.0/1000 = 0.03 mol

$\Delta H_{reaction1}$ = + q / n($NaHCO_3$) (this reaction is endothermic)

$\Delta H_{reaction2}$ = ...

[2]

(b) Ionic equations for neutralisation, **reaction 1**, and **reaction 2** are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	$\Delta H_{neu} = -57.1$ kJ mol^{-1}
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{reaction1}$
$HCO_3^-(aq) + H^+(aq) \rightarrow H_2O(l) + CO_2(g)$	$\Delta H_{reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3 $CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \longrightarrow 2HCO_3^-(aq)$ $\Delta H_{reaction3}$

Using your calculated answers in **(a),** together with the given value of enthalpy change of neutralisation, ΔH_{neu}, construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{reaction3}$.

$$\begin{tikzcd}
CO_2 + 2H_2O + CO_3^{2-} \arrow[r, "\Delta H_{r3}"] & 2HCO_3^- + H_2O \\
HCO_3^- + H^+ + CO_3^{2-} + H_2O \arrow[u, "\Delta H_{r2}"] & 2HCO_3^- + H^+ + OH^- \arrow[l, "\Delta H_{r1}"] \arrow[u, "\Delta H_n"']
\end{tikzcd}$$

$\Delta H_{\text{reaction3}}$ = (– **(a)(ii)**) + (– **(a)(i)**) + (–57.1)

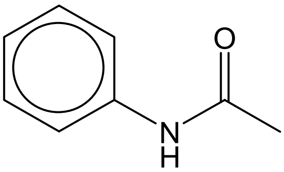
$\Delta H_{\text{reaction3}}$ = ……………………

[3]

[Total: 9]

5 **Planning**

The structure of *N*-phenylethanamide is shown below:



N-phenylethanamide, $C_6H_5NHCOCH_3$

The preparation of *N*-phenylethanamide from phenylamine is termed acylation. Ethanoic anhydride, $(CH_3CO)_2O$ is commonly used as an acylating agent as its low reactivity relative to ethanoyl chloride allows the reaction rate to be more easily controlled.

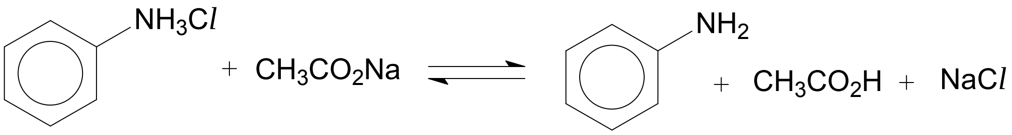
Phenylamine is most conveniently used in the form of the salt phenylammonium chloride, $C_6H_5NH_3Cl$.

The reaction is performed in **two** stages:

Stage **1:**

Phenylamine can be prepared from phenylammonium chloride and sodium ethanoate in an aqueous medium under room temperature.

The reaction is as shown below:



phenylammonium chloride phenylamine

The reaction mixture needs to be continuously stirred for 3 minutes.

Stage **2:**

Phenylamine then reacts with ethanoic anhydride to form solid *N*-phenylethanamide together with ethanoic acid. The addition of ethanoic anhydride to the reaction mixture may be violent.

This mixture is heated under reflux for about 15 minutes, before the crude solid product is removed by filtration and purified by recrystallisation from hot water. The melting point of *N*-phenylethanamide is 114 ^{0}C.

(a) **(i)** State the type of reaction taking place in stage **1**.

Acid base reaction/ neutralisation

[1]

(ii) Write an equation for the reaction of phenylamine with ethanoic anhydride in stage **2.**

$C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3CO_2H$.

[1]

(b) The above reaction between phenylamine and ethanoic anhydride in stage **2** gives an 80% yield.

Assuming phenylammonium chloride is completely converted to phenylamine in stage **1**, determine the mass of phenylammonium chloride required to prepare 2 g of *N*-phenylethanamide.
(A_r: C: 12.0, H: 1.0, N: 14.0, O: 16.0, C*l*: 35.5)

Amount of *N*-phenylethanamide = 2/ 135= 0.01481 mol

Amount of phenylamine = 0.01481 mol

Mass of phenylammonium chloride
= 0.01481 x (72 + 8 + 14 + 35.5) x 100/80
= 2.398 g

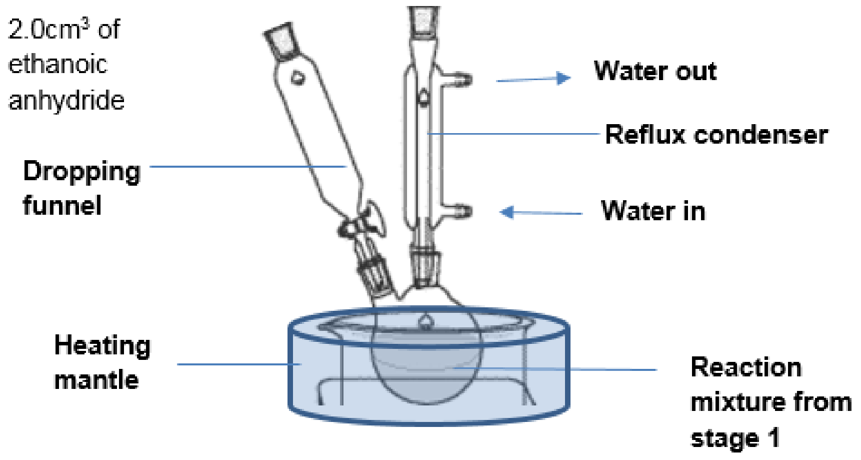
[2]

(c) Write a full description of the procedure to carry out stages **1** and **2**.
You do not need to describe the recrystallization process to obtain a pure sample of N-phenylethanamide *in stage **2**.*

You may assume that you are provided with :

- 30 cm^3 of water for use as solvent
- 6.0 g of hydrated sodium ethanoate
- 2.0 cm^3 of ethanoic anhydride
- Apparatus normally found in a school or college laboratory

Your plan should include details of:
(i) appropriate quantities of reactants
(ii) appropriate choice of apparatus
(iii) drawing of reflux set-up



1. **Weight out** accurately about **2.40 g** of phenylammonium chloride in a clean and dry weighing bottle.
2. **Measure 30 cm^3 of water** using a 100 cm^3 measuring cylinder.
3. **Dissolve/Add** this completely in 30 cm^3 of water in a clean and dry 250 cm^3 round bottom flask.
4. Weigh out **6.0 g** of hydrated sodium ethanoate in a weighing bottle.
5. Add sodium ethanoate to the solution in (3) and **stir the mixture for three minutes** using a magnetic stirrer.
6. Measure **2.0 cm^3 of ethanoic anhydride** using a 10 cm^3 measuring cylinder.
7. Introduce **2.0 cm^3** of ethanoic anhydride slowly using a **dropping funnel/dropwise using dropper /(using ice bath for the reaction)** and connect the reaction mixture to the reflux condenser as shown in the set up below inside a fumehood.
8. Carry out the **reflux for 15minutes**.
9. **Filter off** the crude product and wash it with a little cold water

(d) Suggest a method to check the purity of *N*-phenylethanamide obtained.

Determine the melting point and verify it against literature data/ value of 114 ^{o}C.
If the melting point is within $\underline{+}$ 2 ^{o}C of literature data/ 114 ^{o}C, it is pure

[Total: 10]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

Paper 1 Multiple Choice

24 September 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and tutor's name on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages and **0** blank page.

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

1 Which of the following contains the smallest number of stated atoms at r.t.p.?

A oxygen atoms in 48 dm^3 of NO_2

B sulfur atoms in 48 dm^3 of SO_2

C carbon atoms in 44 g of CO_2

D nitrogen atoms in 44 g of N_2O

2 An isolated gaseous species has paired electrons in at least one of its 3d orbitals and a fully filled 4s subshell.

What could be the identity of the species?

A Cu **B** Fe^{3+} **C** Ni^{2+} **D** Sr^{2+}

3 Which one of the following species is **not** planar?

A BrF_3

B ICl_4^-

C PCl_4^+

D XeF_4

4 Hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2, are both used as rocket propellants because they can produce large volumes of hot gases from a small volume of liquid.

Which of the following statements about these two compounds is correct?

1 The bond angle in N_2H_4 is larger than that in H_2O_2.

2 The N–H bond is shorter than the O–H bond.

3 Hydrazine forms stronger intermolecular hydrogen bonds than hydrogen peroxide.

4 There are σ bonds formed by sp^3 – s orbital overlap in both molecules.

A 1 and 4

B 2 and 3

C 1, 2 and 4

D 1, 3 and 4

5 Which factor is the most significant in explaining the non-ideal behaviour of the gases present in the reaction chamber in the Haber process?

A strong bonds between the atoms in the molecule

B the presence of a catalyst

C the high temperature of 450 °C

D the high pressure of 150 atm

6 A student mixed 25.0 cm^3 of 3.00 mol dm^{-3} hydrochloric acid with an equal volume of 6.00 mol dm^{-3} sodium hydroxide. The initial temperature of both solutions was 15.0 °C. The maximum temperature recorded was 24.5 °C. It was found that 15% of the heat produced during the experiment was lost to the surrounding.

Using these results, what is the enthalpy change of neutralisation?

A –15.6 kJ mol^{-1}

B –22.5 kJ mol^{-1}

C –31.1 kJ mol^{-1}

D –57.3 kJ mol^{-1}

7 A student calculated the lattice energy for calcium oxide using the data in the table below, and relevant data from the *Data Booklet*.

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of calcium	+178
first electron affinity for oxygen	–141
second electron affinity for oxygen	+798
standard enthalpy change of formation of calcium oxide	–635

However, the value calculated by the student for the lattice energy was **more** exothermic than the correct value.

Which error could have been made in the calculation?

A omitting the second electron affinity for oxygen

B omitting the standard enthalpy change of formation of calcium oxide

C using the 1st and 2nd ionisation energies of magnesium instead of calcium

D using the standard enthalpy change of combustion of calcium rather than the standard enthalpy change of formation of calcium oxide

8 A student investigates the kinetics of the following reaction by using a spectrometer. The spectrometer is able to measure the concentration of iodine by measuring the absorbance of the solution.

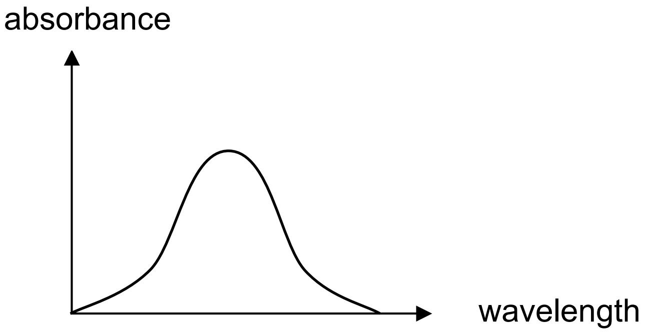
$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The time taken for the absorbance of the reaction mixture to reach a fixed value is measured over a range of hydrogen peroxide concentrations.

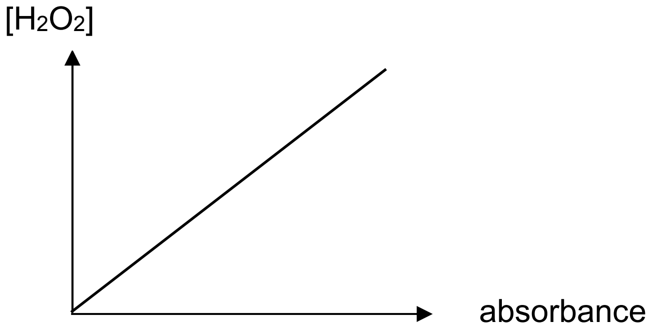
Based on the data obtained, the student correctly drew a graph to prove that order of reaction is one with respect to H_2O_2.

Which graph did the student draw?

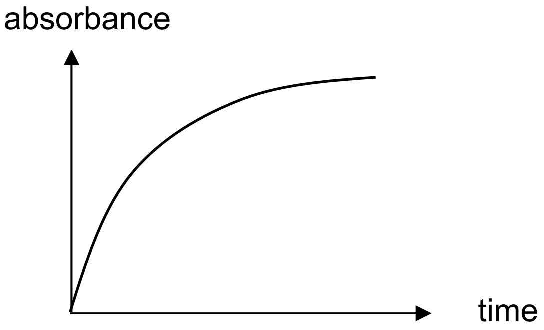
A



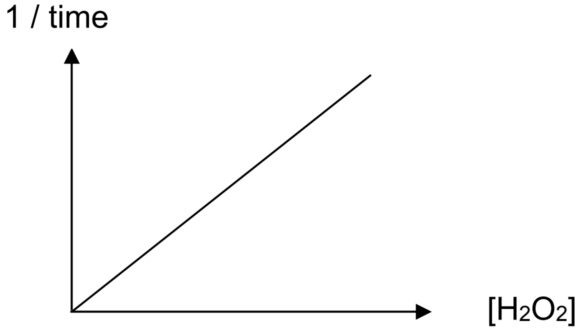
B



C



D



9 The decomposition of hydrogen peroxide follows first order kinetics. A certain solution of hydrogen peroxide undergoes complete decomposition to liberate 96 cm^3 of oxygen gas. It is found that at 25 °C, 48 cm^3 of oxygen was collected in 35 min.

How long will it take for 80 cm^3 of the gas to be produced?

A 87.5 min

B 90.5 min

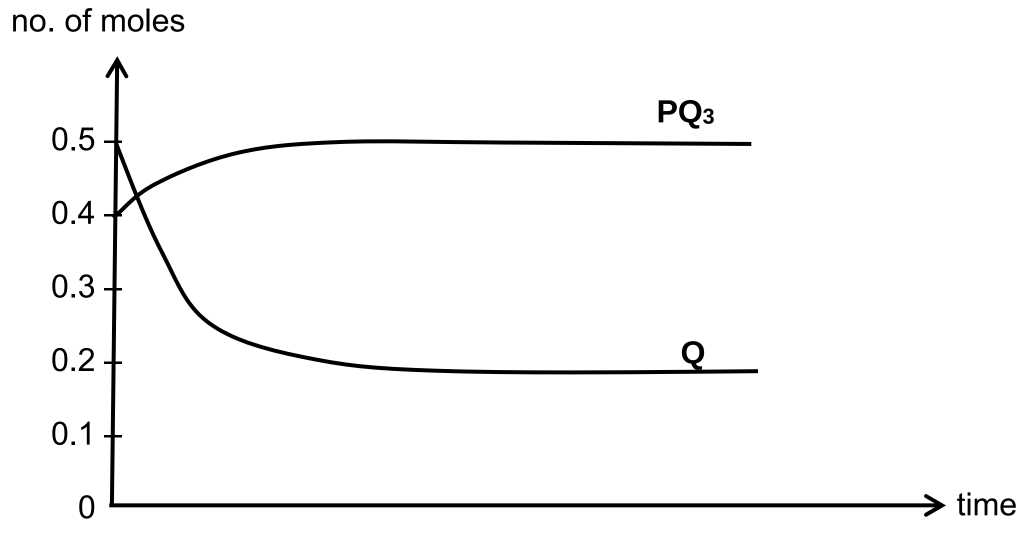
C 97.5 min

D 105 min

10 The system containing P, Q and PQ_3 is allowed to reach equilibrium in a 5 dm^3 vessel at a temperature of 1000 K.

$$P(g) + 3Q(g) \quad PQ_3(g)$$

The diagram below shows the change in number of moles of PQ_3 and Q with time. The initial number of moles of P was 0.2.



What is the equilibrium constant K_c for the reaction?

A $\frac{0.5}{0.1\times(0.2)^3}$ **B** $\frac{0.5}{0.2\times(0.2)^3}$ **C** $\frac{0.5\times5^3}{0.1\times(0.2)^3}$ **D** $\frac{0.5\times5^3}{0.2\times(0.2)^3}$

11 Which statement is correct about a reaction for which the equilibrium constant is independent of temperature?

1 The rate constants for the forward and reverse reactions are both independent of temperature.

2 Temperature has no effect on the position of equilibrium.

3 The forward and reverse reactions have equal activation energies.

4 The entropy change is zero.

A 1 and 2

B 2 and 3

C 3 and 4

D 2, 3 and 4

12 The two simplest carboxylic acids are formic acid and acetic acid. Formic acid is present in the venom of ant and bee stings while acetic acid is the major characterising component of vinegar. The pK_a values of the two acids is given in the table below.

Acid	**Formula**	**pK_a**
Formic acid	HCOOH	3.74
Acetic acid	CH_3COOH	4.76

Which solution has the lowest pH?

A 100 cm^3 of 0.10 mol dm^{-3} acetic acid

B 100 cm^3 of 0.10 mol dm^{-3} sodium acetate

C 100 cm^3 of 1.0 mol dm^{-3} formic acid and 50 cm^3 of 1.0 mol dm^{-3} aqueous sodium hydroxide

D 100 cm^3 of 1.0 mol dm^{-3} formic acid and 75 cm^3 of 1.0 mol dm^{-3} aqueous sodium hydroxide

13 Deuterium oxide, D_2O consists of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium ${}^{2}_{1}D$. It is known as 'heavy water' and is used for research into chemical reactions.

Like H_2O, pure D_2O is weakly ionised.

$$2D_2O \quad D_3O^+ + OD^-$$

For D_2O, we use the terms K_D instead of K_w and pD instead of pH.
At 25 °C, $pK_D = 14.8$

Which statements about D_2O at 25 °C is correct?

1 pD of D_2O is 7.4
2 D_2O is not a neutral liquid.
3 D_2O dissociates to a smaller extent than H_2O.

A 1 only
B 3 only
C 1 and 3
D 2 and 3

14 **W**, **X**, **Y** and **Z** are four consecutive elements in Period 3 but not necessarily in the order presented.

- Chloride of **W** dissolves in water and turns blue litmus red.
- **X** is a good conductor of electricity but is insoluble in water.
- Oxide of **Y** has the highest melting point.
- **Z** has the highest first ionisation energy and largest ionic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

A **X, Y, Z, W**
B **X, Y, W, Z**
C **Y, X, W, Z**
D **Y, X, Z, W**

15 **M** is a Group 2 metal. The carbonate of **M** decomposes when heated in a Bunsen flame to give carbon dioxide and a white solid residue as the only products. This white solid residue is sparingly soluble in water. Even when large amounts of the solid residue are added to water the pH of the saturated solution is less than that of limewater.

What could be the identity of **M**?

A magnesium

B calcium

C strontium

D barium

16 A white powder is a mixture of sodium chloride and sodium iodide. It is dissolved in water in a test-tube. Excess aqueous silver nitrate is added to the test-tube. A precipitate, X, is observed.

Excess concentrated ammonia is then added to the test-tube containing X. After the test-tube has been shaken, a precipitate, Y, is observed.

Which statement about X or Y is correct?

A X is a pure white colour.

B X is pure silver iodide.

C Y is pure silver chloride.

D Y is yellow.

17 Which of the following statements is correct?

1 Enthalpy change of vaporisation of halogens increases down the group.

2 Bond energy of hydrogen halides increases down the group.

3 Oxidising power of halogens increases down the group.

4 Thermal stability of hydrogen halides increases down the group.

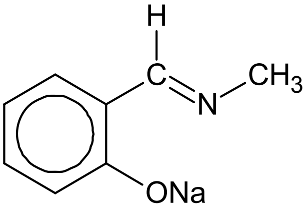
A 1 only

B 1 and 3

C 2 and 4

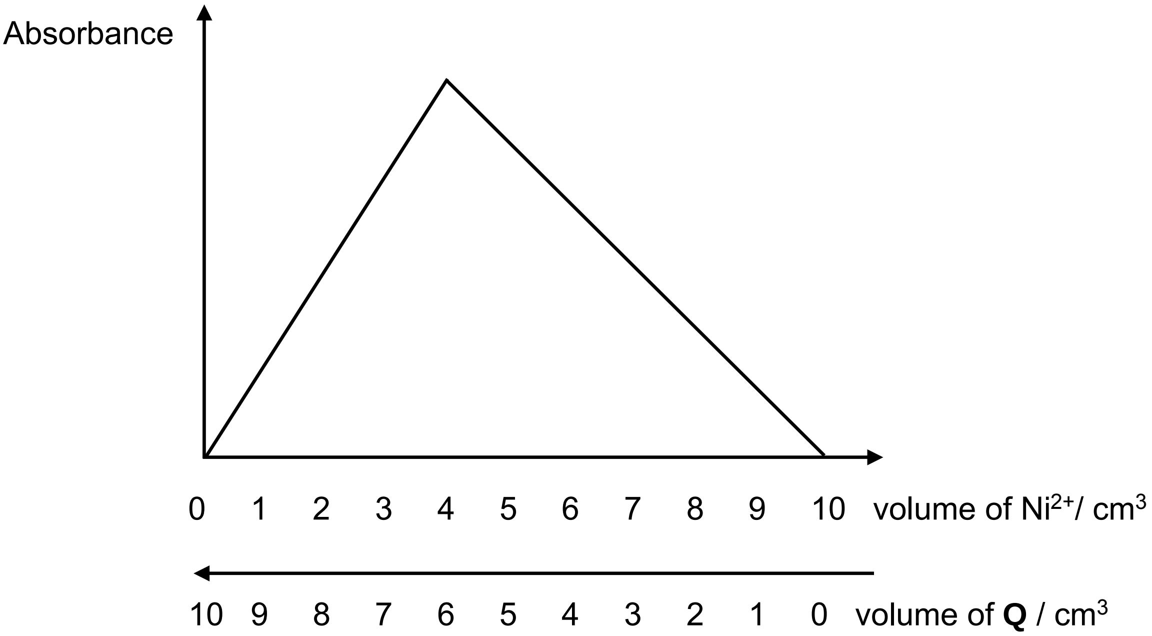
D 3 and 4

18 The complex of nickel with ligand **Q** (shown below) is thermochromic, being coloured red at room temperature but changing to yellow-green when heated to 170 °C.



Q

The following graph was obtained when the colour intensities of mixtures of a 4.0 × 10^{-3} mol dm^{-3} solution of **Q** and a 3.0 × 10^{-3} mol dm^{-3} solution of nickel(II) chloride were measured using a colorimeter at room temperature.



Which of the following statements is correct for the nickel(II) complex ion?

A The complex ion absorbs red light at room temperature.

B The co-ordination number of nickel(II) complex is 4.

C The overall charge of the nickel(II) complex is 2+.

D The shape of the nickel(II) complex ion is linear.

[Turn over

19 If a molecule contains two non-identical chiral carbon atoms, four optical isomers exist.

How many isomers are there with

- molecular formula $C_7H_{14}O$ **and**
- a five-membered ring **and**
- a tertiary alcohol group?

A 7 **B** 8 **C** 9 **D** 10

20 Which of the following trends are **incorrect**?

1 The boiling points of alcohols with the same molecular formula increases from primary to secondary to tertiary.

2 The pH values of the aqueous solutions increases from CH_3CH_2COCl to CH_3CH_2COOH to $CH_3CH_2CONH_2$ to $CH_3CHClCH_2NH_2$.

3 The ease of hydrolysis of the chlorine atoms decreases from chlorobenzene to chloroethane to ethanoyl chloride.

4 The pK_b values increases from ethanoate ion to phenoxide ion to ethoxide ion.

A 2 only

B 1 and 3 only

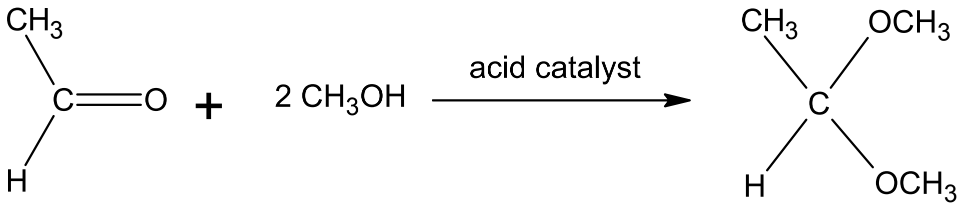
C 2 and 4 only

D 1, 3 and 4 only

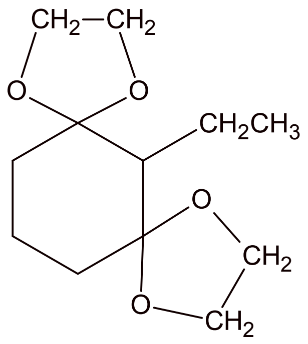
21 Alkenes undergo catalytic oxidation to produce aldehydes and ketones, for example

$$H_2C{=}CH_2 + 1/2\ O_2 \xrightarrow{\text{catalyst}} CH_3CHO$$

Acetals (molecules that contain 2 –OR groups bonded to the same carbon) can be formed from aldehydes and ketones in an acid catalysed process, for example

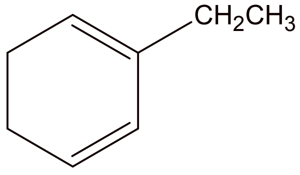


Compound **W** undergoes catalytic oxidation, followed by an acid catalysed reaction with $HOCH_2CH_2OH$ to produce the following as the only product.

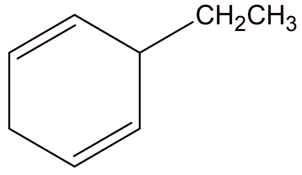


Which of the following best represents the structure of compound **W**?

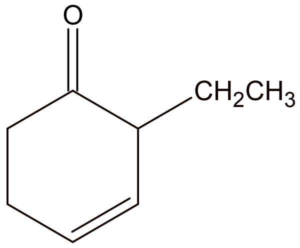
A



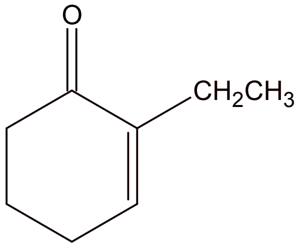
B



C



D



22 The molecular formula of compound **X** is $C_5H_{12}O$.

Compound **X**:
- reacts with alkaline aqueous iodine
- can be dehydrated to form two alkenes only.

What could be the identity of compound **X**?

A $CH_3CH_2CH(CH_3)CH_2OH$

B $(CH_3)_2C(OH)CH_2CH_3$

C $(CH_3)_2CHCH(OH)CH_3$

D $CH_3CH_2CH_2CH(OH)CH_3$

23 $H_2NNHC_6H_3(NO_2)_2$ is the structural formula of 2,4-DNPH.

Many but not all, organic reactions need to be heated before reaction occurs.

Which reaction cannot occur at a good rate at room temperature (20 °C)?

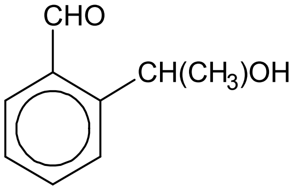
A $CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$

B $CH_3CH_2OH + KBr \rightarrow CH_3CH_2Br + KOH$

C $CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

D $(CH_3)_2CO + H_2NNHC_6H_3(NO_2)_2 \rightarrow (CH_3)_2C{=}NNHC_6H_3(NO_2)_2 + H_2O$

24 Compound **X** is heated under reflux with an excess of acidified $K_2Cr_2O_7$ to form compound **Y**.



compound **X**

Both **X** and **Y** are separately warmed with Fehling's solution and the observations noted.

What are the observations?

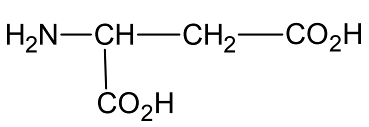
A Both **X** and **Y** give a red precipitate.

B Only **X** gives a red precipitate.

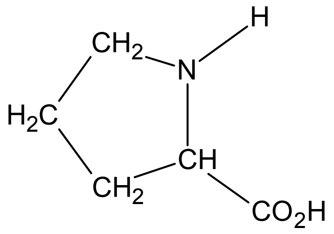
C Only **Y** gives a red precipitate.

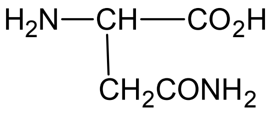
D Neither **X** nor **Y** gives a red precipitate.

25 The following are structures of 3 amino acids.



$H_2N-\underset{\displaystyle CO_2H}{\underset{|}{CH}}-CH_2-CO_2H$

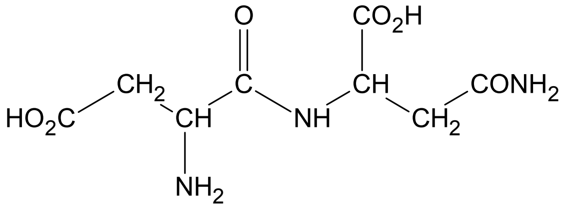




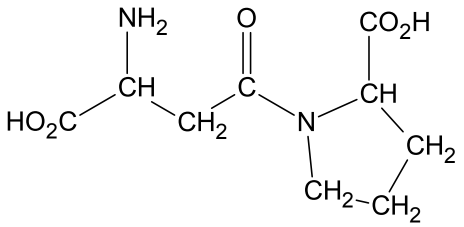
$H_2N-\underset{\displaystyle CH_2CONH_2}{\underset{|}{CH}}-CO_2H$

Which of the following represents dipeptides formed from these amino acids?

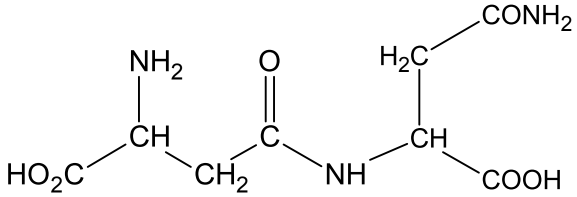
1



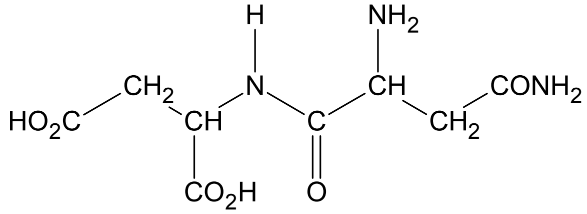
2



3



4



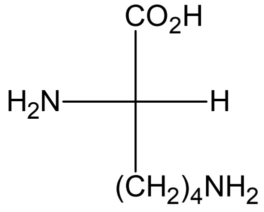
A 1 only

B 1 and 4 only

C 3 and 4 only

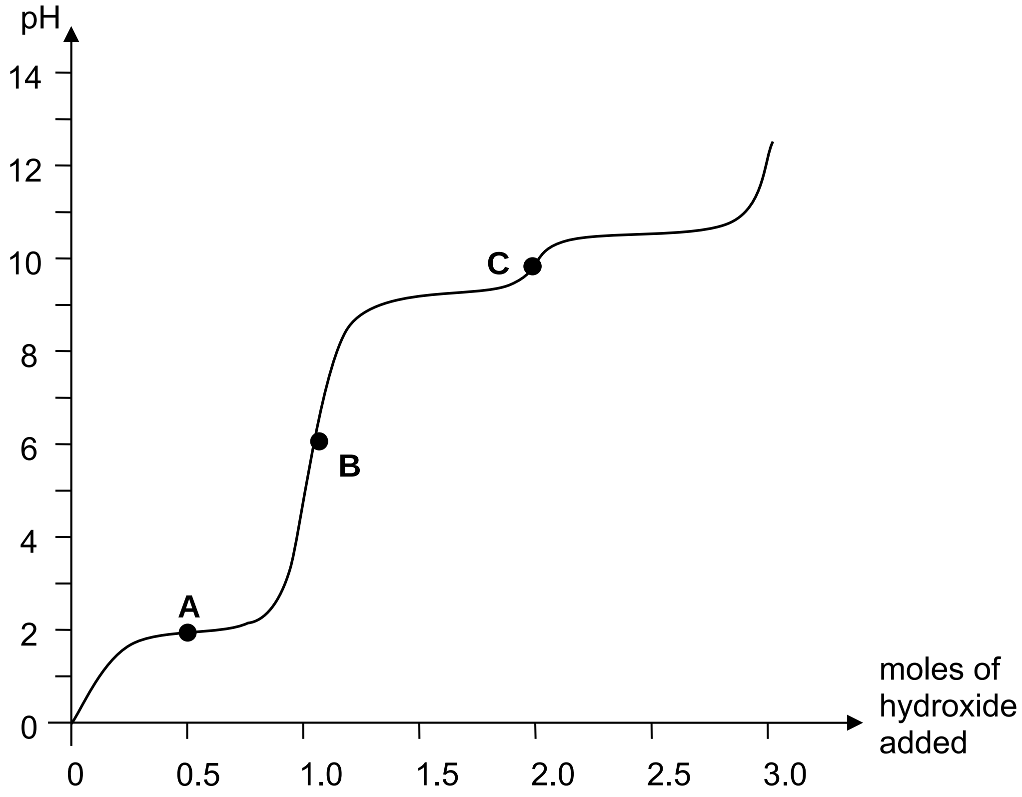
D All are correct

26 Lysine is an essential amino acid found in the body. It has three pK_a values associated with it: 2.2, 9.0 and 10.5



lysine

When one mole of protonated lysine was titrated against hydroxide ions, the following pH curve is obtained:



Which of the following statements are true with respect to the curve above?

1 The α-amino group has a pK_a value of 10.5.

2 Equal amounts of $H_3N^+CH(CO_2H)(CH_2)_4NH_3^+$ and $H_3N^+CH(CO_2H)(CH_2)_4NH_2$ are present at point **A**.

3 The major species present at point **C** has no net charge.

4 The major species present at point **B** will migrate towards the cathode of an electrolytic cell.

A 1 and 3 only

B 2 and 4 only

C 3 and 4 only

D All are correct

27 A carboxylic acid, **P**, has no possible chain isomers. It reacts with an alcohol, **Q**, that has only one other positional isomer.

What could be the ester formed from a reaction between **P** and **Q**?

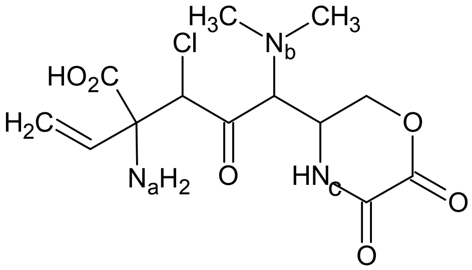
A butyl propanoate

B ethyl butanoate

C pentyl ethanoate

D propyl pentanoate

28 Which of the following statements about compound **W** is correct?



compound **W**

A In the gaseous phase, N_b is a stronger Lewis base than N_a but in the aqueous phase, N_b is a weaker Bronsted-Lowry base than N_a.

B When 96 dm^3 of H_2 gas was reacted with one mole of compound **W**, followed by excess sodium metal, at room conditions, the gas volume expanded by 48 dm^3.

C The reduction of **W** by $LiAlH_4$ will cause the oxidation state of any carbon involved in the reduction to decrease from +3 to −1.

D **W** will require 3 moles of NaOH(aq) for complete reaction if the reaction is to take place with heating.

29 Which of the following changes represent an oxidation process?

A CO_2 to $C_2O_4^{2-}$

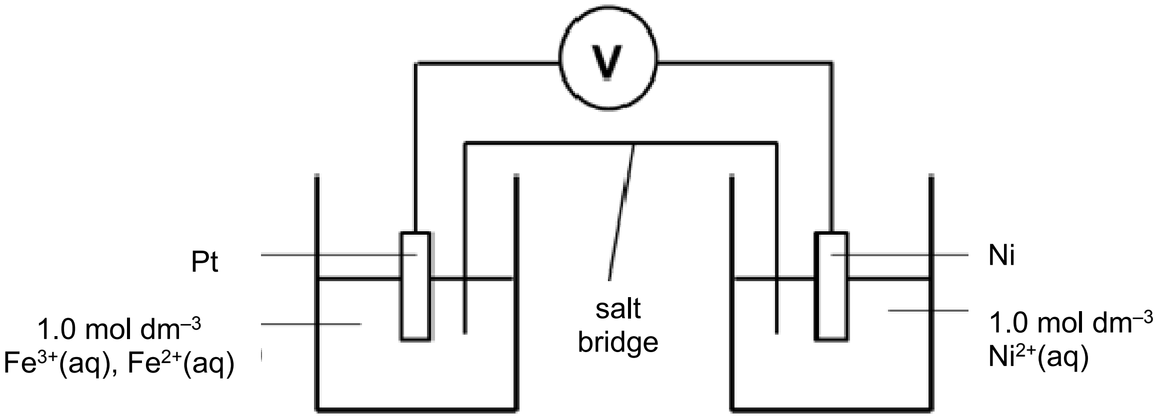
B CrO_4^{2-} to $Cr_2O_7^{2-}$

C Br_2 to BrF_3

D Cl_2 to ICl_3

30 *The use of Data booklet is relevant to this question.*

A Fe^{3+}/Fe^{2+} half-cell was connected to a Ni^{2+}/Ni half-cell as shown in the diagram below under standard conditions.



Which of the following statements is correct?

1 The solution in the Fe^{3+}/Fe^{2+} half-cell turns red-brown.

2 The cathode increases in size.

3 The electron flows from Fe^{3+}/Fe^{2+} half-cell to the Ni^{2+}/Ni half-cell.

4 The standard cell potential is +1.02 V.

A 4 only

B 1 and 3

C 2 and 3

D 1, 3 and 4

Nanyang JC J2 Preliminary Exam 2018
H2 Chemistry 9729/01
Paper 1 MCQ Answers and Comments

Qn	Ans	Qn	Ans	Qn	Ans	Qn	Ans	Qn	Ans	Qn	Ans
1	**C**	6	**C**	11	**B**	16	**D**	21	**D**	26	**C**
2	**D**	7	**C**	12	**A**	17	**A**	22	**C**	27	**A**
3	**C**	8	**D**	13	**C**	18	**B**	23	**B**	28	**A**
4	**A**	9	**B**	14	**C**	19	**C**	24	**D**	29	**C**
5	**D**	10	**C**	15	**A**	20	**D**	25	**B**	30	**A**

---

1 C

A: 2 mol of NO_2 gives 4 mol of O atoms
B: 2 mol of SO_2 gives 2 mol of S atoms
C: 1 mol of CO_2 gives 1 mol of C atoms
D: 1 mol of N_2O gives 2 mol of N atoms

---

2 D

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^1$
Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Ni^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$
Sr^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

---

3 C

A BrF_3 : T-shaped (3bp, 2 lp)
B ICl_4^- : square planar (4bp, 2 lp)
C PCl_4^+: tetrahedral (4 bp, 0 lp)
D XeF_4: square planar (4bp, 2 lp)

---

4 A
(1 and 4 are correct)

1 True, bond angle in N_2H_4 is 107^{O} while bond angle in H_2O_2 is 105^{O}

2 False, the N–H bond is *longer* than the O–H bond as the O–H covalent bond in more polar. Students can also check the DB to compare the 2 bond energies.

3 False, hydrazine forms *weaker* intermolecular hydrogen bonds than hydrogen peroxide as N is less electronegative than O.

4 True, both N and O are sp^3 hybridised, and form σ bonds by overlapping with the s orbital of H.

---

5 D

Gases deviate from non-ideal behaviour at low temperature or high pressure hence option D is true.

Explanation for option D: At high pressure, volume of container decreases hence volume of gas particles is more significant compared to volume of container, therefore gas behave less ideally.

Note for option A, it should be the significant intermolecular hydrogen bonds between molecules that result in deviation from ideal gas behaviour (not the intramolecular covalent bonds between atoms).

6 C

amount of water formed

$$= \frac{25.0}{1000} \times 3.00 = 0.07500 \text{ mol}$$

heat produced

$$= (25.0 + 25.0) \times 4.18 \times 9.5 \times \frac{100}{85}$$

$$= 2335 \text{ J mol}^{-1}$$

$$\Delta H_n = -\frac{2335\times10^{-3}}{0.07500}$$

$$= -31.14$$

$$= -31.1 \text{ kJ mol}^{-1}$$

---

7 C

$\Delta H^{\ominus}_{lattice\ energy}$ CaO
= – ($\Delta H^{\ominus}_{atomisation}$ Ca + 1st and 2nd ionisation energies of calcium + $\Delta H^{\ominus}_{atomisation}$ O + first and second electron affinity for oxygen) + $\Delta H^{\ominus}_{formation}$ CaO

Option A: Less exothermic
Option B: Less exothermic
Option C: More exothermic since 1st and 2nd ionisation energies of magnesium are more endothermic than calcium
Option D: No change since standard enthalpy change of combustion of calcium is equal to the standard enthalpy change of formation of calcium oxide.

---

8 D

1/ time presents rate of reaction
Since first order wrt H_2O_2, hence
$[H_2O_2] \alpha 1 / \text{time}$

---

9 B

$$\frac{96-80}{96} = \left(\frac{1}{2}\right)^{t/35}$$

t = 90.5 min

---

10 C

$[Q]_{eqm} = 0.2 / 5$ mol dm^{-3}
$[PQ_3]_{eqm} = 0.5 / 5$ mol dm^{-3}
Initial P = 0.2 mol

Since P and PQ_3 have the same mole ratio in the equation,
|change in P| = |change in PQ_3| = 0.1
(read off from graph)

Alternatively, you can also find change in P = 1/3 change in Q.

Hence $[P]_{eqm}$ = (0.2 – 0.1) = 0.1 / 5 mol dm^{-3}

$$K_c = \frac{[PQ_3]}{[Q]^3[P]} = \frac{(\frac{0.5}{5})}{(\frac{0.2}{5})^3(\frac{0.1}{5})} = \frac{0.5\times5^3}{0.2^3\times0.1}$$

---

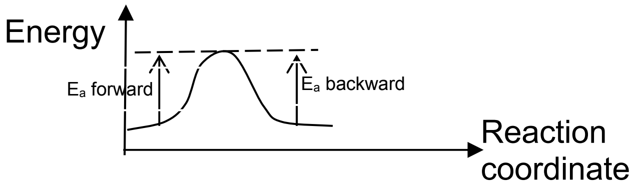
11 B

If equilibrium constant is independent of temperature, it means when temperature changes, neither forward nor backward reaction is favoured and this is only possible if ΔH is zero.

1. All rate constants are affected by temperature according to Arrhenius equation: $k = A^{-Ea/RT}$.

2. Temperature would have no effect on POE if ΔH is zero.

3. When ΔH is zero, activation energies for forward and backward reaction are equal as shown in the energy profile diagram below:



4. We cannot deduce any information about ΔS unless some information about how value of equilibrium constant changes with pressure is provided.

---

12 A

A pH of 0.010 mol dm^{-3} acetic acid = - lg ($\sqrt{10^{-4.76}(0.10)}$) = 2.88
B The solution contains a basic salt hence pH > 7.
C A buffer at maximum buffering capacity of formic acid and its salt is formed. pH = pKa = 3.74
D As more hydroxide is added compared to option C, pH of D > C but pH D < 7 as it is an acidic buffer.

---

13 C

1: $K_D = 10^{-14.8}$
$[D^+] = \sqrt{10^{-14.8}} = 3.98\times10^{-8}$
pD = 7.4

2: Since $[H^+]=[OH^-]$, D_2O is netural.

3: $K_D = 10^{-14.8} < K_w = 10^{-14}$ hence D_2O dissociates to a smaller extent than H_2O.

---

14 C

Chloride of **W** dissolves in water and turns blue litmus red: **W** is not Na (NaCl is neutral)

X is a good conductor of electricity but insoluble in water. **X** can be Mg or Al (However, since **Y** is Mg, **X** must be Al)

Oxide of **Y** has the highest melting point: MgO (**Y** is Mg)

Z has the highest first ionisation energy and largest ionic radius. (**Z** is P)

Since the four elements in Period 3 must be consecutive, **W** must be Si.

Hence the order is **Y**, **X**, **W**, **Z**.
(Mg, Al, Si, P)

---

15 A

$\mathbf{M}CO_3 \rightarrow \mathbf{M}O + CO_2$
Down the group, solubility of oxides increases and pH of the solution increases.
$MgO + H_2O \quad Mg(OH)_2$
$BaO + H_2O \rightarrow Ba(OH)_2$
MgO dissolves sparingly in water to form weak base $Mg(OH)_2$ whereas BaO dissolves readily in water to form strong base, $Ba(OH)_2$.
Since pH of the saturated solution is less than that of limewater, $Ca(OH)_2$, **M** must be Mg.

---

16 D

$Ag^+(aq) + Cl^-(aq) \quad AgCl(s)$ – white ppt
$Ag^+(aq) + I^-(aq) \quad AgI(s)$ – yellow ppt
$Ag^+(aq) + 2NH_3 \quad [Ag(NH_3)_2]^+$
Only AgCl dissolves in conc NH_3, AgI remains insoluble in conc NH_3. Hence Y is AgI(s) – yellow ppt.

---

17 A

Enthalpy change of vaporisation is inversely proportional to boiling point.

Halogens have simple molecular structure with weak instantaneous dipole-induced dipole forces (id-id) between molecules. As the number of electrons or size of electron cloud increases, the electron cloud gets more polarised, id-id forces increases down the group. More energy required to overcome id-id forces. Boiling point increases and hence ΔH_{vap} decreases down the group.

Thermal stability of HX decreases down group 17 due to decreasing bond strength of H–X (increasing H–X bond length)

Electrode reaction	$E^\ominus$/ V
$F_2 + 2e^- \quad 2F^-$	+2.87
$Cl_2 + 2e^- \quad 2Cl^-$	+1.36
$Br_2 + 2e^- \quad 2Br^-$	+1.07
$I_2 + 2e^- \quad 2I^-$	+0.54

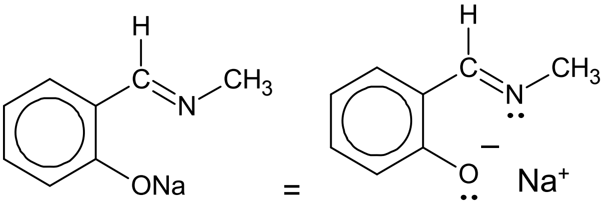
$E^\ominus(X_2|X^-)$ becomes less positive down the group, oxidising power of elements decreases down the group.

---

18 B

A The red complex ion absorbs complementary colour (green) at room temperature.

B



$$n(Ni^{2+}) = 3.0\times10^{-3}\times\frac{4}{1000} = 1.2\times10^{-3}\text{ mol}$$

$$n(Q) = 4.0\times10^{-3}\times\frac{6}{1000} = 2.4\times10^{-3}\text{ mol}$$

$$\frac{n(Ni^{2+})}{n(Q)} = \frac{1.2\times10^{-3}}{2.4\times10^{-3}} = \frac{1}{2}$$

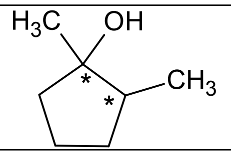
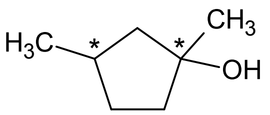
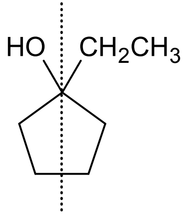
Since **Q** is a bidentate ligand (lone pair on N and lone pair on O^- for dative bonding), the co-ordination number of nickel(II) complex is 4.

C The overall charge of the nickel(II) complex is 0 as there are 2 ligands of **Q** to one nickel(II) ion.

D The shape of the nickel(II) complex ion is not linear as the co-ordination number is not 2.

---

19 C

	
4 optical isomers	4 optical isomers
	
no cis-trans isomer no optical isomer as contains an internal line of symmetry	

---

20 D (1,3 and 4)

Option 1 (incorrect)

The surface area decreases from primary (elongated) to secondary to tertiary alcohol (spherical). Hence strength of id-id forces of attraction decreases from primary to secondary to tertiary.

Option 2 (correct)

CH_3CH_2COCl hydrolyses in water to produce a strong acid, HCl. Hence the pH of its aqueous solution is the lowest. $CH_3CH_2CONH_2$ contains an amide functional group which is neutral. $CH_3CH(Cl)CH_2NH_2$ contains an amine functional group which is basic and hence its pH value is the highest.

Option 3 (incorrect)

The ease of hydrolysis of the chlorine atoms ~~decreases~~ increases from chlorobenzene to chloroethane to ethanoyl chloride.

Option 4 (incorrect)

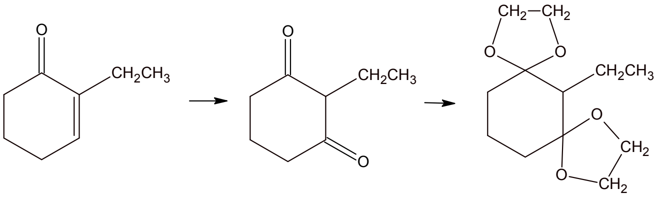
Acidity decreases from ethanoic acid to phenol to ethanol.

Ethanoic acid is the strongest among the three, hence its conjugate base, ethanoate ion will be the weakest, with the largest pK_b value.

Ethanol is the weakest among the three, hence its conjugate base, ethoxide ion will be the strongest, with the smallest pK_b value.

---

21 D



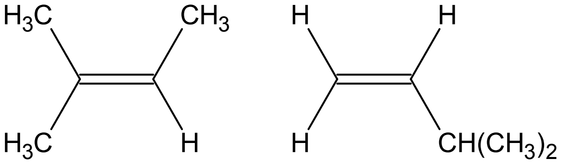
---

22 C

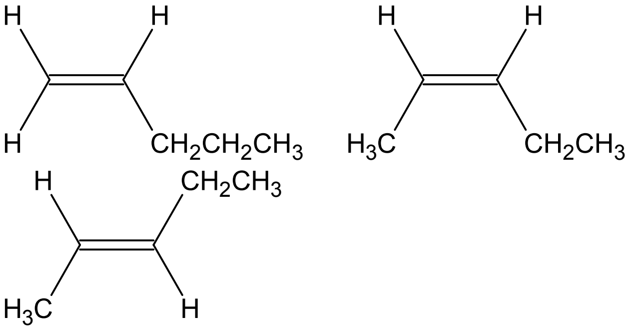
A and **B** do not contain methyl alcohol, hence will not be able to react with alkaline aqueous iodine.

C, $(CH_3)_2CH\mathbf{CH(OH)CH_3}$ and **D**, ($CH_3CH_2CH_2\mathbf{CH(OH)CH_3}$) contain methyl alcohol, hence will react with alkaline aqueous iodine.

When **C** undergoes dehydration, it produces two alkenes only as shown below.



When **D** undergoes dehydration, it produces three alkenes as shown below.



---

23 B

All can occur at a good rate at room temperature (20 °C) except

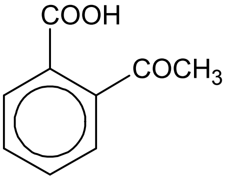
$CH_3CH_2OH + KBr \rightarrow CH_3CH_2Br + KOH$ as conc. H_2SO_4 needs to be added to react with KBr with heating to produce HBr which will then reacts with CH_3CH_2OH to produce CH_3CH_2OH.

---

24 D

X contains an aromatic aldehyde that does **not** give a red ppt when warmed with Fehling's solution.

X reacts with acidified $K_2Cr_2O_7$ to give **Y** as shown below.

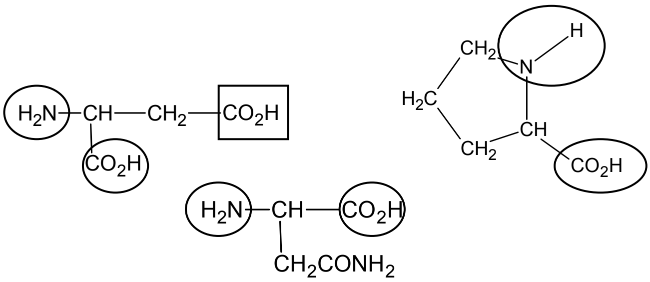


So **Y** also does **not** give a red ppt when warmed with Fehling's solution.

---

25 B

A dipeptide (formed in the body) should be formed between the carboxylic acid and amino group bonded directly to the α C i.e. see circles in black



Hence, only Option 1 and 4 is correct. Option 2 and 3 show structures that are bonded by the carboxylic acid group in the side chain of the 1st amino acid (look at the –COOH in the rectangle box) and are not classified as dipeptides formed in the body. Option 3 is incorrect.

---

26 C (3 and 4)

Option 1:

The α–amino group should have a pK_a value of 9.0 because it is closer to the –COOH group which is withdrawing in nature.

Option 2:

Equal amounts of $H_3N^+CH(CO_2H)(CH_2)_4NH_3^+$ and $H_3N^+CH(CO_2^-)(CH_2)_4NH_3^+$ are present at point **A**.

Option 3:

At point C, $H_2NCH(CO_2^-)(CH_2)_4NH_3^+$ is present, which is a zwitterion with no net charge

Option 4:

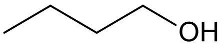
At point B, $H_3N^+CH(CO_2^-)(CH_2)_4NH_3^+$ is present which has net positive charge, hence will migrate to cathode

---

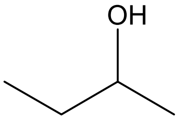
27 A

A butyl propanoate is formed by butan-1-ol and propanoic acid

The positional isomer of butan-1-ol is butan-2-ol as shown below.



butan-1-ol



butan-2-ol

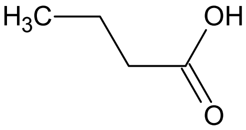
Propanoic acid has no chain isomerism.

Both conditions fulfilled.

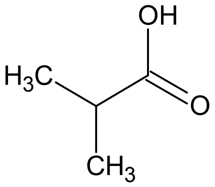
B ethyl butanoate is formed by ethanol and butanoic acid

Ethanol has no positional isomer.

Butanoic acid has 1 chain isomer as shown below.



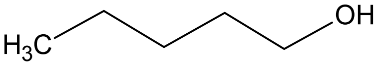
butanoic acid



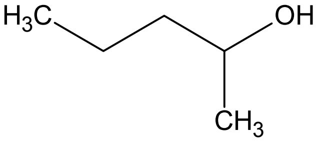
2-methylpropanoic acid

C pentyl ethanoate is formed by pentan-1-ol and ethanoic acid

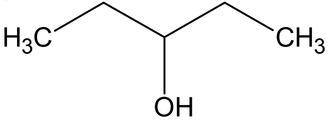
Pentan-1-ol has 2 positional isomers as shown below.



pentan-1-ol



pentan-2-ol

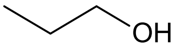


pentan-3-ol

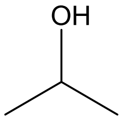
Ethanoic acid has no chain isomerism.

D Propyl pentanoate is formed by propan-1-ol and pentanoic acid

Propan-1-ol has 1 positional isomer.

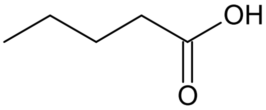


propan-1-ol

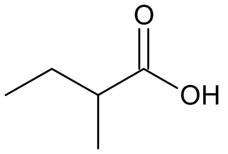


propan-2-ol

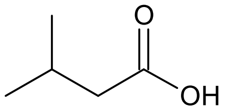
Pentanoic acid has 3 chain isomers as shown below.



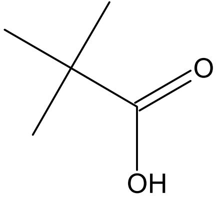
pentanoic acid



2-methylbutanoic acid



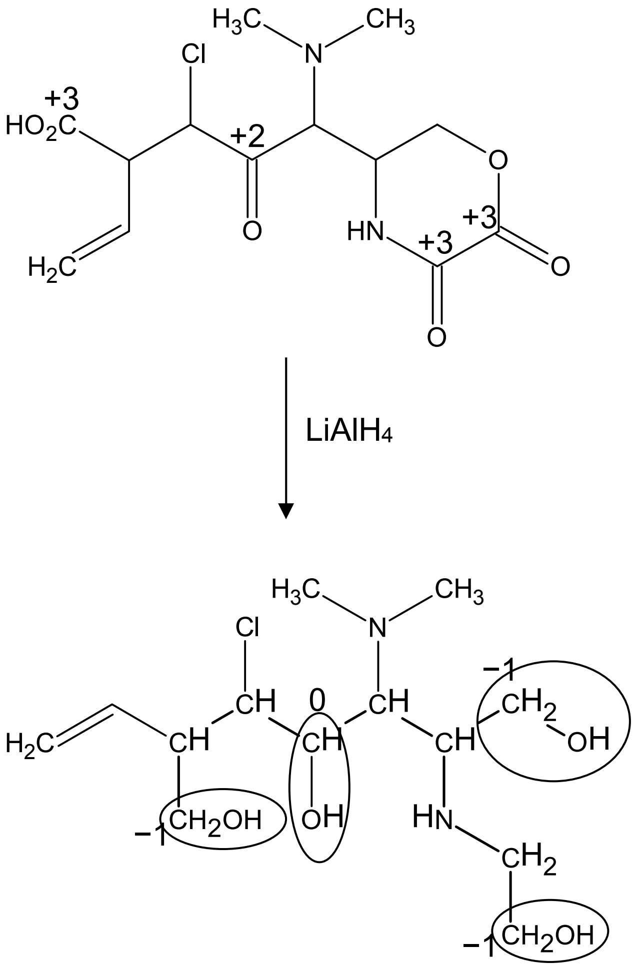
3-methylbutanoic acid



2,2-dimethylpropanoic acid

---

28 A



A (Correct) As a Lewis base, N_b has more electron-donating grps than N_a which increases the electron density on the N atom and hence the availability of the lone pair of electrons for donation to a Lewis acid. So N_b is a stronger Lewis base than N_a.

As a Bronsted-Lowry base, N_b experiences steric hindrance from the presence of 3 bulky alkyl grps, hence protons from the aq soln will have difficulty going near the lone pairs to form dative bond. So N_b is a weaker Bronsted-Lowry base than N_a.

B (Incorrect) When 96 dm^3 of H_2 gas was reacted with one mole of compound **W**, followed by excess sodium metal, at room conditions, the gas volume ~~expanded~~ contracted by ~~48~~24 dm^3.

96 dm^3 is equivalent to 4 mol of H_2 gas.
Only the alkene and ketone function grp will be reduced by $H_2(g)$ using up 2 out of the 4 mol of $H_2(g)$ present.
Alkene will be reduced to alkane while ketone will be reduced to 2° alcohol. The 2° alcohol and −COOH grp present will then react with Na to produce 1 mol of $H_2(g)$.
The final volume of $H_2(g)$ is 72 dm^3.
The gas volume contracted by 24 dm^3.

C Incorrect. The numbers written beside the C atom (as shown above) shows the oxidation state of the carbon before and after the reduction by $LiAlH_4$.

D Functional groups in **W** that will react with NaOH with heating are –COOH, RCl, amide and ester. So will need 4 mol of NaOH.
Functional groups in **W** that will react with NaOH without heating is –COOH. So will need 1 mol of NaOH.

---

29 C

A: O.S. of C changes from +4 to +3 (reduction)
B: O.S. of Cr remains unchanged at +6
C: O.S. of Br changes from 0 to +3 (oxidation)
D: O.S. of Cl changes from 0 to –1 (reduction)

---

30 A

$Fe^{3+} + e \rightarrow Fe^{2+}$ +0.77V → +ve → [R]
$Ni + 2e \rightarrow Ni^{2+}$ -0.25V → -ve → [O]

Fe^{3+} is yellow and Fe^{2+} is pale green.

Reduction occurs at the Fe^{3+}/Fe^{2+} half-cell.

E_{cell} = +0.77 – (-0.25) = +1.02 V.

Electrons flow from the anode (Ni^{2+}/Ni half-cell) to the cathode (Fe^{3+}/Fe^{2+} half-cell).

Pt cathode size remains unchanged.

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/24**
2	**/11**
3	**/9**
4	**/13**
5	**/18**
Total	**/75**

This document consists of **17** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1(a) An unknown sample was found to contain the anions, Cl^-, ClO_3^- and NO_3^-. A student weighed a sample into a beaker and recorded the following data.

mass of beaker and sample / g	68.962
mass of empty beaker / g	67.620

The sample was dissolved and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In **experiment 1**, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The AgCl precipitated was transferred onto a dry filter paper and was placed under an infra-red lamp. The dry AgCl precipitate was weighed and the following data was obtained.

Experiment 1

mass of dry filter paper and AgCl / g	0.737
mass of dry filter paper / g	0.620

In **experiment 2**, a gas was bubbled into another 50 cm^3 portion of solution **L** to convert ClO_3^- to Cl^- before the addition of excess silver nitrate solution. The AgCl precipitated was also dried and weighed. The following data was obtained.

Experiment 2

mass of dry filter paper and AgCl / g	0.799
mass of dry filter paper / g	0.651

(i) Write the half equation for the reduction of ClO_3^- to Cl^-.

.... [1]

(ii) Determine the mass of Cl^- in 50 cm^3 of solution **L**.

[1]

(iii) Determine the mass of Cl^- converted from ClO_3^- in **experiment 2**.

[2]

(iv) Hence, determine the percentage mass of ClO_3^- in the unknown sample.

[3]

(v) The *E* (ClO_3^-/Cl^-) has a value of +1.47 V. From the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce ClO_3^- to Cl^-. Explain your answer.

....

....

....

.... [2]

(b) **(i)** An aqueous solution of HCl has a density of 1.15 g cm^{-3} and is 30% by mass of HCl.

Calculate the concentration in mol dm^{-3} of this solution of HCl.

[2]

(ii) Calculate the volume of this solution required to prepare 5 dm^3 of 0.20 mol dm^{-3} HCl by dilution with water.

[1]

(c) The gelatin silver process is the photographic process used with black-and-white films. The following information pertains to the process of taking photographs and developing films.

Taking photographs

- A 35 mm cartridge of black-and-white print film contains a long strip of plastic that has layered coatings on each side.
- On the front side of the film, the layers are made of gelatin which contain grains of silver chloride crystals.
- When the shutter of the camera is opened for a fraction of a second to allow the film to be exposed to light, these crystals undergo decomposition thereby producing an image on the film.

Developing films

- After the photographs have been taken, the film is developed in a dark room under a light source that emits low energy light.
- Firstly, the film is soaked in water before adding phenidone. Phenidone makes the image more visible by reacting with the exposed silver chloride crystals to produce silver atoms and two other by-products.
- This reaction can only proceed at high pH.
- After some time, the reaction will then be quenched.
- Finally, the film will be soaked in ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is used as a fixer to make the image permanent and light resistant. This is done through the reaction between the unexposed silver chloride crystals and the fixer.

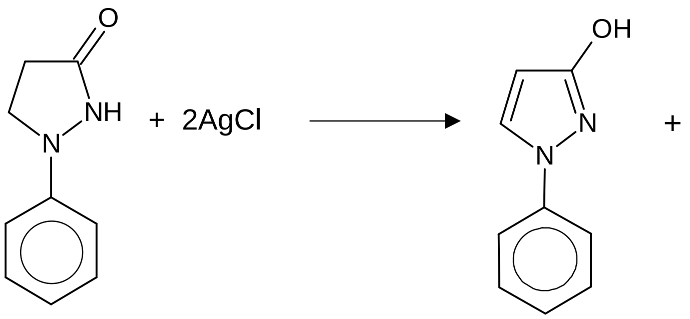
(i) Write the balanced equation for the decomposition of silver chloride crystals when it is exposed to light.

.... [1]

(ii) Suggest a suitable colour of the light source that is used in a dark room.

.... [1]

(iii) Complete the equation for the reaction between the developing agent, phenidone, and the exposed silver chloride crystals. Hence, state the role of phenidone in this reaction.



phenidone

role of phenidone .... [2]

(iv) Suggest a suitable reagent, other than excess cold water, that can be used to quench the development of the film. Explain.

....

....

....

.... [2]

(v) When the non-exposed silver chloride crystals react with the fixer, $(NH_4)_2S_2O_3$, a silver complex compound **M** is formed together with a chloride salt, **N**. Both **M** and **N** have the same cation. The silver-containing complex ion has a coordination number of 2 and is chlorine-free.

Suggest the formulae of compounds **M** and **N**.

compound **M**: .... compound **N**: .... [2]

(vi) State the shape of the silver-containing ion in compound **M**.

.... [1]

(vii) Complete the electronic configuration of silver in compound **M**. Hence, deduce the colour of compound **M**.

compound **M** [Ar]$3d^{10}4s^2$ ....

....

....

....

....

.... [2]

(viii) Explain why the fixer, $(NH_4)_2S_2O_3$, is able to make the image permanent and light resistant on the film.

....

....

.... [1]

[Total: 24]

2 Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, is the chemical compound N_2O_4. It is a useful reagent in chemical synthesis.

(a) Colourless N_2O_4 readily dissociates to form brown NO_2 and the following equilibrium is reached fairly quickly in the gaseous phase.

$$N_2O_4(g) \qquad 2NO_2(g) \qquad\qquad \Delta H > 0$$

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

[3]

(ii) Describe and explain what you would observe when the stoppered flask is placed into a basin of boiling water.

....

....

....

....

.... [1]

(b) N_2O_4 is also used in the large scale manufacture of nitric acid. It reacts with water to give both nitrous acid and nitric acid.

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The two acids have different acid strengths. To determine the acid strength of the two acids, two separate solutions containing 0.10 mol dm^{-3} of each acid were prepared. The pH was found to be 2.17 and 1.00 for the solutions containing nitrous acid and nitric acid respectively.

(i) Use the data provided to prove nitrous acid is a weak acid and hence, determine its K_a value.

[2]

(ii) Suggest a reason why nitrous acid is a weaker acid than nitric acid.

....

....

....

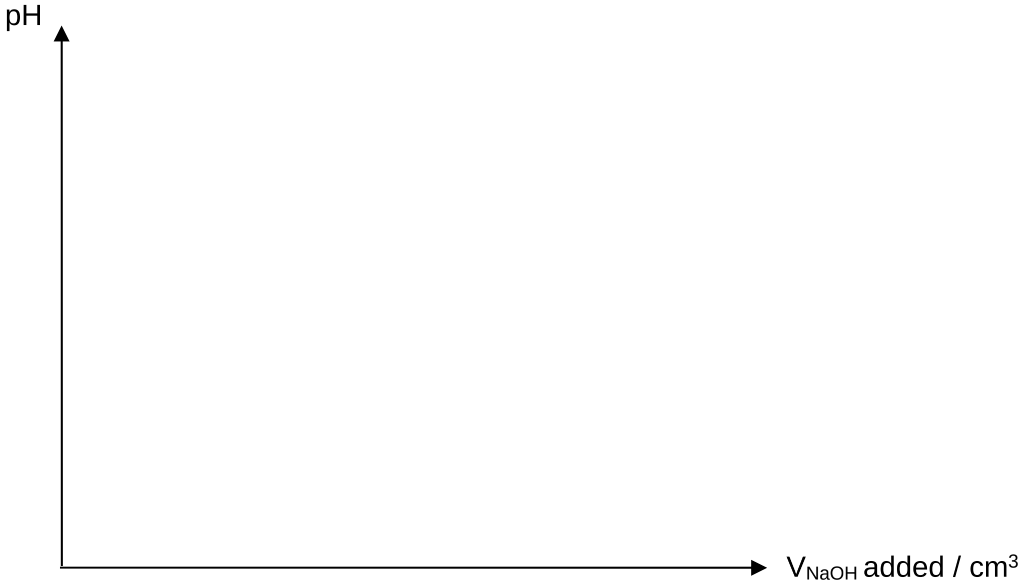
.... [1]

25.0 cm^3 of the prepared 0.10 mol dm^{-3} nitrous acid was titrated with 0.10 mol dm^{-3} aqueous sodium hydroxide.

(iii) Using your value of K_a calculated in part **(i)**, calculate the pH when 25.00 cm^3 of aqueous sodium hydoxide has been added.

[2]

(iv) On the given axes below, sketch the pH-volume added graph you would expect to obtain when the above titration was performed. Label the appropriate pH at various key points on the graph.



[2]

[Total: 11]

3 The equation for the reaction between bromine and methanoic acid is as follows:

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

It is hypothesised that the reaction is elementary. To prove this hypothesis, volumes of the two reactants were varied and the rate of the reaction is measured in terms of the rate at which the bromine concentration changes. When the total volume is kept constant, the following relationship is true.

$$\text{rate of reaction } \alpha \ \frac{\text{volume of bromine used}}{\text{time for color of bromine to disappear}}$$

The temperature of the reaction mixture was maintained at 25 °C.

The following results were obtained in three repeated experiments:

Expt	Volume of 1.0 mol dm^{-3} Br_2 / cm^3	Volume of 10.0 mol dm^{-3} HCOOH / cm^3	Volume of water added / cm^3	Relative time for colour of bromine to disappear
1	10	10	0	1.4
2	40	20	20	2.8
3	5	10	5	1.4

(a) By comparing the rates of reactions, explain how the results of the three experiments support the hypothesis that the reaction is elementary.

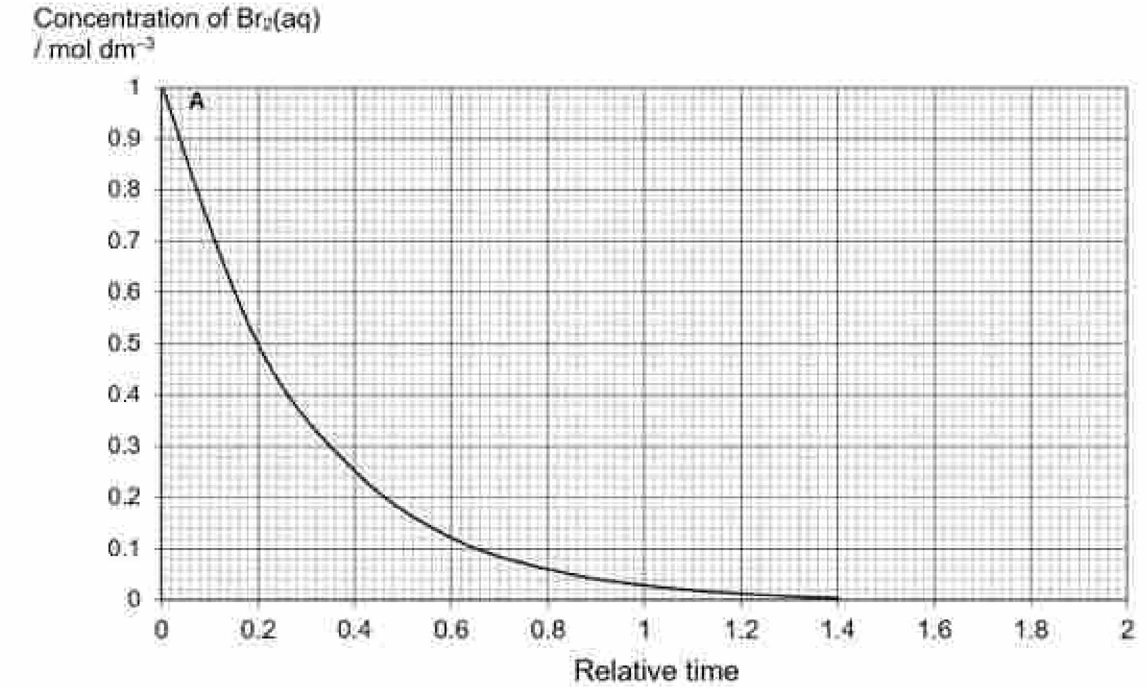
....

....

....

.... [3]

(b) During another experiment, the concentration of Br_2 was monitored over time and the following graph (Run **A**) was obtained. The concentration of HCOOH used was 10.0 mol dm^{-3}.



(i) Define the term "half-life".

....

.... [1]

(ii) The experiment was repeated using 0.8 mol dm^{-3} of Br_2(aq) and 10.0 mol dm^{-3} of HCOOH. On the axes above, draw the concentration-time graph of Br_2(aq) for the new experiment and label it 'Run **B'**.

On your graph, clearly state and label the half-life of Br_2(aq). [1]

(iii) The experiment was repeated again using 1.0 mol dm^{-3} of Br_2(aq) and 5.0 mol dm^{-3} of HCOOH (Run **C**). In comparison to Run **A**, state how the half-life of the experiment will change.

....

....

.... [1]

(c) By drawing a suitable illustration, estimate and explain the change in rate of reaction when temperature is increased to 35 °C.

....

....

....

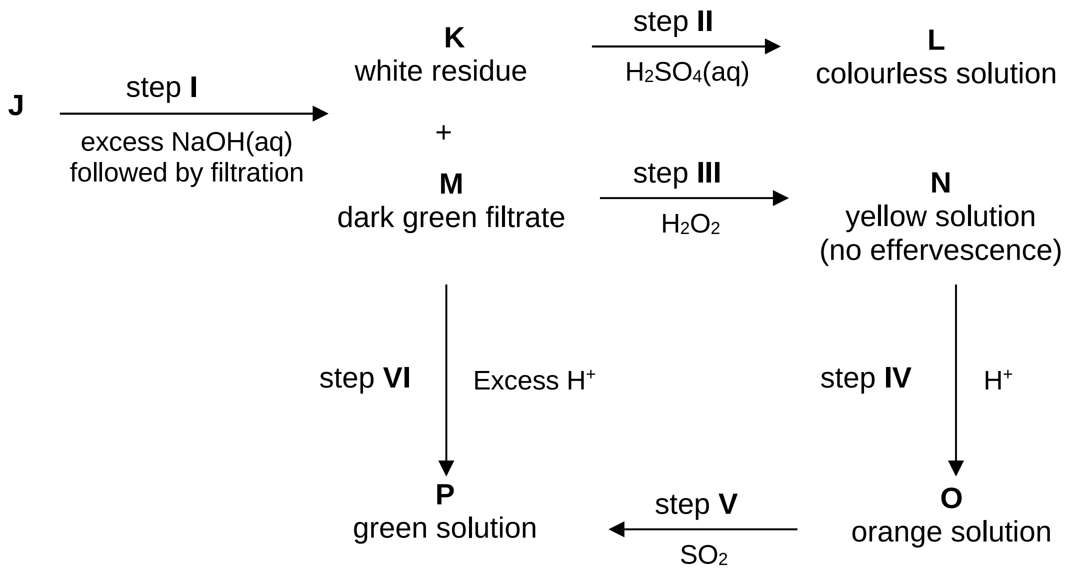
....

....

.... [3]

[Total: 9]

4(a) Solution **J** contains a Group 2 ion and a transition metal ion. The following reaction scheme shows how **J** reacts with some common reagents in the laboratory.



(i) State the identities of **K**, **L**, **M**, **N**, **O** and **P.**

K.. **L**..

M .... **N**..

O.. **P**..

[3]

(ii) State the roles of H_2O_2 and SO_2 in steps **III** and **V** respectively.

H_2O_2 in step **III**: ....

SO_2 in step **V**:.. [1]

(iii) Write an ionic equation to explain the formation of solution **P** in step **V**.

.... [1]

(iv) Explain how solution **P** can be formed in step **VI**.

....

....

....

....

....

....

.... [2]

(b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.
For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

(i) Explain why the melting points of these elements decrease from carbon to germanium.

....

....

....

....

....

.... [2]

(ii) Explain how first ionisation energy changes from carbon to germanium.

....

....

....

....

....

.... [2]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts violently with water.

(iii) Write a balanced equation for the reaction of $SiCl_4$ with water.

.... [1]

(iv) Suggest an explanation for the inertness of CCl_4 to water.

....

....

.... [1]

[Total: 13]

5 Azo dyes are made in large quantites from benzene, C_6H_6, via nitrobenzene, $C_6H_5NO_2$ (density = 1.20 g cm^{-3}), and phenylamine, $C_6H_5NH_2$.

(a) The preparation of nitrobenzene requires benzene to be warmed under reflux at about 55 ^oC with a mixture of concentrated nitric and sulfuric acids. Some information about these substances is given below:

Benzene: immiscible with water; highly flammable; extremely toxic by ingestion or inhalation; known carcinogen.

Concentrated nitric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent. The acid contains about 30 % water by volume.

Concentrated sulfuric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent; dilution with water is very exothermic and can be dangerous.

(i) Nitric acid is placed in a suitable flask and sulfuric acid is added slowly with cooling of the flask. Explain why cooling is necessary.

....

.... [1]

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55 ^oC for 45 minutes under reflux with vigorous stirring of the reaction mixture.

Explain why the reflux condenser is necessary and also why the mixture is vigorously stirred.

....

....

.... [2]

(iii) State, with a reason, **one** other precaution (other than wearing protective wear) that would be necessary when carrying out the experiment.

....

.... [1]

(iv) The reaction mixture is then poured into a large excess of cold water, the liquid nitrobenzene layer is separated and *washed* with sodium carbonate solution.
Explain why this washing is necessary.

....

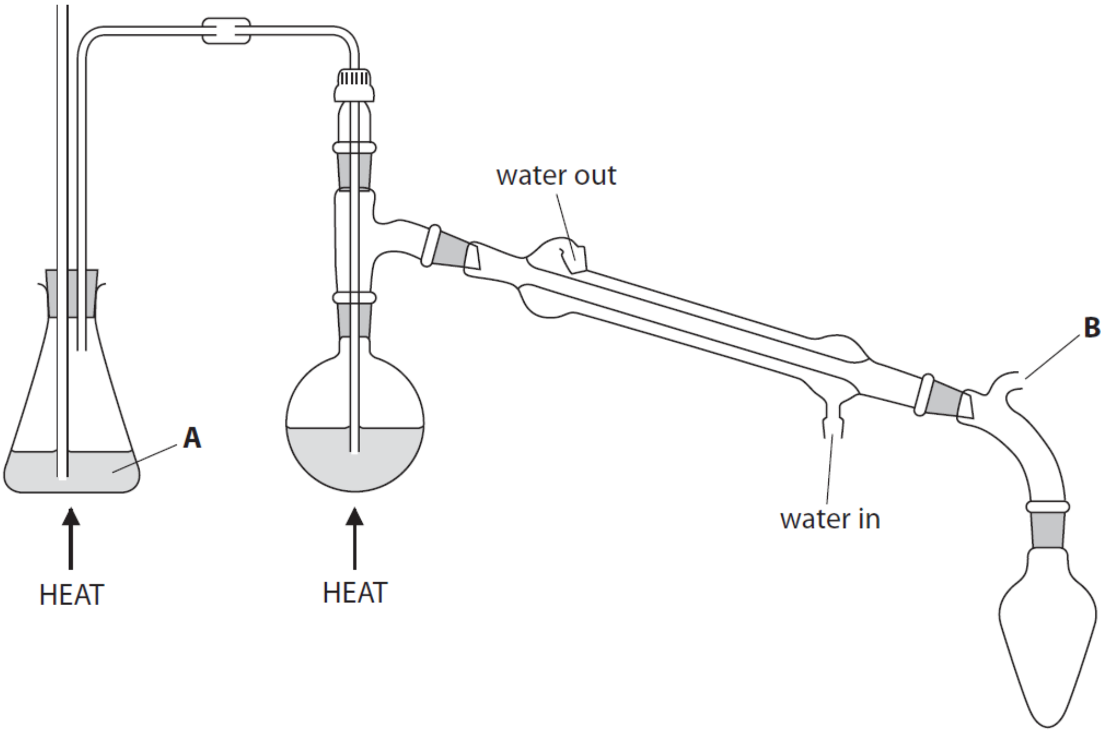
.... [1]

(v) The nitrobenzene layer is dried before being distilled to purify it.
Identify a suitable drying agent.

.... [1]

(b) Steam distillation is a purification process to separate nitrobenzene from the reaction mixture. During the process of steam distillation, a current of steam is blown through a mixture containing the desired organic substance to be distilled. This caused the desired organic substance to vaporise. The vapour containing the desired organic substance can then be condensed and collected. This method is used predominantly to purify liquids that are not very volatile and are immiscible with water.

The diagram below shows a steam distillation apparatus used to extract nitrobenzene from the reaction mixture.



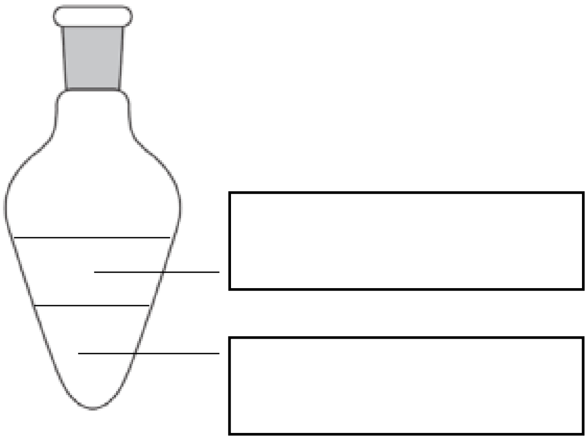
(i) Identify substance **A**.

.... [1]

(ii) Explain the purpose of the part of the apparatus labelled **B**.

.... [1]

(iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.

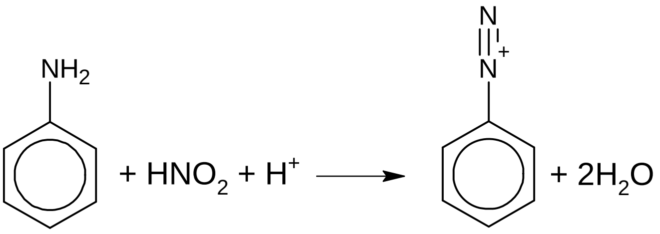


[1]

(c) The purified nitrobenzene is then reduced to phenylamine, $C_6H_5NH_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0 °C and 10 °C. Nitrous acid is generated in the reaction mixture from sodium nitrite and hydrochloric acid.

The ionic equation for the diazotisation of phenylamine to produce benzenediazonium ion is as shown below.

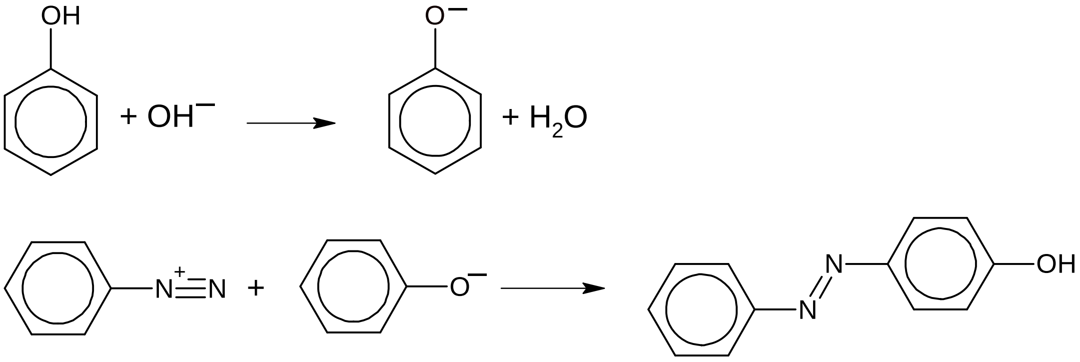


benzenediazonium ion

If the above reaction is warmed, benzenediazonium ion will undergo hydrolysis to give phenol. A gas will also be produced and the resulting mixture is acidic.

Reaction of the benzenediazonium compound with an alkaline solution of a phenol, C_6H_5OH, will produce a solid azo dye, which is purified by recrystallisation.

The equations for the reaction between benzenediazonium ion and phenol to produce the solid azo dye are shown below.



azo dye

(i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.

.... [1]

(ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0 °C.

.... [1]

(iii) Write an equation to show benzenediazonium ion undergoing hydrolysis upon warming.

.... [1]

[Turn Over

(d) Purification by recrystallisation requires the following steps:

1. The azo dye is dissolved in a minimum volume of hot solvent.
2. The solution is filtered through a pre-heated funnel.
3. The solution is cooled and filtered using a Buchner funnel.
4. The solid is washed with a small amount of cold solvent.
5. The solid is dried in a desiccator.

(i) Explain why a **minimum** volume of hot solvent is used in step 1.

....

.... [1]

(ii) Explain why the funnel must be pre-heated.

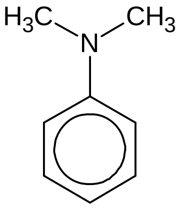
.... [1]

(iii) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

.... [1]

(e) This question compares the acidity and basicity of some organic compounds.

(i) Explain why an aqueous solution of of N,N-dimethylphenylamine is more basic than an aqueous solution of phenylamine.



N,N-dimethylphenylamine

....

....

....

.... [1]

(ii) Explain why an aqueous solution of azo dye is more acidic than an aqueous solution of phenol.

....

....

....

.... [2]

[Total: 18]

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	Teachers' Mark Scheme

CLASS		TUTOR'S NAME	

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

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For Examiner's Use	
1	**/24**
2	**/11**
3	**/9**
4	**/13**
5	**/18**
Total	**/75**

This document consists of **17** printed pages and **1** blank page.

[Turn over

Answer **all** questions in the spaces provided.

1(a) An unknown sample was found to contain the anions, Cl^-, ClO_3^- and NO_3^-. A student weighed a sample into a beaker and recorded the following data.

mass of beaker and sample / g	68.962
mass of empty beaker / g	67.620

The sample was dissolved and diluted in a 250 cm³ volumetric flask to obtain solution **L**.

In **experiment 1**, a 50 cm³ portion of solution **L** was reacted with excess silver nitrate solution. The AgCl precipitated was transferred onto a dry filter paper and was placed under an infra-red lamp. The dry AgCl precipitate was weighed and the following data was obtained.

Experiment 1

mass of dry filter paper and AgCl / g	0.737
mass of dry filter paper / g	0.620

In **experiment 2**, a gas was bubbled into another 50 cm³ portion of solution **L** to convert ClO_3^- to Cl^- before the addition of excess silver nitrate solution. The AgCl precipitated was also dried and weighed. The following data was obtained.

Experiment 2

mass of dry filter paper and AgCl / g	0.799
mass of dry filter paper / g	0.651

(i) Write the half equation for the reduction of ClO_3^- to Cl^-.

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$ [1] ....[1]

(ii) Determine the mass of Cl^- in 50 cm³ of solution **L**.

mass of AgCl precipitate in expt 1 = 0.737 – 0.620 = 0.117 g

mass of Cl^- present in 50 cm³ portion

$= \frac{35.5}{35.5+107.9} \times 0.117 = 0.02896 \text{ g} \approx 0.0290 \text{ g}$ [1]

[1]

(iii) Determine the mass of Cl^- converted from ClO_3^- in **experiment 2**.

mass of AgCl precipitate in expt 2 = 0.799 – 0.651 = 0.148 g

mass of Cl^- present in 50 cm³ portion $= \frac{35.5}{35.5+107.9} \times 0.148 = 0.03663 \text{ g}$ [1]

mass of Cl^- from ClO_3^- in 50 cm³ = 0.03663 – 0.02896

= 0.007674 g ≈ 0.00767 g [1]

[2]

(iv) Hence, determine the percentage mass of ClO_3^- in the unknown sample.

Since n(ClO_3^-) : n(Cl^-) is 1 : 1,

mass of ClO_3^- present in 50 cm^3 = $0.007674 \times \frac{35.5+3(16)}{35.5}$ = 0.01805 g [1]

mass of ClO_3^- present in 250 cm^3 = $0.01805 \times \frac{250}{50}$ = 0.1805 g [1]

% ClO_3^- present in unknown compound = $\frac{0.1805}{68.962-67.620}$ x 100%

= 13.45% ≈ 13.5% [1]

[3]

(v) The E (ClO_3^-/Cl^-) has a value of +1.47 V. From the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce ClO_3^- to Cl^-. Explain your answer.

E (H^+/H_2) = 0.00 V

H_2 gas is an appropriate reducing agent. [1]

(also accept E (NO_3^-/NO_2) or E (SO_4^{2-}/SO_2) as their E < +1.47V)

E_{cell} = (+1.47) – (0.oo) = +1.47 V > 0

Since, E_{cell} > 0, the reaction is feasible. [1]

....

.... [2]

(b) **(i)** An aqueous solution of HCl has a density of 1.15 g cm^{-3} and is 30% by mass of HCl.

Calculate the concentration in mol dm^{-3} of this solution of HCl.

mass of HCl in 1 cm^3 = $\frac{30}{100}$ x 1.15 = 0.3450 g [1]

[HCl] = $\frac{0.3450}{1.0+35.5}$ x 1000 = 9.45 mol dm^{-3} [1]

[2]

(ii) Calculate the volume of this solution required to prepare 5 dm^3 of 0.20 mol dm^{-3} HCl by dilution with water.

volume of HCl required = $\frac{5 \times 0.20}{9.452}$ = 0.106 dm^{-3} = 106 cm^3 [1]

[1]

(c) The gelatin silver process is the photographic process used with black-and-white films. The following information pertains to the process of taking photographs and developing films.

Taking photographs

- A 35 mm cartridge of black-and-white print film contains a long strip of plastic that has layered coatings on each side.
- On the front side of the film, the layers are made of gelatin which contain grains of silver chloride crystals.
- When the shutter of the camera is opened for a fraction of a second to allow the film to be exposed to light, these crystals undergo decomposition thereby producing an image on the film.

Developing films

- After the photographs have been taken, the film is developed in a dark room under a light source that emits low energy light.
- Firstly, the film is soaked in water before adding phenidone. Phenidone makes the image more visible by reacting with the exposed silver chloride crystals to produce silver atoms and two other by-products.
- This reaction can only proceed at high pH.
- After some time, the reaction will then be quenched.
- Finally, the film will be soaked in ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is used as a fixer to make the image permanent and light resistant. This is done through the reaction between the unexposed silver chloride crystals and the fixer.

(i) Write the balanced equation for the decomposition of silver chloride crystals when it is exposed to light.

$$2AgCl \xrightarrow{\text{light}} 2Ag + Cl_2$$ [1]

.... [1]

(ii) Suggest a suitable colour of the light source that is used in a dark room.

Red. (Also accept orange or yellow) [1] .... [1]

(iii) Complete the equation for the reaction between the developing agent, phenidone, and the exposed silver chloride crystals. Hence, state the role of phenidone in this reaction.

+ 2Ag + 2HCl [1]

phenidone

role of phenidone reducing agent [1]... [2]

(iv) Suggest a suitable reagent, other than excess cold water, that can be used to quench the development of the film. Explain.

Acetic acid / Citric acid / Any plausible acids. e.g. HCl, HNO_3, H_2SO_4 [1]

When acid is added, the pH will be lowered. Hence, the reaction will not proceed at lower pH. [1]

.... [2]

(v) When the non-exposed silver chloride crystals react with the fixer, $(NH_4)_2S_2O_3$, a silver complex compound **M** is formed together with a chloride salt, **N**. Both **M** and **N** have the same cation. The silver-containing complex ion has a coordination number of 2 and is chlorine-free.

Suggest the formulae of compounds **M** and **N**.

compound **M**: $(NH_4)_3[Ag(S_2O_3)_2]$ [1]....... compound **N**: NH_4Cl [1] ....[2]

(vi) State the shape of the silver-containing ion in compound **M**.

Linear [1]...[1]

(vii) Complete the electronic configuration of silver in compound **M**. Hence, deduce the colour of compound **M**.

compound **M** $[Ar]3d^{10}4s^{2}4p^{6}4d^{10}$ [1] ....

Since the 4d orbitals are fully occupied, d–d transition cannot occur. [1]

Hence, compound **M** is colourless. [1]

....

.... [2]

(viii) Explain why the fixer, $(NH_4)_2S_2O_3$, is able to make the image permanent and light resistant on the film.

The fixer is able to remove any remaining unexposed AgCl. Hence, there is <u>no AgCl remaining on the film to undergo decomposition through the exposure of light</u> to change the image on the film. [1]

....

....

.... [1]

[Total: 24]

2 Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, is the chemical compound N_2O_4. It is a useful reagent in chemical synthesis.

(a) Colourless N_2O_4 readily dissociates to form brown NO_2 and the following equilibrium is reached fairly quickly in the gaseous phase.

$$N_2O_4(g) \qquad 2NO_2(g) \qquad\qquad \Delta H > 0$$

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

- Initial no of moles of N_2O_4 = 4.60 / (14.0 × 2 + 16.0 × 4) = 0.0500 mol

ICE table/eqm amounts:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Initial / mol	0.0500	0
Eqm / mol	0.0500 – x	+2x

- PV = nRT

$(101325)(1.48 \times 10^{-3}) = n\,(8.31)(300)$

n(gases at eqm) = 0.06015 = 0.0602 mol

- Solve for x and find eqm amts

0.0500 – x + 2x = 0.06015

x = 0.01015

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Eqm / mol	0.03985	0.0203

- $$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{\left(\frac{0.02030}{0.06015}\times 1\right)^2}{\frac{0.03985}{0.06015}\times 1} = 0.172 \text{ atm}$$

4 points 3 marks; 3 points: 2 marks; 2 points: 1 mark

<u>Alternative solution in terms of partial pressure ICE table.</u>

$$P(N_2O_4 \text{ initial}) = \frac{0.05(8.314)(300)}{1.48\times 10^{-3}} = 84220\,Pa = 0.08312\,atm$$

ICE table/eqm partial pressures:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Initial / atm	0.08312	0
Eqm / atm	0.08312 – x	+2x

0.08312 – x + 2x = 1

x =0.1687 atm

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.1687 \times 2)^2}{0.8312 - 0.1687} = 0.172 \text{ atm}$$

[3]

(ii) Describe and explain what you would observe when the stoppered flask is placed into a basin of boiling water.

Temperature of system increases and by Le Chatelier's Principle, the forward endothermic reaction is favoured. Position of equlibrium shifts to the right to absorb added heat and more NO_2 is formed. Hence the reaction mixture becomes more brown. **[1]**

....

.... [1]

(b) N_2O_4 is also used in the large scale manufacture of nitric acid. It reacts with water to give both nitrous acid and nitric acid.

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The two acids have different acid strengths. To determine the acid strength of the two acids, two separate solutions containing 0.10 mol dm^{-3} of each acid were prepared. The pH was found to be 2.17 and 1.00 for the solutions containing nitrous acid and nitric acid respectively.

(i) Use the data provided to prove nitrous acid is a weak acid and hence, determine its K_a value.

$[H^+]$ in solution of HNO_2 = $10^{-2.17}$ = 0.00676 $moldm^{-3}$
which is less than $[HNO_2]$ = 0.10 $moldm^{-3}$.
Hence HNO_2 only dissociates partially and it is a weak acid. **[1]**

OR for the same concentration of acid, HNO_2 dissociates to produce a lower $[H^+]$ (as shown by the higher pH of the solution). Hence, it dissociates to a smaller extent and is a weak acid. ☒ higher pH so weaker acid.

(FYI. Not required in answer: $[H^+]$ in solution of HNO_3 = $10^{-1.00}$ = 0.100 mol dm^{-3} = $[HNO_3]$ hence Not required it is completely dissociated and HNO_3 is a strong acid.)

$$K_a = \frac{[NO_2^-][H^+]}{[HNO_2]} = \frac{(0.00676)^2}{0.10 - 0.00676} = 4.90\times10^{-4} \text{ mol dm}^{-3}$$ **[1]**

[Note if students use $[H^+] = \sqrt{K_a . c}$ or $K_a = \frac{(0.00676)^2}{0.10} = 4.57\times10^{-4}$]

[2]

(ii) Suggest a reason why nitrous acid is a weaker acid than nitric acid.

Nitric acid is a stronger acid as NO_3^- is a more stable conjugate base than NO_2^- as the negative charge is more effectively dispersed over a greater number of electronegative oxygen atoms (or vice versa). **[1]**

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [1]

25.0 cm^3 of the prepared 0.10 mol dm^{-3} nitrous acid was titrated with 0.10 mol dm^{-3} aqueous sodium hydroxide.

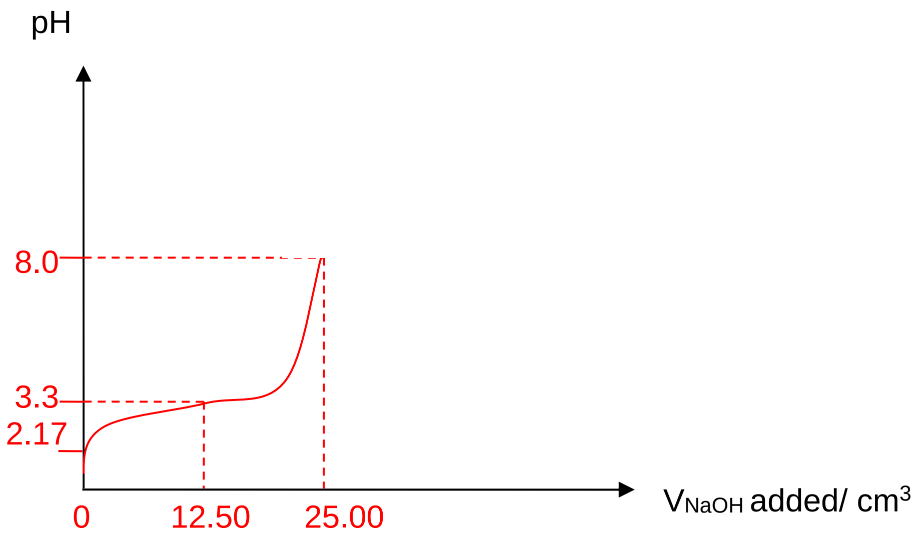
(iii) Using your value of K_a calculated in part **(i)**, calculate the pH when 25.00 cm^3 of aqueous sodium hydoxide has been added.

Equivalence volume = 25.00 cm^3
At equivalence point, solution contains basic salt only.

$K_b = 10^{-14} / 4.90 \times 10^{-4} = 2.040 \times 10^{-11}$
[salt] = 25.0 x 0.1 / 50.0 = 0.05 $moldm^{-3}$
$[OH^-] = \sqrt{K_b.c} = \sqrt{2.040\times10^{-11}(0.05)} = 1.010\times10^{-6}$
pH = 14 – pOH = 14 – (–lg(1.010×10^{-6})) = 8.0
4 points [2], 2 points [1] ecf K_a value

[2]

(iv) On the given axes below, sketch the pH-volume added graph you would expect to obtain when the above titration was performed. Label the appropriate pH at various key points on the graph.



Label following values
- Initial pH (given in question)
- Maximum buffering capacity occurs at 12.50 cm^3: pH = pK_a (–lg(4.90×10^{-4}) = 3.3)
- Equivalence point (calculated in iii)

Correct shape (relatively flat at buffer region)
*don't penalize if students sketch graph beyond 25.00 cm^3
4 points [2], 2-3 points [1]

[2]

[Total: 11]

3 The equation for the reaction between bromine and methanoic acid is as follows:

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

It is hypothesised that the reaction is elementary. To prove this hypothesis, volumes of the two reactants were varied and the rate of the reaction is measured in terms of the rate at which the bromine concentration changes. When the total volume is kept constant, the following relationship is true.

$$\text{rate of reaction } \alpha \ \frac{\text{volume of bromine used}}{\text{time for color of bromine to disappear}}$$

The temperature of the reaction mixture was maintained at 25 °C.

The following results were obtained in three repeated experiments:

Expt	Volume of 1.0 mol dm^{-3} Br_2 / cm^3	Volume of 10.0 mol dm^{-3} HCOOH / cm^3	Volume of water added / cm^3	Relative time for colour of bromine to disappear
1	10	10	0	1.4
2	40	20	20	2.8
3	5	10	5	1.4

(a) By comparing the rates of reactions, explain how the results of the three experiments support the hypothesis that the reaction is elementary.

Expt	Vol. of 1.0 mol dm^{-3} Br_2 / cm^3	Vol. of 10.0 mol dm^{-3} HCOOH / cm^3	Vol. of water added / cm^3	Relative time for colour of bromine to disappear	Rate
1	10	10	0	1.4	10/1.4=7.14
2	40	20	20	2.8	
2a	40/4=10	20/4=5	20/4=5	2.8	10/2.8=3.57
3	5	10	5	1.4	5/1.4=3.57

Using expt 1 and 3,

When vol of Br_2 halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to Br_2, 1st order wrt Br_2.

Using expt 1 and 2a,

When vol of HCOOH halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to HCOOH, 1st order wrt HCOOH.

Since orders of reaction correspond to stoichiometric ratio of the overall equation, the reaction is elementary.

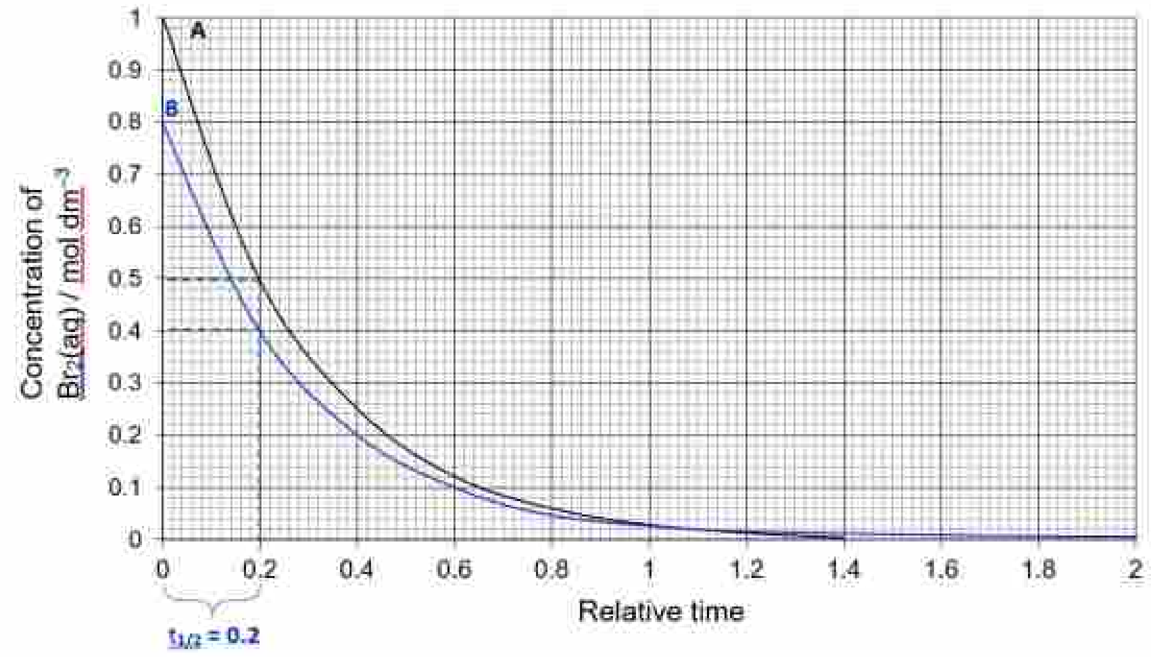
1 mark for finding order wrt Br_2

1 mark for finding order wrt HCOOH and deducing the hypothesis correctly

....

.... [3]

(b) During another experiment, the concentration of Br_2 was monitored over time and the following graph (Run **A**) was obtained. The concentration of HCOOH used was 10.0 mol dm^{-3}.



(i) Define the term "half-life".

Time taken for concentration of reactant to reach half its original concentration.

.... [1]

(ii) The experiment was repeated using 0.8 mol dm^{-3} of $Br_2(aq)$ and 10.0 mol dm^{-3} of HCOOH. On the axes above, draw the concentration-time graph of $Br_2(aq)$ for the new experiment and label it 'Run **B**'.

On your graph, clearly state and label the half-life of $Br_2(aq)$. [1]

Curve must show at least 2 constant half-lives. Only one half-life needs to be clearly labelled.

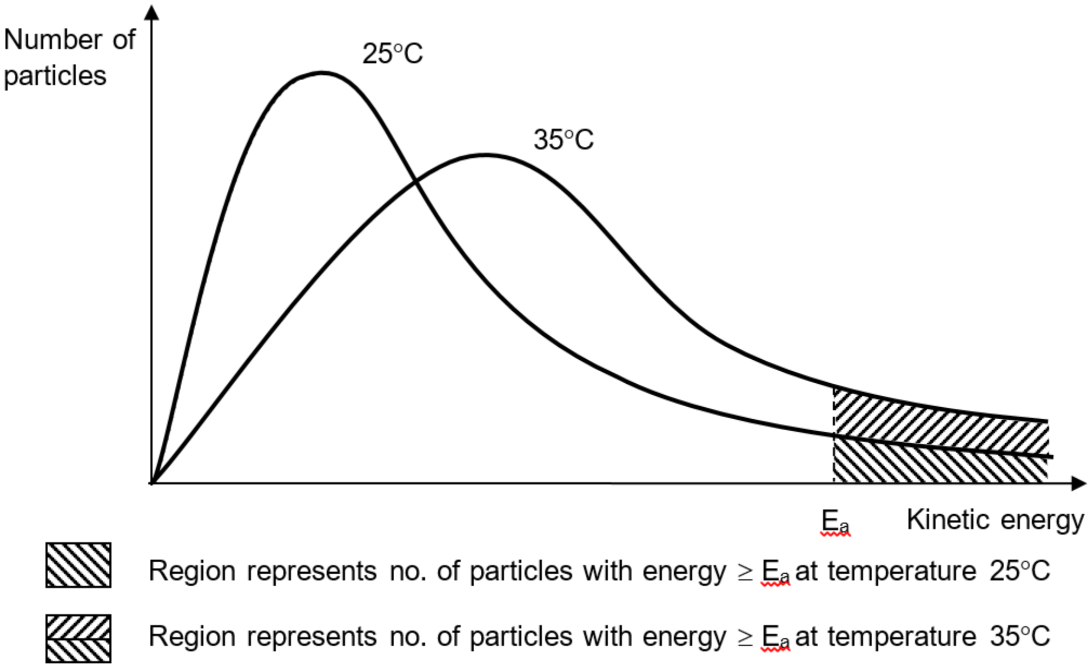
(iii) The experiment was repeated again using 1.0 mol dm^{-3} of $Br_2(aq)$ and 5.0 mol dm^{-3} of HCOOH (Run **C**). In comparison to Run **A**, state how the half-life of the experiment will change.

The reaction is a pseudo-first order reaction in which $\mathbf{t}_{1/2} = \dfrac{\ln 2}{k[HCOOH]}$

Hence if [HCOOH] halves, $t_{1/2}$ will double from 0.2 to 0.4.

.... [1]

(c) By drawing a suitable illustration, estimate and explain the change in rate of reaction when temperature is increased to 35 °C.



When the temperature increases by 10 °C,

⇒ the average kinetic energy of particles doubles

⇒ the shape of the Maxwell-Boltzmann curve flattens out such that double the number particles have energy ≥ E_a

⇒ the frequency of effective collisions doubles

⇒ Rate constant doubles, hence rate doubles

....

....

....

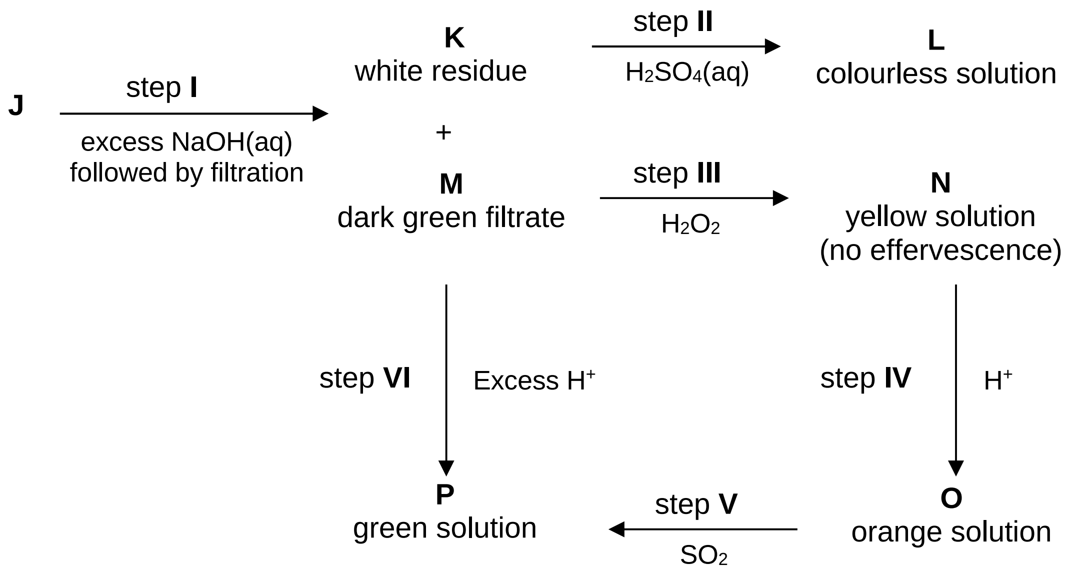
....

....

.... [3]

[Total: 9]

4(a) Solution **J** contains a Group 2 ion and a transition metal ion. The following reaction scheme shows how **J** reacts with some common reagents in the laboratory.



(i) State the identities of **K**, **L**, **M**, **N**, **O** and **P.**

K $Mg(OH)_2$.. **L** $MgSO_4$ or Mg^{2+}..........................

M $[Cr(OH)_6]^{3-}$.. **N** CrO_4^{2-} ....

O $Cr_2O_7^{2-}$ .... **P** Cr^{3+} or $[Cr(H_2O)_6]^{3+}$....................

[3]

6 correct [3]; 4, 5 correct [2]; 2, 3 correct [1] (Note: also accept Be for K & L)

[3]

(ii) State the roles of H_2O_2 and SO_2 in steps **III** and **V** respectively.

H_2O_2 in step **III**: oxidising agent ....

SO_2 in step **V**: reducing agent .... [1]

(iii) Write an ionic equation to explain the formation of solution **P** in step **V**.

$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1] .... [1]

(iv) Explain how solution **P** can be formed in step **VI**.

$Cr^{3+}(aq) + 3OH^-(aq) \quad Cr(OH)_3(s)$ (1)
or $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \quad Cr(H_2O)_3(OH)_3(s) + 3H_2O$
$Cr(OH)_3(s) + 3OH^-(aq) \quad Cr(OH)_6^{3-}(aq)$ (2)
When H^+ is added, it removes the excess $OH^-(aq)$ which was added. Position of equilibrium (2) will shift to the left to form grey-green ppt of $Cr(OH)_3$. [1]
When excess H^+ is added, it removes all the $OH^-(aq)$ in the solution. Position of equilibrium (1) will shift to the left forming green solution of Cr^{3+}. [1]

....

.... [2]

(b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.
For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

(i) Explain why the melting points of these elements decrease from carbon to germanium.

They have giant covalent structures with strong covalent bonds between atoms in a 3-dimensional network. [1] From carbon to germanium, the atomic radius increase and the bond length increase (C–C bond length < Si–Si bond length < Ge–Ge bond length), hence the covalent bond strength decrease from carbon to silicon to germanium. [1] Since the melting of these elements require breaking the covalent bonds between the respective atoms, the melting point decreases since less energy is required to break the weaker covalent bonds.

.... [2]

(ii) Explain how first ionisation energy changes from carbon to germanium.

Down the group from carbon to germanium,

- the number of protons increases, nuclear charge increases.
- As the number of electron shells increases, shielding effect increases significantly.
- The outermost electron is further away from the nucleus, hence attraction between the nucleus and outermost electron decreases
- The first ionisation energy decreases down a group.

4 points – [2]; 2,3 points – 1

.... [2]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts violently with water.

(iii) Write a balanced equation for the reaction of $SiCl_4$ with water.

$SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl$ [1] .... [1]

(iv) Suggest an explanation for the inertness of CCl_4 to water.

Water molecules could not form co-ordinate/dative bonds with the central carbon atom of CCl_4 because carbon is in period 2 and does not have energetically accessible low lying orbitals to accommodate lone pair of electrons from O atom in H_2O. [1]

....

.... [1]

[Total: 13]

5 Azo dyes are made in large quantites from benzene, C_6H_6, via nitrobenzene, $C_6H_5NO_2$ (density = 1.20 g cm^{-3}), and phenylamine, $C_6H_5NH_2$.

(a) The preparation of nitrobenzene requires benzene to be warmed under reflux at about 55 °C with a mixture of concentrated nitric and sulfuric acids. Some information about these substances is given below:

Benzene: immiscible with water; highly flammable; extremely toxic by ingestion or inhalation; known carcinogen.

Concentrated nitric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent. The acid contains about 30 % water by volume.

Concentrated sulfuric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent; dilution with water is very exothermic and can be dangerous.

(i) Nitric acid is placed in a suitable flask and sulfuric acid is added slowly with cooling of the flask. Explain why cooling is necessary.

To avoid the temperature rising too much OR the reaction between sulfuric acid and water is exothermic as the sulfuric acid is diluted by the water in nitric acid

....

.... [1]

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55 °C for 45 minutes under reflux with vigorous stirring of the reaction mixture.

Explain why the reflux condenser is necessary and also why the mixture is vigorously stirred.

Prevents escape of benzene / volatile liquids [1]
reactants are immisicible/do not mix/form separate layers so they need to be stirred to make reaction rate acceptable or increase frequency of effective collisions or increase the surface area of contact between the two immiscible layers or to enable the reactant molecules to collide with the correct orientation [1]

....

.... [2]

(iii) State, with a reason, **one** other precaution (other than wearing protective wear) that would be necessary when carrying out the experiment.

EITHER
benzene is toxic so use fume cupboard
OR
benzene/nitrobenzene is flammable so use heating mantle/water bath

....

.... [1]

(iv) The reaction mixture is then poured into a large excess of cold water, the liquid nitrobenzene layer is separated and *washed* with sodium carbonate solution. Explain why this washing is necessary.

sodium carbonate removes/neutralises (residual) acid [1]

.... [1]

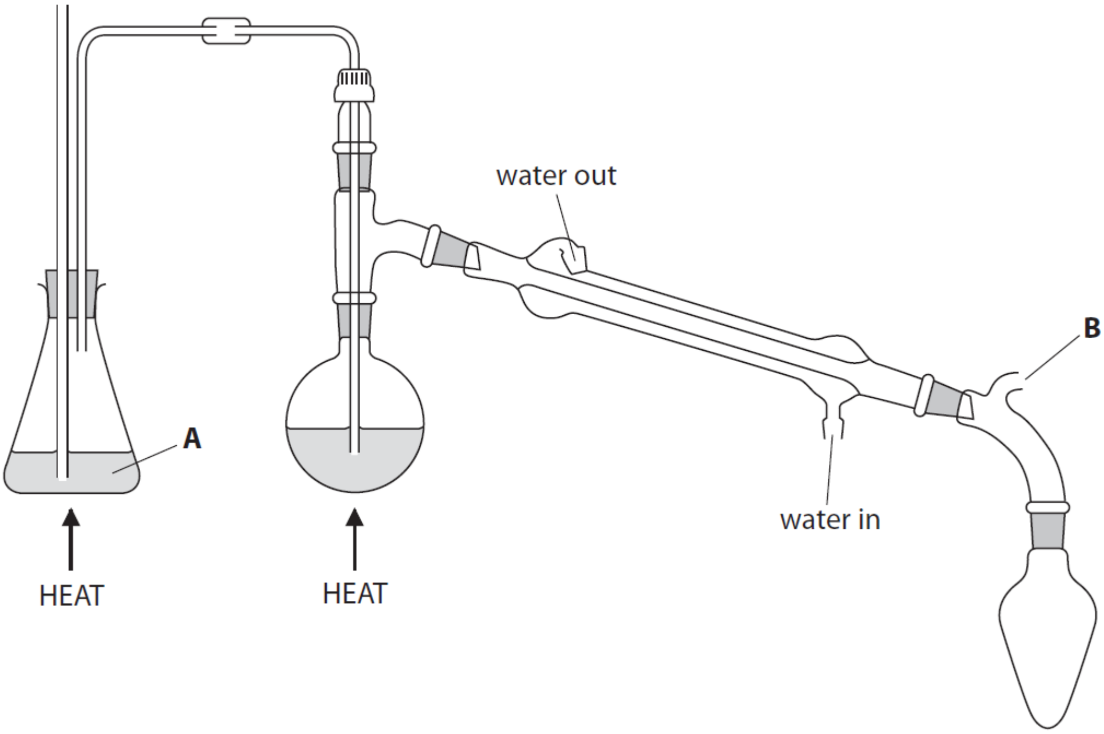
(v) The nitrobenzene layer is dried before being distilled to purify it. Identify a suitable drying agent.

(anhydrous) sodium sulfate / magnesium sulfate OR
(anhydrous) calcium chloride OR silica gel

.... [1]

(b) Steam distillation is a purification process to separate nitrobenzene from the reaction mixture. During the process of steam distillation, a current of steam is blown through a mixture containing the desired organic substance to be distilled. This caused the desired organic substance to vaporise. The vapour containing the desired organic substance can then be condensed and collected. This method is used predominantly to purify liquids that are not very volatile and are immiscible with water.

The diagram below shows a steam distillation apparatus used to extract nitrobenzene from the reaction mixture.



(i) Identify substance **A**.

water (to produce steam) .... [1]

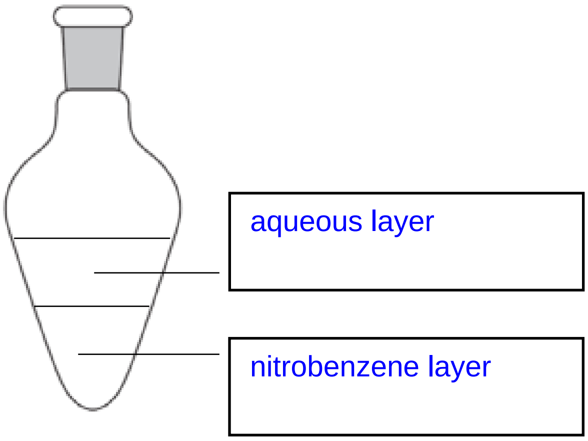
(ii) Explain the purpose of the part of the apparatus labelled **B**.

prevents pressure building up (by allowing gases/vapour to escape)
allow to prevent explosion

reject to allow gases/vapours to escape only
ignore the reference to 'air' for gases / vapours

.... [1]

(iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.



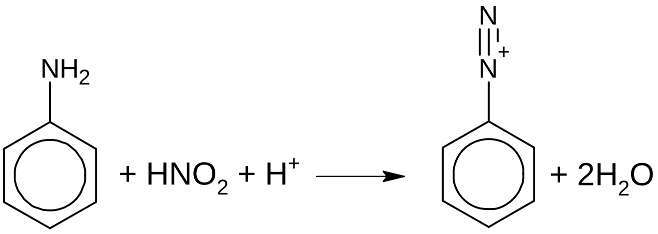
[1]

aqueous layer on top while nitrobenzene on bottom [1]

(c) The purified nitrobenzene is then reduced to phenylamine, $C_6H_5NH_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0 °C and 10 °C. Nitrous acid is generated in the reaction mixture from sodium nitrite and hydrochloric acid.

The ionic equation for the diazotisation of phenylamine to produce benzenediazonium ion is as shown below.

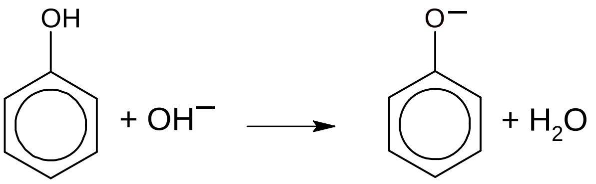


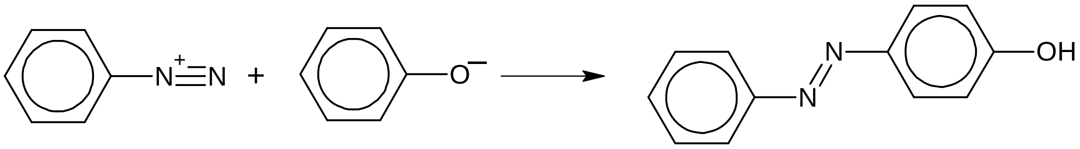
benzenediazonium ion

If the above reaction is warmed, benzenediazonium ion will undergo hydrolysis to give phenol. A gas will also be produced and the resulting mixture is acidic.

Reaction of the benzenediazonium compound with an alkaline solution of a phenol, C_6H_5OH, will produce a solid azo dye, which is purified by recrystallisation.

The equations for the reaction between benzenediazonium ion and phenol to produce the solid azo dye are shown below.





(i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.

Sn, conc. HCl, under under reflux (followed by addition of NaOH(aq) [1]

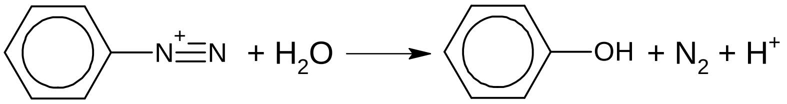
.... [1]

(ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0 °C.

< 0 °C reaction is too slow [1]
allow mixture freezes

.... [1]

(iii) Write an equation to show benzenediazonium ion undergoing hydrolysis upon warming.



.... [1]

(d) Purification by recrystallisation requires the following steps:

1. The azo dye is dissolved in a minimum volume of hot solvent.
2. The solution is filtered through a pre-heated funnel.
3. The solution is cooled and filtered using a Buchner funnel.
4. The solid is washed with a small amount of cold solvent.
5. The solid is dried in a desiccator.

(i) Explain why a **minimum** volume of hot solvent is used in step 1.

To prevent (much of the) azo dye remaining in solution on cooling
OR
Gives a saturated solution

....

.... [1]

(iii) Explain why the funnel must be pre-heated.

To prevent crystallization (of the azo dye) [1]

.... [1]

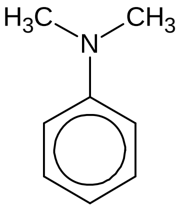
(iv) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

Decomposition could occur if the compound were to be heated
OR
Compound might melt

.... [1]

(e) This question compares the acidity and basicity of some organic compounds.

(i) Explain why an aqueous solution of N,N-dimethylphenylamine is more basic than an aqueous solution of phenylamine.



N,N-dimethylphenylamine

There are 2 electron-donating $-CH_3$ groups [pt 1] attached to the N atom in N,N-dimethylphenylamine. Hence the electron density on the N atom in N,N-dimethylphenylamine is higher [pt 2] than that in phenylamine. The lone pair of electrons on the N atom in N,N-dimethylphenylamine is more available [pt 3] for dative bonding with a H^+.

....

.... [1]

(ii) Explain why an aqueous solution of azo dye is more acidic than an aqueous solution of phenol.

This group, $C_6H_5N=N-$ is an electron-withdrawing [pt 4] group which further disperses the negative charge on the O atom [pt 5] in the conjugate base of azo dye. The conjugate base formed by the azo dye is further stabilized [pt 6]. The azo dye donates proton more readily [pt 7].

....

.... [2]

7 pts – 3 marks
5 – 6 pts – 2 marks
3 – 4 pts – 1 mark

[Total: 18]

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9~~64~~729/03

Paper 3 Free Response

~~21~~ 18 September 2018~~6~~

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2 hours

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, ~~highlighters,~~ glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
~~Answer any **four** questions.~~
~~A Data Booklet is provided.~~
~~You are reminded of the need for good English and clear presentation in your answers.~~

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

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Section A

Answer **all** questions in this section.

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1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C. ~~[3]~~

The details of the use of ~~No details regarding use of~~ specific glassware for measurement are **not** required. [3]

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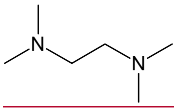
(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of NH_3 (aq), each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.
In your mechanism, show appropriate curly arrows, lone pairs and dipoles.
[3]

(v) State the rate equation for the above ligand exchange reaction. [1]

(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced ~~by~~with a fluoride ion. [1]

(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be ~~the~~ more spontaneous. Explain your reasoning. [3]

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard Cl_2|~~/~~Cl^- electrode and a standard Co^{2+}~~/~~|Co electrode. Indicate the direction of the electron flow. [3]

(ii) Calculate the $E^{\ominus}_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction. [~~1~~2]

(iii) Using your answer in **(ii)**, calculate ΔG for the cell reaction. [1]

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the Co^{2+}|~~/~~Co half cell. Explain your answer. [1]

[Total: 2~~1~~2]

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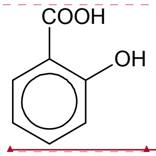
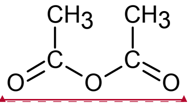
~~**Answer any four questions.**~~

~~1~~2**(a)** Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.

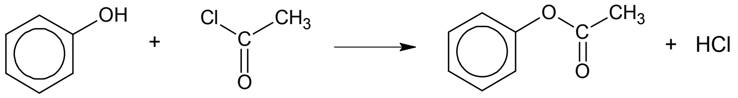


2-hydroxybenzoic acid



ethanoic anhydride

Ethanoyl chloride and phenol can undergo condensation reaction.



Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [3]

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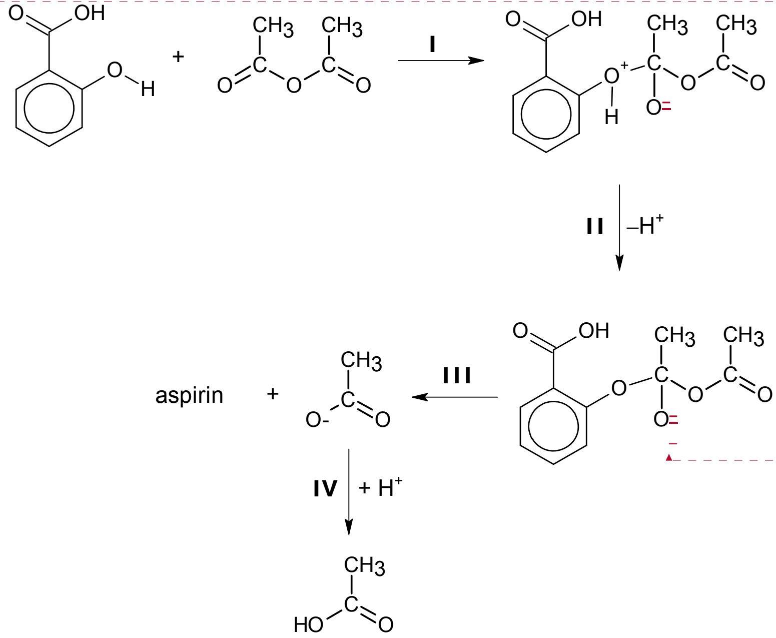
The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:



(iii) Using the information given above, state the type of mechanism in step **I**. [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.

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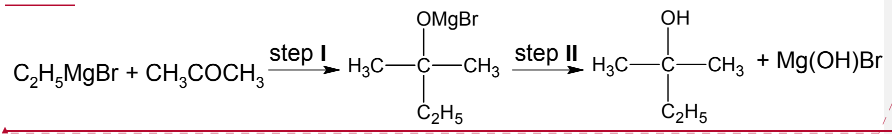
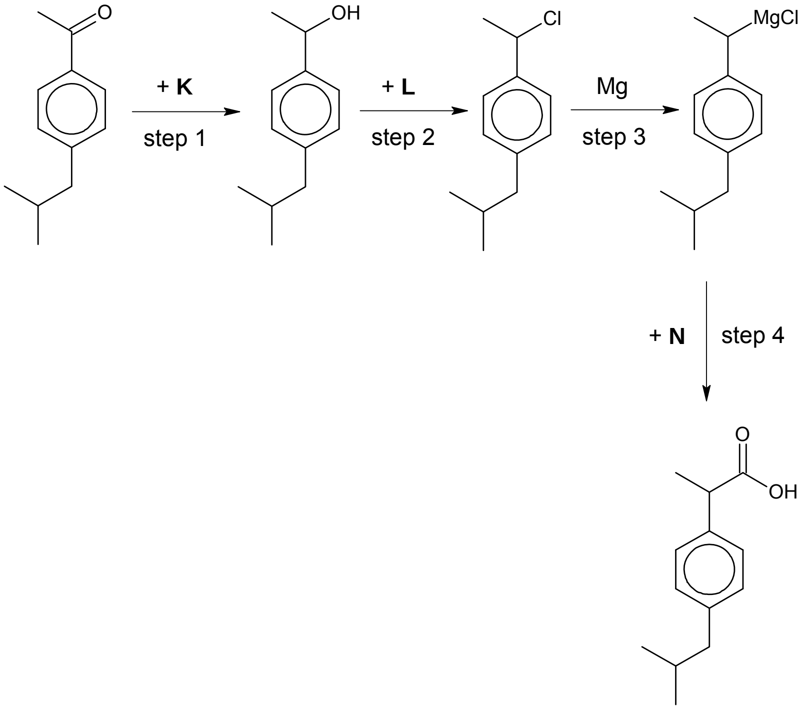


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step } \mathbf{I}} H_3C-\underset{C_2H_5}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{\text{step } \mathbf{II}} H_3C-\underset{C_2H_5}{\overset{OH}{C}}-CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step **II**. [1]

(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.



ibuprofen

(i) Suggest the identity of the reagent **K** in step 1. [1]

(ii) Suggest the identity of the reagent **L** in step 2. [1]

(iii) Suggest the identity of the reagent **N** in step 4. [1]

(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for **each** compound. [3]

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[Total: 16]

~~Copper(I) sulfate, Cu_2SO_4, can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.~~

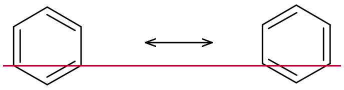
~~**(i)** Suggest, with a reason, the colour of copper(I) sulfate. [2]~~

~~**(ii)** Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]~~

~~**(b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $PdN_2H_6Cl_2$. Two of these, **A** and **B**, are non-ionic, with M_r = 211. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having M_r = 422, and contains palladium in both its cation and anion.~~

~~For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]~~

~~**(c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.~~

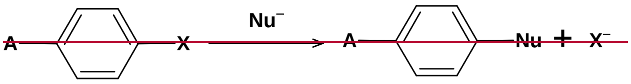


Benzene (two resonance forms)

~~The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.~~

~~Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.~~

~~An example of a reaction is as follows:~~

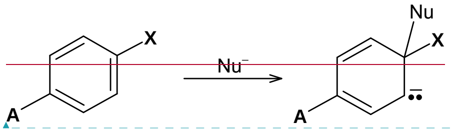


~~where **A** is an electron withdrawing group and **X** is a halogen~~

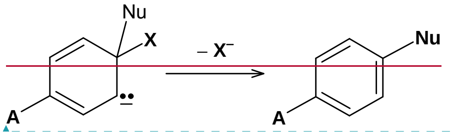
~~The mechanism of this reaction has two steps:~~

- ~~addition of the nucleophile~~
- ~~elimination of the halogen leaving group~~

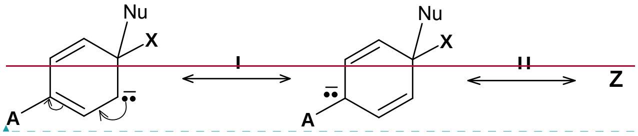
~~3 **Step 1** involves the addition of the nucleophile (Nu⁻). The Nu⁻ attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.~~



~~**Step 2** involves the loss of the halogen **X**, reforming the aromatic ring.~~

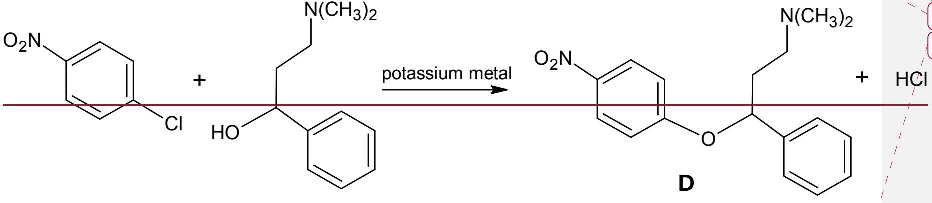


~~Two other resonance structures of the intermediate in **Step 1** are shown below:~~



~~**(i)** Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**.~~ ~~[2]~~

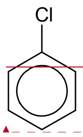
~~The reaction below shows the synthesis of compound, **D**.~~

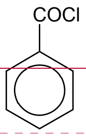


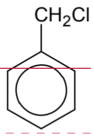
~~**(ii)** Suggest the role of potassium metal in the reaction.~~ ~~[1]~~

~~**(iii)** Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons.~~ ~~[3]~~

~~**(d)** Describe and explain the relative ease of hydrolysis of the following three chloro-compounds.~~ ~~[3]~~







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~~**2** Sulfuric acid, H_2SO_4, can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.~~

~~**(a)** Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]~~

~~**(b)** The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:~~

~~$2SO_2(g) + O_2(g)$ Ý $2SO_3(g)$ $\Delta H = –197$ kJ $mol^{–1}$~~

~~Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.~~

~~**(i)** Write an expression for the equilibrium constant, K_p, of the reaction.~~ [1]

~~**(ii)** Calculate the value of K_p at 400 °C, stating its units.~~ [3]

~~**(iii)** How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]~~

~~**(c)** Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO, BaO and SiO_2 .~~

~~State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid.~~ [4]

~~**(d)** Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:~~

~~$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(l)$ ΔH_1~~

~~Using the data below and data from **(b)**, construct an energy cycle to calculate~~

~~**(i)** the enthalpy change of formation of $SO_2(g)$, and hence~~

~~**(ii)** the enthalpy change of reaction, ΔH_1 for the above reaction.~~

~~Enthalpy change of formation of $H_2O(l)$ = –286 kJ $mol^{–1}$~~
~~Enthalpy change of formation of $H_2SO_4(l)$ = –811 kJ $mol^{–1}$~~
~~Enthalpy change of formation of $SO_3(g)$ = –493 kJ $mol^{–1}$~~
~~[4]~~

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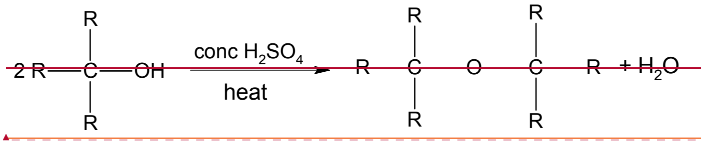
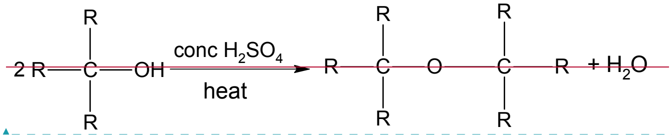
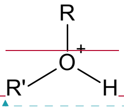
~~**(e)** Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.~~





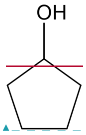
~~The mechanism occurs via 3 steps:~~

~~**Step 1:**~~
~~An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.~~

~~**Step 2:**~~
~~A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates an oxonium ion~~  ~~intermediate.~~

~~**Step 3:**~~
~~Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.~~

~~**(i)** Draw the ether formed when cyclopentanol undergoes the above reaction.~~



~~cyclopentanol~~
~~[1]~~

~~**(ii)** Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.~~ ~~[3]~~

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3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

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~~Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.~~

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:

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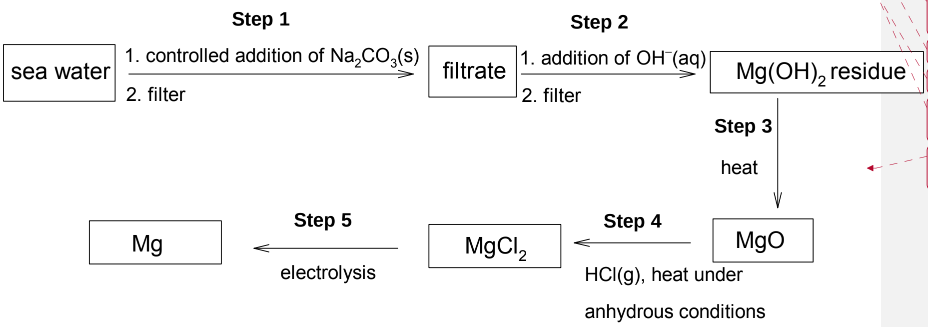

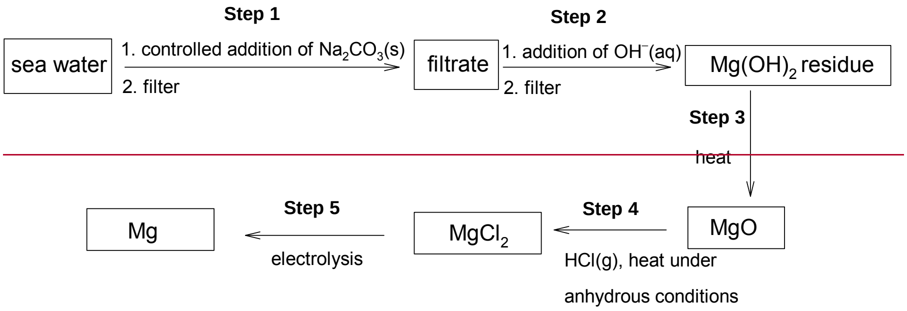

Concentration of common ions in sea water:

ion	**concentration / mol dm^{-3}**
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

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The numerical values of solubility products are given below:

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compound	**value of solubility product**
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}

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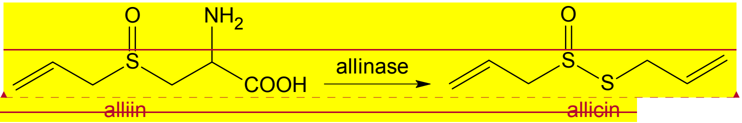
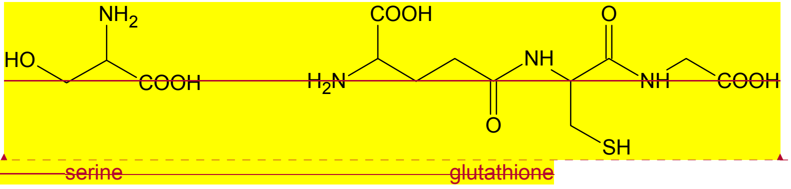
magnesium hydroxide	5.61×10^{-12}
calcium hydroxide	5.50×10^{-6}

~~When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.~~



~~Allicin can also be biosynthesised by using serine and glutathione.~~



~~(i) Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]~~

(i) Explain why the addition of sodium carbonate ~~ions~~ in **step 1** has to be controlled. [1]

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

~~(under controlled conditions)~~

~~sodium~~

[2]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in ~~S~~**step 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

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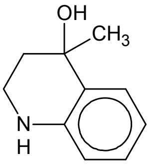
(c) ~~A is an organic compound.~~ When 0.46~~7~~8 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.

A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar~~ecular~~ mass of **A** is 177 g mol^{-1}. [1]

(ii) Hence, d~~D~~educe the structural formulae of all the above structures, and explain the chemistry involved. [6]

(iii) State the type of isomerism exhibited by **B** and **C.** Explain why **B** and **C** both give the same product **D** when reacted with HBr. [2]

[Total: 22]

~~**(ii)** When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae.~~
~~Draw the structural formula of **each** of these esters. [2]~~

~~**(iii)** Draw the structural formulae of the products when glutathione is hydrolysed. [3]~~

~~Alliin has pK_a values of 1.84 and 8.45.~~

~~**(iv)** Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]~~

- ~~pH 1~~
- ~~pH 7~~
- ~~pH 11~~

~~v) Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]~~

~~**(vi)** With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]~~

~~**(vii)** Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin.~~
~~Briefly describe how you have calculated the various key points on the curve. [4]~~

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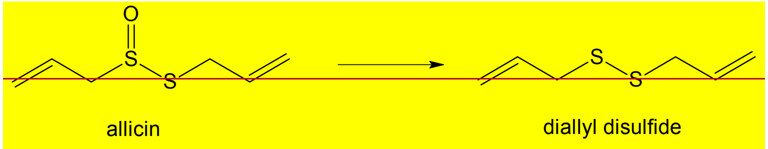
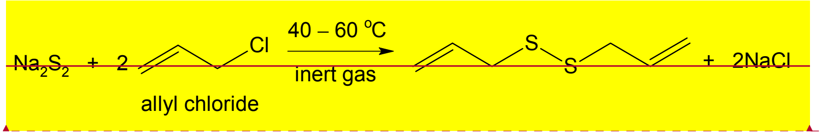
~~**(b)** Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of allicin.~~



~~Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 ¼C in an inert atmosphere.~~



~~(i) Give the *IUPAC* name of allyl chloride. [1]~~

~~(ii) Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]~~

~~(iii) State the type of reaction when diallyl disulfide is converted back to allicin. [1]~~

~~[Total: 20]~~

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Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term “homologous series”. [1]

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

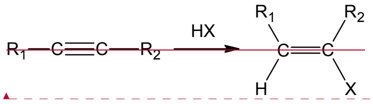
~~Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of~~ ~~C_nH_{2n-2}~~ ~~i.e.~~

~~$R_1-C\equiv C-R_2$~~

~~where R_1 and R_2 = H or alkyl or aryl groups~~

~~Alkynes exhibit similar chemical properties to alkenes.~~

~~e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes~~



~~e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids~~

~~$R_1-C\equiv C-R_2 \xrightarrow{KMnO_4} R_1COOH + R_2COOH$~~

~~However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.~~

~~$RC\equiv CH + NaNH_2 \longrightarrow RC\equiv C^-Na^+ + NH_3$~~

~~**(a)** Ethyne, C_2H_2, is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.~~

~~**(i)** Write an equation for the first stage. [1]~~

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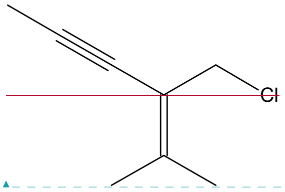
~~**(ii)** Suggest a structure for the dihalide formed. [1]~~

~~**(iii)** When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products.~~
~~Write an equation to explain the formation of these inorganic by-products. [1]~~

~~**(b)** Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).~~



~~Compound **A**~~

~~One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]~~

(c) ~~Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, $NaNH_2$ followed by heating under reflux to form compound **C**, C_8H_{10}. Compound **C** reacts with hot concentrated $KMnO_4$ to produce butane-1,4-dioic acid only.~~ Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

Cyclopropane is a colourless gas with a "petroleum-like" odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its "ring strain energy" using the formula below:

Ring strain energy =

$$\begin{matrix}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{matrix} \times \left(\left| \begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix} \right| - \left| \begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix} \right| \right)$$

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~~$\text{number of carbon atoms in cyclic alkane, A} \times \left(\left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix}\right| - \left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix}\right| \right)$~~

$$\begin{matrix}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{matrix} \times \left(\left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix}\right| - \left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix}\right| \right)$$

$$\begin{matrix}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{matrix} \times \left(\left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix}\right| - \left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix}\right| \right)$$

$$\begin{matrix}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{matrix} \times \left(\left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix}\right| - \left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix}\right| \right)$$

~~$\text{number of carbon atoms in cyclic alkane} \times \left(\left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane}\end{matrix}\right| - \left|\begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix}\right| \right)$~~

(d) Given that the ΔH_f of CO_2 is –94.05 kcal mol^{-1} and ΔH_f of water is –68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. ~~calculate the enthalpy change of formation of cyclopropane.~~ [2~~1~~]

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]

(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2. ~~Formation of methylene, CH_2, and N_2 from diazomethane, CH_2N_2.~~

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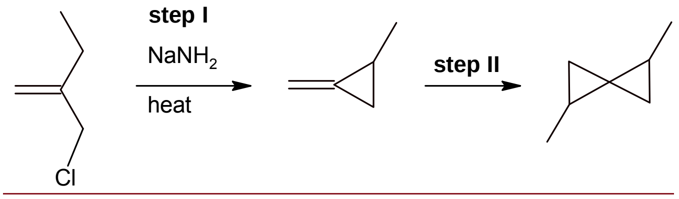
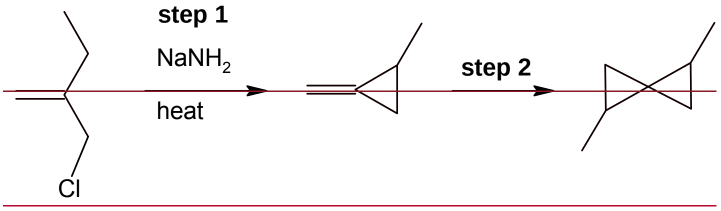
Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, d~~D~~raw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule. [1]

(ii) Draw the structure of the cyclic molecule formed in **s~~S~~tep 2**, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]

~~(h)~~ Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.





A **B**

(iii~~i~~) **Step I~~1~~** involves the reaction of molecule **A** with $NaNH_2$ to form NH_3 and a negatively-charged~~n~~ organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I~~1~~** and draw the organic intermediate that was formed. [2]

(iv~~i~~) By considering the reactivity of the Cl atom, explain why~~if~~ molecule **C** cannot be used to replace molecule **A** in the synthesis above.

[1~~2~~]

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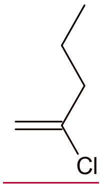
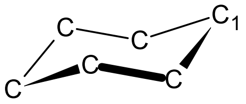


C

(v) Using the above information,
s~~S~~uggest a suitable reagent for **step II~~2~~**. [1]

(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the "chair shape" arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing ~~in~~ the 3-D arrangement of hydrogen atoms bonded to~~for~~ C_1, explain why cyclohexane does not experience ring strain.

[2~~2~~]

~~**(i)** Explain the reaction with $NaNH_2$. [1]~~

~~**(ii)** Hence, explain the formation of compound **C**. [1]~~

~~**(iii)** Suggest skeletal structures for compounds **B** and **C**. [2]~~

~~When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH=CHCO_2K$) for 15 minutes, it was found that 110 cm³ H_2, measured at r.t.p, was collected at the cathode. The following reaction took place.~~

$$\cancel{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$$

~~**(d)** State the relationship between the Faraday constant, *F* and the Avogadro's constant, *L*. [1]~~

~~**(e)** Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]~~

~~**(f)** Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:~~

- ~~mass of NaOH before experiment = 10.501 g~~
- ~~mass of NaOH after experiment = 10.904 g~~
- ~~initial reading on syringe = 10.0 cm³~~
- ~~final reading on syringe = 120.0 cm³~~

~~**(i)** State the oxidation state of carbon in ethyne. [1]~~

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~~**(ii)** With the help of an equation, explain the purpose of passing the anode gas through NaOH. [1]~~

~~**(iii)** Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]~~

~~**(iv)** Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]~~

~~**(g)** When aqueous potassium maleate was acidified, maleic acid, $HO_2CCH=CHCO_2H$ (pK_{a1} = 1.90 and pK_{a2} = 6.07) was liberated. Fumaric acid (pK_{a1} = 3.03 and pK_{a2} = 4.44) is a stereoisomer of maleic acid.~~

~~With a suitable illustration, suggest a reason why maleic acid has a lower pK_{a1} but higher pK_{a2} than fumaric acid.~~

~~[2]~~

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5(a) ~~Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.~~

The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail ~~for~~ this difference. [1]

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is –24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

~~Below is a synthetic route involving L-DOPA and dopamine:~~

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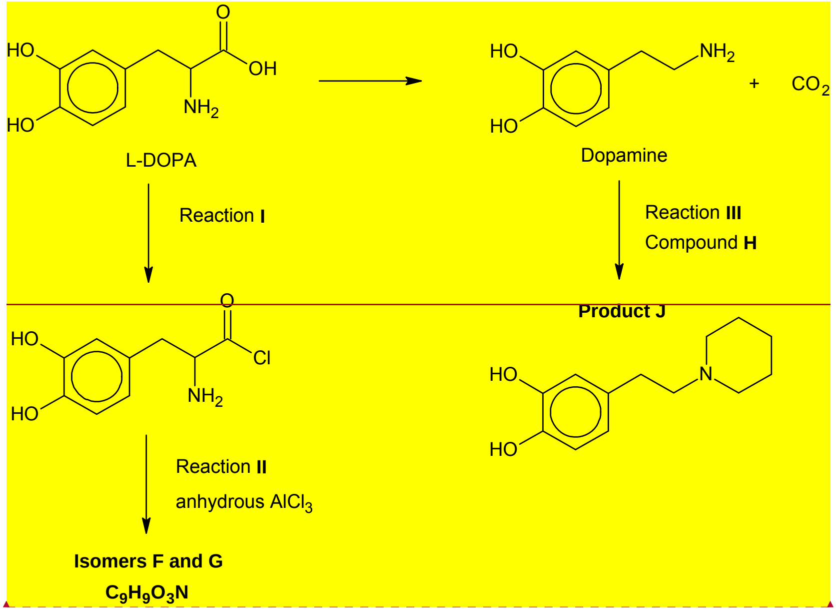
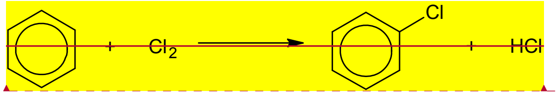


~~**(i)** State the reagents and conditions and any observations in Reaction **I**. [1]~~

~~**(ii)** Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.~~



~~The reaction occurs in several steps.~~

- ~~The first step is the reaction between Cl_2 and $AlCl_3$.~~

~~$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$~~

- ~~The benzene ring is then attacked by the Cl^+ cation in the second step.~~

~~$AlCl_3$ reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.~~

~~Predict the structures of isomers **F** and **G** in Reaction **II**. [2]~~

~~**(iii)** In Reaction **III**, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]~~

(iii) Explain why your answer in **(ii)** ~~does not correspond~~is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

(b) ICl reacts with pure water to form HCl and HI:

$$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g) \qquad \Delta H_r = +171.2\ kJ\ mol^{-1}$$

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Using ΔH_r, the following data, as well as relevant data from **a(ii)**, draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]

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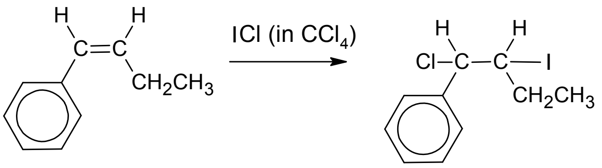
(~~b~~c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.

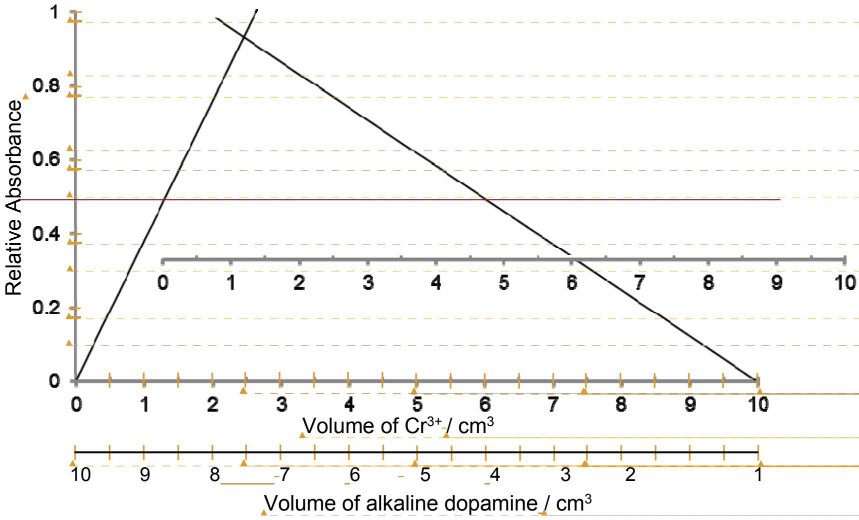


E

(i) Describe the mechanism for the formation of **E**. [3]

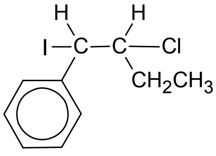
~~**(ii)** Dopamine is a bidentate ligand. When different volumes of 0.0030 mol dm^{-3} of aqueous Cr(III) and 0.0020 mol dm^{-3} of alkaline dopamine solution were mixed, a complex R is formed. Analysis of R shows that its formula is [Cr($C_8H_9NO_2$)$_x$(H_2O)$_y$]$^{z+}$, where x, y and z are integers.~~

~~To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.~~



~~**(i)** Use the graph and the information given to determine the formula of complex R. Show your workings clearly.~~ [3]

With the aid of a diagram, explain why **E** is formed and not **F**. [2]



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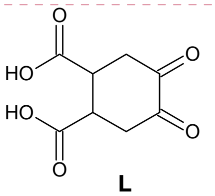
(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

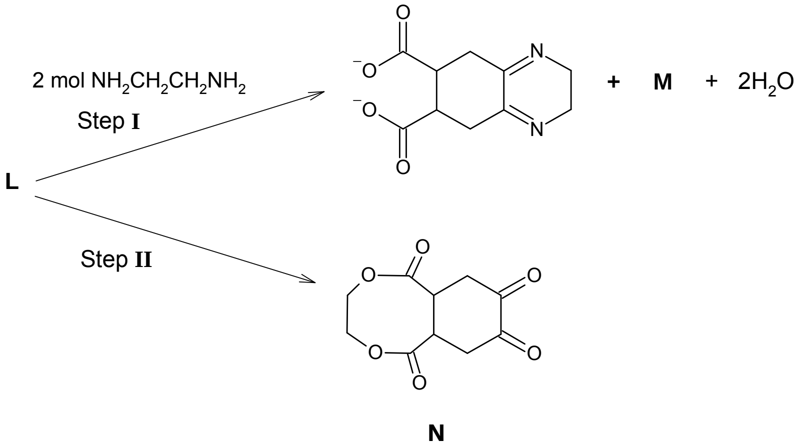
K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.



L

Suggest structures for **J** and **K** and explain the reactions described. [5]

(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



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(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

~~**(ii)** The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o. The relationship between Δ_o and colours of complexes can be described in the equation below:~~

$$\cancel{\Delta_o = \frac{hc}{\lambda}}$$

~~where h is Planck's constant, *c* is the speed of light and λ is the wavelength of light absorbed~~

~~colour~~	~~absorbed λ / nm~~
~~violet~~	~~410~~
~~indigo~~	~~430~~
~~blue~~	~~480~~
~~blue-green~~	~~500~~
~~green~~	~~530~~
~~yellow~~	~~580~~
~~orange~~	~~610~~
~~red~~	~~680~~

~~Given that Δ_o for complex **R** is 4.125 x 10^{-22} kJ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**.~~ [2]

~~**(c)** Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:~~

$$\cancel{I^-(aq) + I_2(s) \rightleftharpoons I_3^-(aq)}$$

~~**(i)** Draw a fully labelled experimental set-up for a voltaic cell made up of a $Cr_2O_7^{2-}$ / Cr^{3+} half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons.~~ [3]

~~**(ii)** By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to the I_2/I^- half-cell.~~ [3]

~~**(d)** Explain the following statements.~~

~~**(i)** BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity.~~ [2]

~~**(ii)** $SiCl_4$ reacts violently in water but CCl_4 has no reaction with water.~~ [1]

~~**(iii)** Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist.~~ [1]

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NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9~~64~~729/03

Paper 3 Free Response

~~21 ~~18 September 2018~~6~~

2 hours

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Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, ~~highlighters, ~~glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
~~Answer any **four** questions.~~
~~A Data Booklet is provided.~~
~~You are reminded of the need for good English and clear presentation in your answers.~~

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

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Section A

Answer **all** questions in this section.

1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt-(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

- The presence of ligands causes the energy level of the five 3d orbitals to be split into two different levels (crystal field splitting).
- The energy difference, ΔE, corresponds to wavelengths in the visible spectrum.
- When light energy is absorbed by the substance, an electron is promoted from a d orbital of lower to one of higher energy (d-d transition)
- Unabsorbed wavelengths are transmitted and the colour of the complex is complementary to the colour absorbed.

[3] for 4 marking points
[2] for 3 marking points
[1] for 2 marking points

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

- Different ligands give rise to a difference in the splitting of the *d*-orbitals, cause a different energy gap (ΔE).
- A different wavelengths of visible light is absorbed and thus a different wavelength of light is observed.

[1] for 2 marking points

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C.

~~[3]~~

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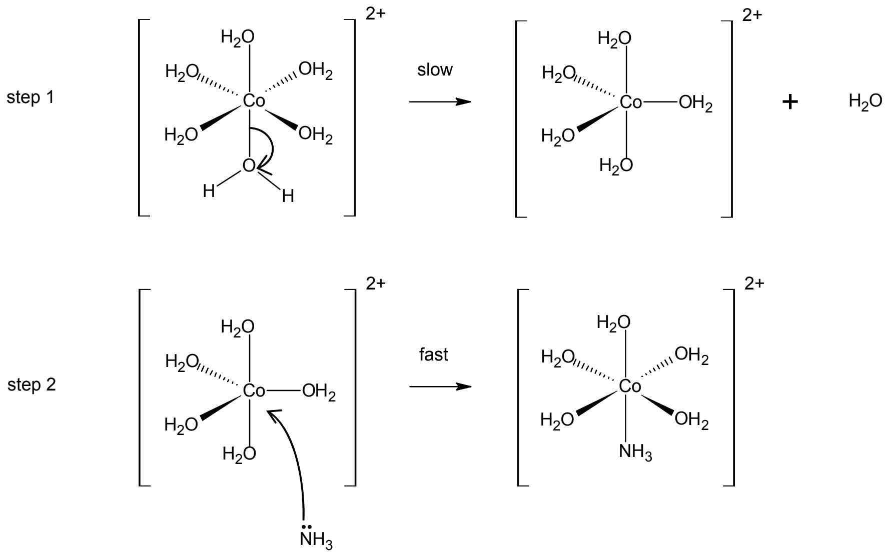
The details of the use of ~~No details regarding use of~~ specific glassware for measurement are **not** required. [3]

- Spectrometer is set up to absorb the wavelength of violet (monitoring product) or green (monitoring reactant) and maintain the temperature of the sample at 5 °C.
- Separate solutions of $[Co(H_2O)_6]^{2+}$ and NH_3 are cooled to 5 °C in an ice-water bath.
- Stoichiometric amounts of $[Co(H_2O)_6]^{2+}$ and NH_3 (or excess NH_3) are mixed and swirled. A few cm^3 of the coloured solution is quickly placed into the spectrometer.
- A stop watch is started.
- The concentration of $[Co(H_2O)_6]^{2+}$ (or $[Co(NH_3)_6]^{2+}$) is then determined by measuring the absorbance of the reaction mixture at time = 0 minute and then at regular time intervals (e.g. every 5 minutes), to obtain at least 5 measurements.
- A graph of absorbance value against time is plotted.
- The initial rate is found by drawing a tangent at time = 0 minute.

7 marking points
[1] for 2 marking points

(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of NH_3(aq), each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.
In your mechanism, show appropriate curly arrows, lone pairs and dipoles. [3]



Square pyramidal intermediate is accepted as well.

[1] for correct shapes
[1] for arrows and lone pair on NH_3

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[1] for intermediate and side product

(v) State the rate equation for the above ligand exchange reaction. [1]

rate = k $[[Co(H_2O)_6]^{2+}]$ [1]

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(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced ~~by~~with a fluoride ion. [1]

The rate of reaction remains constant as the rate is independent of the incoming ligand. [1]

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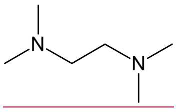
(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be ~~the~~ more spontaneous. Explain your reasoning. [3]

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$

$[Co(H_2O)_6]^{2+} + 3TMEDA \rightleftharpoons [Co(TMEDA)_3]^{2+} + 6H_2O$

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ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ is similar in magnitude and sign due to the breaking of 6 similar Co—O bonds and forming of 6 similar Co—N bonds. [1]

ΔS for formation of $[Co(TMEDA)_3]^{2+}$ would be more positive than that of $[Co(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles when $[Co(TMEDA)_3]^{2+}$ is formed, allowing more ways of arranging the particles. [1]

Since ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ are similar in magnitude and sign and ΔS for formation of $[Co(TMEDA)_3]^{2+}$ is more positive than that of $[Co(NH_3)_6]^{2+}$, ΔG for formation of $[Co(TMEDA)_3]^{2+}$ would be more negative than that of $[Co(NH_3)_6]^{2+}$ and hence more spontaneous. [1]

~~ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ is similar in magnitude due to breaking of similar Co—O bonds and forming of similar Co—N bonds. [1]~~

~~ΔS for formation of $[Co(TMEDA)_3]^{2+}$ would be more positive than that of $[Co(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles as $[Co(TMEDA)_3]^{2+}$ is formed, allowing more ways of arranging the particles. [1]~~

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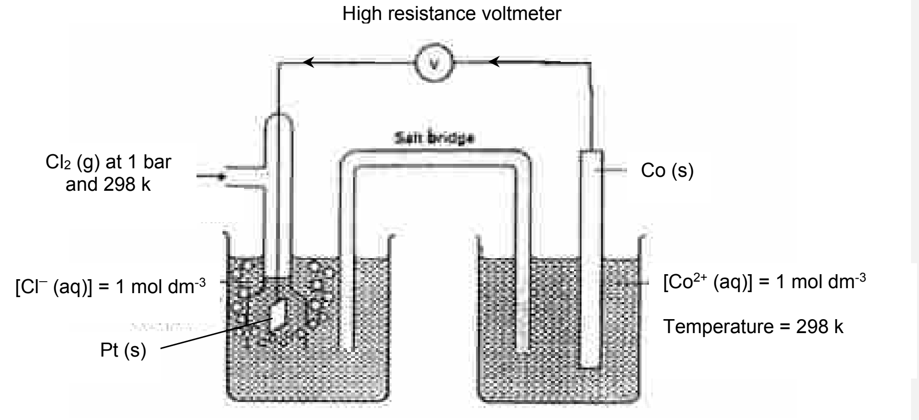
~~Since ΔH for formation of [Co(NH$_3$)$_6$]$^{2+}$ and [Co(TMEDA)$_3$]$^{2+}$ are similar in magnitude and ΔS for formation of [Co(TMEDA)$_3$]$^{2+}$ is more positive than that of [Co(NH$_3$)$_6$]$^{2+}$, ΔG for formation of [Co(TMEDA)$_3$]$^{2+}$ would be more negative than that of [Co(NH$_3$)$_6$]$^{2+}$ and hence more spontaneous. [1]~~

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard Cl$_2$|~~/~~Cl$^-$ electrode and a standard Co^{2+}~~/~~|Co electrode. Indicate the direction of the electron flow. [3]



[1] correct set-up
[1] concentration of ions, 298 and 1 bar
[1] electron flow

(ii) Calculate the $E^{\ominus}_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction.
[~~1~~2]

E_{cell} = +1.36 – (–0.28) = +1.64 V [1]

$Co + Cl_2 \rightarrow Co^{2+} + 2Cl^-$
~~$Co^{2+} + 2Cl^- \rightarrow Co + Cl_2$ [1]~~

(iii) Using your answer in **(ii)**, calculate ΔG for the cell reaction. [1]

Overall 2 mol of electrons are transferred.

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$\Delta G = -nFE_{cell} = -2 \times 96500 \times 1.64 = -317\,000$ J $mol^{-1} = -317$ kJ mol^{-1}

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the Co^{2+}|~~/~~Co half cell. Explain your answer. [1]

$Co^{2+} + 2e \rightleftharpoons Co \qquad E^{\ominus} = -0.28$ V

$[Co(NH_3)_6]^{2+} + 2e \rightleftharpoons Co + 6NH_3 \qquad E^{\ominus} = -0.43$ V

In the presence of ammonia ligands, Co^{2+} undergoes ligand exchange to form a more stable complex ion of $[Co(NH_3)_6]^{2+}$. The $E^{\ominus}$(Co^{2+}|Co) becomes more negative and the Ecell becomes more positive.

Or

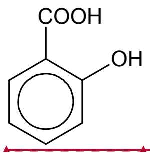
The formation of $[Co(NH_3)_6]^{2+}$ decreases the concentration of Co^{2+}. This caused the position of equilibrium for $Co^{2+} + 2e \rightleftharpoons Co$ to shift left. The $E^{\ominus}$(Co^{2+}|Co) becomes more negative and the Ecell becomes more positive.

[Total: 2~~1~~2]

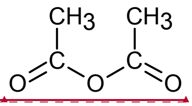
~~**Answer any four questions.**~~

~~1~~2(a) Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.

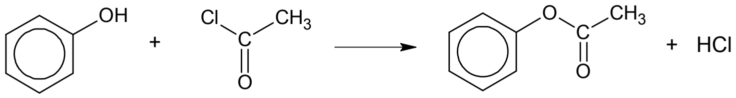


2-hydroxybenzoic acid



ethanoic anhydride

Ethanoyl chloride and phenol can undergo condensation reaction.



Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

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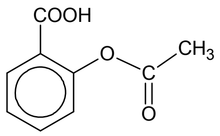
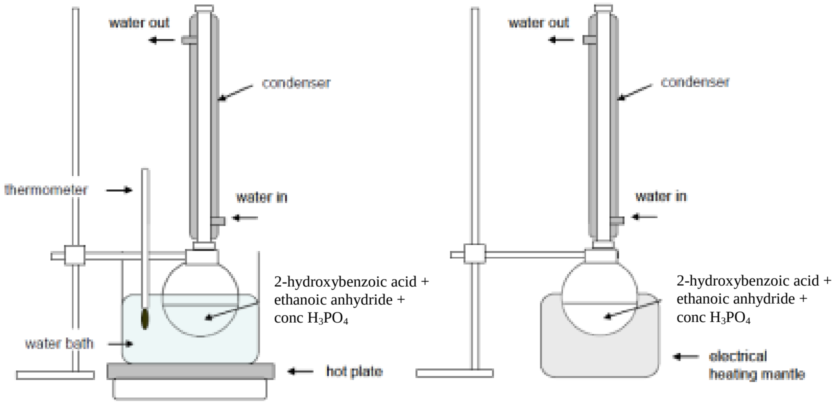


(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [3]



[1] flask fitted with Liebig condenser
[1] clear label of water entering and leaving the condenser in a correct manner
[1] correct heat source (thermostated water bath if thermometer is not drawn)

The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:

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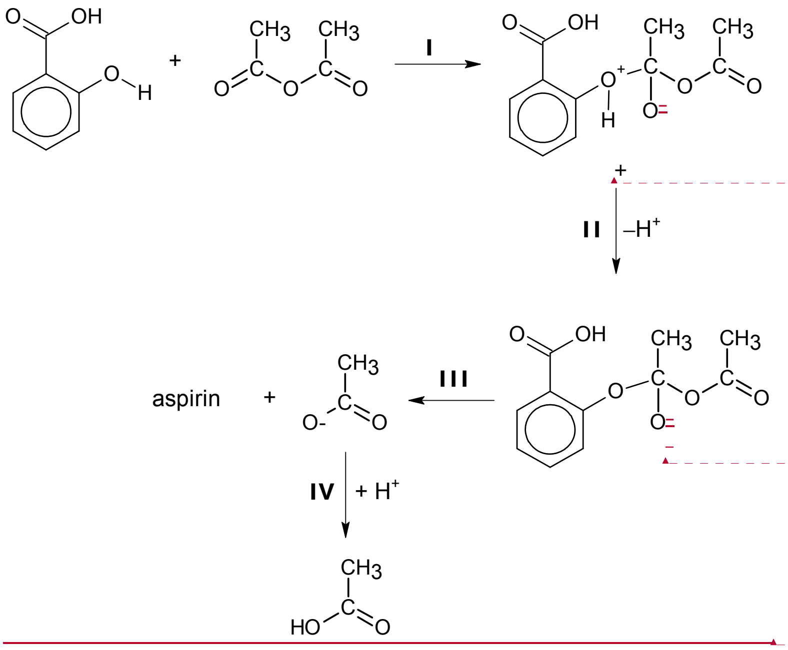

(iii) Using the information given above, state the type of mechanism in step **I**. [1]

Nucleophilic addition [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

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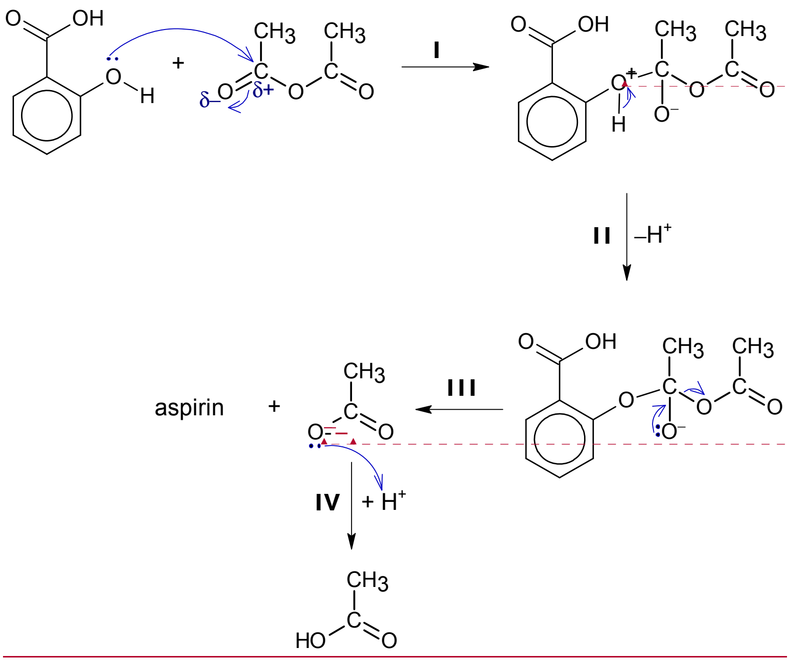
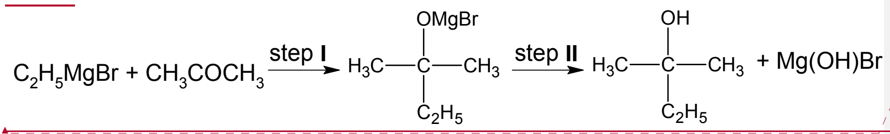


4 steps: 3 marks; 3 steps: 2 mark; 2 steps: 1 mark

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

Safer because ethanoic anhydride is less corrosive as it does not produce corrosive and poisoning / toxic fumes of HCl [1] and less readily hydrolysed.

(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C-\overset{\overset{\large OMgBr}{|}}{\underset{\underset{\large C_2H_5}{|}}{C}}-CH_3 \xrightarrow{\text{step II}} H_3C-\overset{\overset{\large OH}{|}}{\underset{\underset{\large C_2H_5}{|}}{C}}-CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step **II**. [1]

Hydrolysis [1]

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(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.

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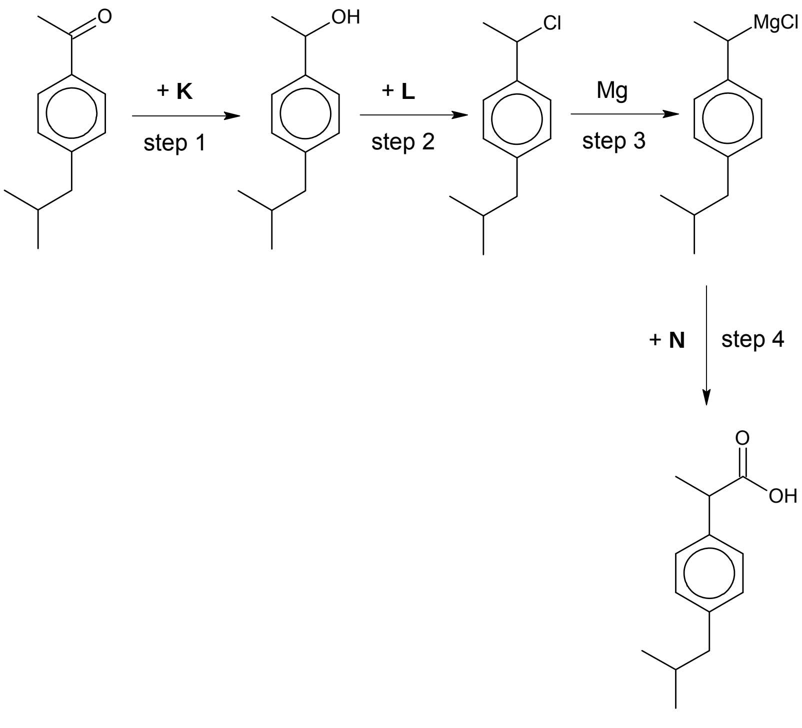

ibuprofen

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(i) Suggest the identity of the reagent **K** in step 1. [1]

$NaBH_4$ [1]

(ii) Suggest the identity of the reagent **L** in step 2. [1]

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PCl_5 or $SOCl_2$ [1]

(iii) Suggest the identity of the reagent **N** in step 4. [1]

CO_2 [1]

(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for **each** compound. [3]

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1. Add H_2SO_4(aq), heat [1] – test
2. Distill

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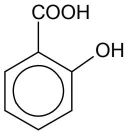


Product obtained from aspirin: CH_3COOH,

3. Add Br_2(aq).

Orange Br_2 decolourises with aspirin; Orange Br_2 remains for ibuprofen. [1]

[Total: 16]

~~Copper(I) sulfate, Cu_2SO_4, can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.~~

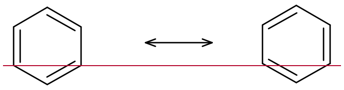
~~**(i)** Suggest, with a reason, the colour of copper(I) sulfate. [2]~~

~~**(ii)** Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]~~

~~**(b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $PdN_2H_6Cl_2$. Two of these, **A** and **B**, are non-ionic, with M_r = 211. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having M_r = 422, and contains palladium in both its cation and anion.~~

~~For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]~~

~~**(c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.~~

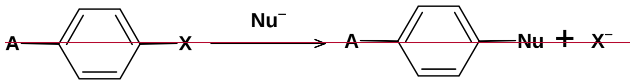


Benzene (two resonance forms)

~~The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.~~

~~Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.~~

~~An example of a reaction is as follows:~~



~~where **A** is an electron withdrawing group and **X** is a halogen~~

~~The mechanism of this reaction has two steps:~~
- ~~addition of the nucleophile~~
- ~~elimination of the halogen leaving group~~

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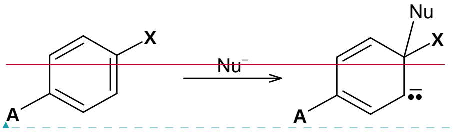
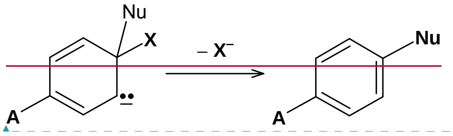
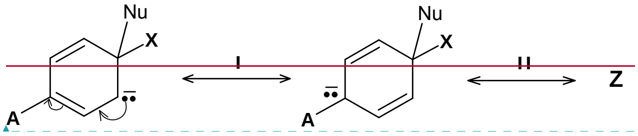
3 ~~**Step 1** involves the addition of the nucleophile (Nu⁻). The Nu⁻ attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.~~



~~**Step 2** involves the loss of the halogen **X**, reforming the aromatic ring.~~

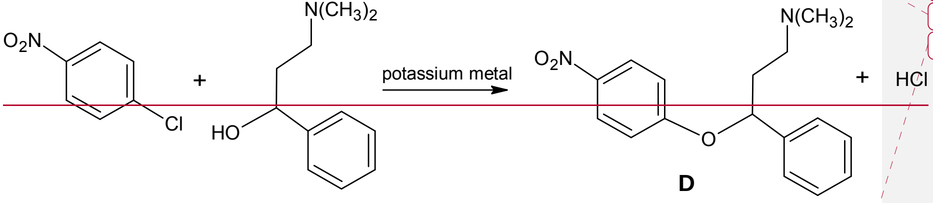


~~Two other resonance structures of the intermediate in **Step 1** are shown below:~~



~~**(i)** Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**.~~ ~~[2]~~

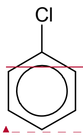
~~The reaction below shows the synthesis of compound, **D**.~~

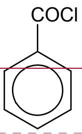


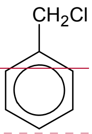
~~**(ii)** Suggest the role of potassium metal in the reaction.~~ ~~[1]~~

~~**(iii)** Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons.~~ ~~[3]~~

~~**(d)** Describe and explain the relative ease of hydrolysis of the following three chloro-compounds.~~ ~~[3]~~







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~~**2** Sulfuric acid, H_2SO_4, can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.~~

~~**(a)** Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom.~~ ~~[2]~~

~~**(b)** The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:~~

~~$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\Delta H = -197\ \text{kJ mol}^{-1}$~~

~~Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.~~

~~**(i)** Write an expression for the equilibrium constant, K_p, of the reaction.~~ ~~[1]~~

~~**(ii)** Calculate the value of K_p at 400 °C, stating its units.~~ ~~[3]~~

~~**(iii)** How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain.~~ ~~[2]~~

~~**(c)** Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO, BaO and SiO_2.~~

~~State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid.~~ ~~[4]~~

~~**(d)** Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:~~

~~$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(l)$ ΔH_1~~

~~Using the data below and data from **(b)**, construct an energy cycle to calculate~~

~~**(i)** the enthalpy change of formation of $SO_2(g)$, and hence~~

~~**(ii)** the enthalpy change of reaction, ΔH_1 for the above reaction.~~

~~Enthalpy change of formation of $H_2O(l)$ = $-286\ \text{kJ mol}^{-1}$~~
~~Enthalpy change of formation of $H_2SO_4(l)$ = $-811\ \text{kJ mol}^{-1}$~~
~~Enthalpy change of formation of $SO_3(g)$ = $-493\ \text{kJ mol}^{-1}$~~
~~[4]~~

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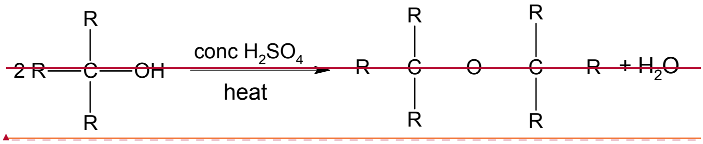
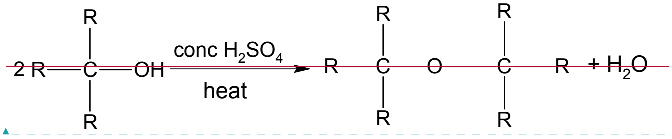
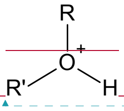
~~**(e)** Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.~~





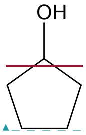
~~The mechanism occurs via 3 steps:~~

~~**Step 1:**~~
~~An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.~~

~~**Step 2:**~~
~~A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates an oxonium ion~~  ~~intermediate.~~

~~**Step 3:**~~
~~Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.~~

~~**(i)** Draw the ether formed when cyclopentanol undergoes the above reaction.~~



~~cyclopentanol~~
~~[1]~~

~~**(ii)** Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]~~

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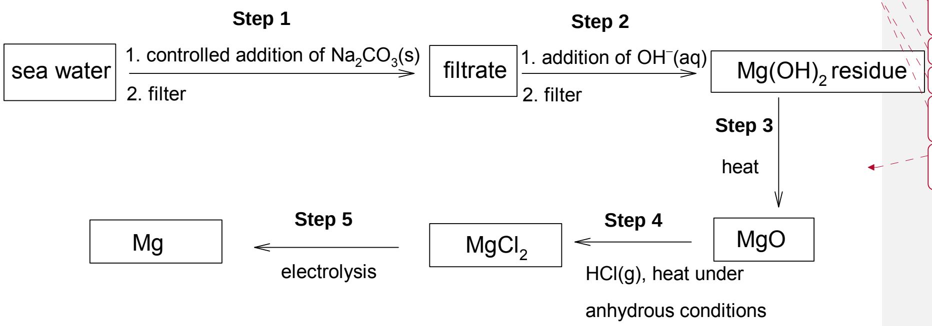
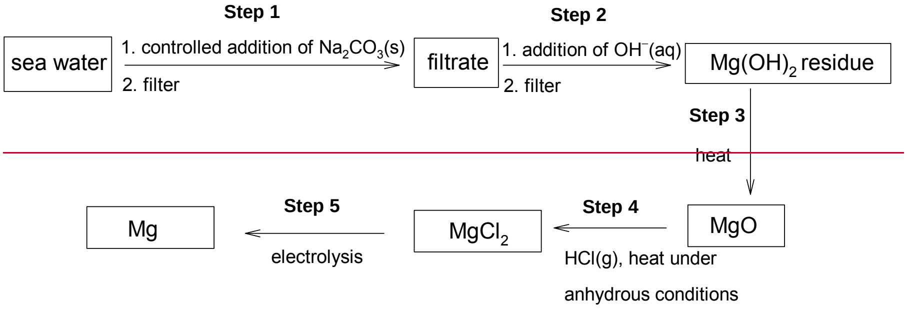
3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

~~Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.~~

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:





Concentration of common ions in sea water:

ion	**concentration / mol dm^{-3}**
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

The numerical values of solubility products are given below:

compound	**value of solubility product**
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}

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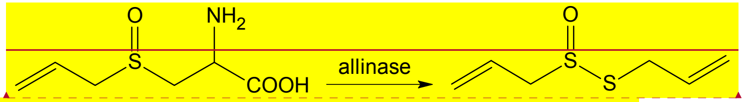
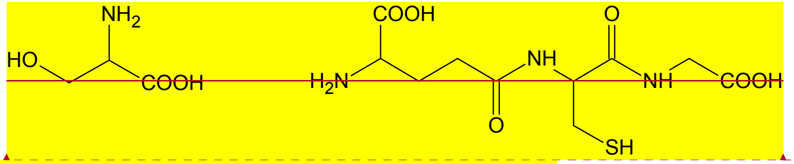
magnesium hydroxide	5.61×10^{-12}
calcium hydroxide	5.50×10^{-6}

~~When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.~~



~~alliin~~ ~~allicin~~

~~Allicin can also be biosynthesised by using serine and glutathione.~~



~~serine~~ ~~glutathione~~

~~**(i)** Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]~~

(i) Explain why the addition of sodium carbonate ~~ions~~ in **step 1** has to be controlled. [1]

If too much carbonate ions was added, both $MgCO_3$ and $CaCO_3$ will be precipitated.

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

Na^+ and Mg^{2+}

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

The $[CO_3^{2-}]$ must be controlled such that only calcium carbonate precipitates out, leaving $MgCO_3$ in the solution.

$$K_{sp} = \left[Mg^{2+}\right]\left[CO_3^{2-}\right]$$

$$\text{maximum}\left[CO_3^{2-}\right] = \frac{K_{sp}}{\left[Mg^{2+}\right]} = \frac{1.0\times10^{-5}}{0.056} = 1.785\times10^{-4} \quad [1]$$

$$m_{CaCO_3} = 1.785\times10^{-4}\times100.1 = 0.0179\text{ g} \quad [1]$$

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

~~(under controlled conditions)~~

~~sodium~~

[2]

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Comparing the K_{sp} of the 2 carbonates, $CaCO_3$ is less soluble and will be precipitated out first, leaving the Mg^{2+} ions in solution, and can be further purified via other steps. [1]

If hydroxide ions was added before carbonate ions, $Mg(OH)_2$ having a smaller K_{sp} value than $Ca(OH)_2$ will be less soluble and precipitate out first, together with other solid impurities in sea water, leading to an impure product. [1]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

Assume $[Mg^{2+}] = 0.056$ mol dm^{-3} (from table)

After adding equal volume of hydroxide ions, $[Mg^{2+}]_{new} = \frac{0.056}{2} = 0.028 \text{ mol dm}^{-3}$

$$K_{sp} = \left[Mg^{2+}\right]\left[OH^{-}\right]^2$$

$$\left[OH^{-}\right] = \sqrt{\frac{K_{sp}}{\left[Mg^{2+}\right]}} = \sqrt{\frac{5.61\times10^{-12}}{0.028}} = 1.415\times10^{-5} \quad [1]$$

$$\left[OH^{-}\right]\text{required} = 1.415\times10^{-5}\text{ x } 2$$

$$\text{pOH}=-\log\left(1.415\times10^{-5}\text{ x } 2\right) = 4.55$$

$$\text{pH} = 9.45 \text{ [1] 2dp ans}$$

(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in ~~S~~s**tep 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

Cathode: Mg^{2+} (l) + 2e → Mg (l) [1]

Anode : $2Cl^{-}$ (l) → Cl_2(g) + 2e [1]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

$$Q = It = nzF$$

$$\frac{95\times1000\times24\times60\times60}{100}\times90 = n\times2\times96500$$

$$n = 38.28 \times10^{4} \quad [1]$$

$$m = 38.28\times10^{4}\times24.3 = 930{,}000g = 930kg \quad [1]$$

(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

$MgCl_2$ has a lower melting point than MgO, hence the electrolysis can be carried out at a lower temperature, saving operation costs. [1]

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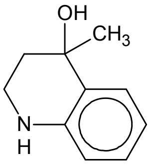
(c) ~~A is an organic compound.~~ When 0.46~~7~~8 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.

A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar~~ecular~~ mass of **A** is 177 g mol^{-1}. [1]

From Data Booklet, at s.t.p, V_m = 22.7 dm^3 mol^{-1} at 10^5 Pa and 273 K

Either

$$10^5 \times 60 \times 10^{-6} = \frac{0.468}{M} \times 8.31 \times 273$$

$$M = 176.9 = 177 \text{ g mol}^{-1} \text{ [1]}$$

Or

$n(A) = 60 / 22700 = 2.643 \times 10^{-7}$ mol

$M_r(A) = 0.468 / 2.643 \times 10^{-7} = 177.06 \approx 177$ g mol^{-1}

Comments

- Generally well-done.
- Common mistake include:
  Using incorrect V_m such as V_m = 24 dm^3 or V_m = 22.4 dm^3
- A small number of students did not use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of **A**. These students used the following approach, which is NOT acceptable for this question.

  1 mol of **A** undergoes reduction to give 1 mol of **E**.
  molar mass of **E** = 163.0 g mol^{-1}
  A has amide.
  molar mass of **A** = 163.0 – 2(1.0) + 16.0 = 177.0 g mol^{-1}

  Note that you are expected to use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of **A**.

(ii) Hence, d~~D~~educe the structural formulae of all the above structures, and explain the

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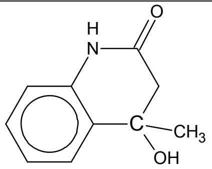
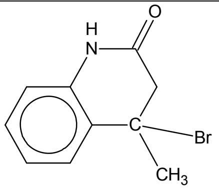
chemistry involved. [6]



A



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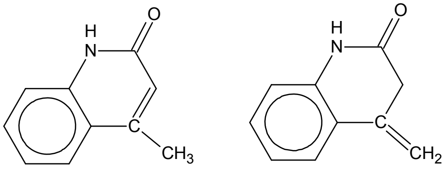

B & C

1 mk for each structure [4]

1/2 mk for each point (max of 2 mks):

1) From the molar mass of 177 g mol^{-1}, the molecular formula is likely to be $C_{10}H_{11}O_2N$.

2) **A** undergoes basic hydrolysis with NaOH (aq) to give –COO⁻ (–COOH + NaOH) and –NH_2. –COO⁻ is an ionic salt that ~~is soluble in~~dissolves in water by forming ion-dipole interactions with water. ⇒ **A** contains an amide group to give an amine and carboxylic salt when hydrolysed.

Some students wrote that the compounds form from the hydrolysis of **A** dissolves in water to via formation of hydrogen bonds with water. It may seem correct, but note that **A** contains an amide in a cyclic structure, hence after hydrolysis, there will be only one single product.

3) **A** undergoes elimination with Al_2O_3 to give alkenes **B** and **C** ⇒ **A** contains an alcohol group

4) The amide group in **A** undergoes reduction with $LiAlH_4$ to give an amine in **E**

5) Alkenes **B** and **C** undergo electrophilic addition with HBr to give halogenoalkane/alkyl halide/bromoalkane **D**.

6) **D** contains a chiral carbon and hence exists as a pair of enantiomers.

Comments

Out of the above 6 statements, the following key points are expected to gain credit.

- **A** undergoes (basic) hydrolysis with NaOH ⇒ **A** contains an amide group
- **A** undergoes elimination with Al_2O_3 to give alkenes **B** and **C** ⇒ **A** contains an alcohol group
- The amide group in **A** undergoes **reduction** with $LiAlH_4$ to give an amine in **E**
- Alkenes **B** and **C** undergo **electrophilic addition** with HBr to give **halogenoalkane/alkyl halide/bromoalkane D**

OR

- **D contains a chiral carbon** and hence exists as a pair of enantiomers.

4 bullet pts correct – 2 marks
2 bullet pts correct (minimum) – 1 mark

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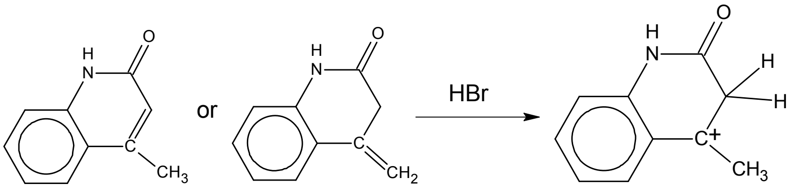
(iii) State the type of isomerism exhibited by **B** and **C.** Explain why **B** and **C** both give the same product **D** when reacted with HBr. [2]

Constitutional isomerism. [1]

When alkenes B and C undergo electrophilic addition with HBr, both form the same carbocation. The carbocation will be attacked by Br⁻ , which leads to the formation of D.



B **or** **C** **carbocation**

[1] for explanation & structure of carbocation

[Total: 22]

~~**(ii)** When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae.~~
~~Draw the structural formula of **each** of these esters. [2]~~

~~**(iii)** Draw the structural formulae of the products when glutathione is hydrolysed. [3]~~

~~Alliin has pK_a values of 1.84 and 8.45.~~

~~**(iv)** Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]~~

- ~~pH 1~~
- ~~pH 7~~
- ~~pH 11~~

~~**v)** Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]~~

~~**(vi)** With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]~~

~~**(vii)** Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin.~~
~~Briefly describe how you have calculated the various key points on the curve. [4]~~

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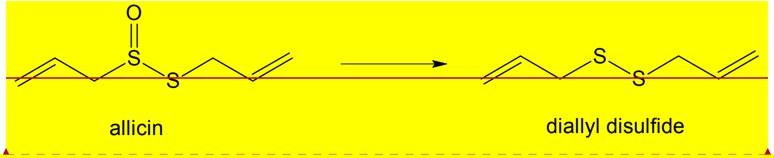
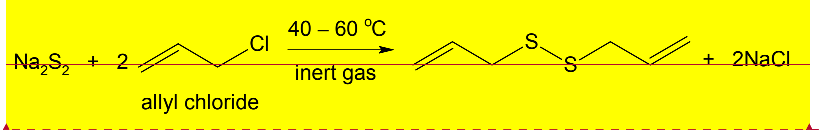
~~**(b)** Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of allicin.~~



~~Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 ¼C in an inert atmosphere.~~



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~~**(i)** Give the *IUPAC* name of allyl chloride. [1]~~

~~**(ii)** Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]~~

~~**(iii)** State the type of reaction when diallyl disulfide is converted back to allicin. [1]~~

~~[Total: 20]~~

Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term "homologous series". [1]

Group of organic compounds with

- Same functional group
- Differ by a CH_2 group

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

- Alkanes have simple molecular structure with weak instantaneous dipole-induced dipole (id-id) forces between molecules
- From ethane to heptane, the electron cloud gets bigger and more easily polarised, hence id-id forces become stronger.
- More energy needed to break the id-id forces, hence boiling point increases
- From ethane to heptane, the molecule increases by a CH_2 group
- This results in more C – C bonds and C – H bonds to break and more C=O and O – H bonds to form, hence more heat given off during combustion.

✓✓✓

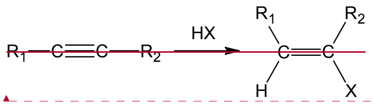
~~Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.~~

~~$R_1-C\equiv C-R_2$~~

~~where R_1 and R_2 = H or alkyl or aryl groups~~

~~Alkynes exhibit similar chemical properties to alkenes.~~

~~e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes~~



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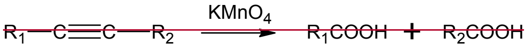
~~e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids~~



~~However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.~~

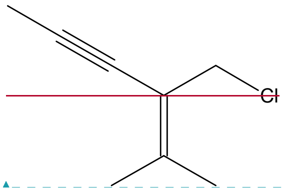
~~**(a)** Ethyne, C_2H_2, is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.~~

~~**(i)** Write an equation for the first stage. [1]~~

~~**(ii)** Suggest a structure for the dihalide formed. [1]~~

~~**(iii)** When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products.~~
~~Write an equation to explain the formation of these inorganic by-products. [1]~~

~~**(b)** Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).~~



~~Compound **A**~~

~~One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]~~

(c) ~~Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, $NaNH_2$ followed by heating under reflux to form compound **C**, C_8H_{10}. Compound **C** reacts with hot concentrated $KMnO_4$ to produce butane-1,4-dioic acid only.~~Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

As the alkane increases in molecular mass, the alkane becomes liquid and liquid phase reactions are slower than gas phase reactions. Hence combustion tends to be incomplete.

Cyclopropane is a colourless gas with a "petroleum-like" odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its "ring strain energy" using the formula below:

Ring strain energy =

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$$\text{number of carbon atoms in cyclic alkane, A} \times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane, A} \right| - \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$$

~~$\text{number of carbon atoms in cyclic alkane, A} \times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane, A} \right| - \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$~~

$$\text{number of carbon atoms in cyclic alkane, A} \times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane, A} \right| - \right.$$

$$\left. \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$$

$$\text{number of carbon atoms in cyclic alkane, A}$$

$$\times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane, A} \right| - \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$$

$$\text{number of carbon atoms in cyclic alkane, A}$$

$$\times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane, A} \right| - \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$$

~~$\text{number of carbon atoms in cyclic alkane} \times \left(\left| \text{enthalpy change of combustion of a } CH_2 \text{ group in the cyclic alkane} \right| - \left| \text{enthalpy change of combustion of a } CH_2 \text{ group in an unstrained n-alkane} \right| \right)$~~

(d) Given that the ΔH_f of CO_2 is –94.05 kcal mol^{-1} and ΔH_f of water is –68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. ~~calculate the enthalpy change of formation of cyclopropane.~~ [2~~1~~]

$3C(s) + 3H_2(g) \rightarrow C_3H_6(g)$

$\Delta H_f = [3(–94.05) + 3(–68.3)] – (–499.8) = +12.75$ kcal mol^{-1}

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

Enthalpy change of combustion of CH_2 group in unstrained molecule
= –530.4 – (–373.0) = –157.4 kcal mol^{-1} (can use other values to subtract)
Enthalpy change of combustion of CH_2 group in cyclopropane
= 1/3 (–499.8) = –166.6 kcal mol^{-1}
Strain energy of cyclopropane = 3 × (166.6 – 157.4) = +27.6 kcal mol^{-1}

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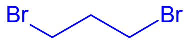
(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]



(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

Cyclopropane has a C – C – C angle of 60° which is smaller than the optimal angle of 109.5° in sp^3 carbons. As a result, bond pairs are much closer to each other and experience greater repulsion, hence weakening the C – C bonds, which breaks easily during addition.

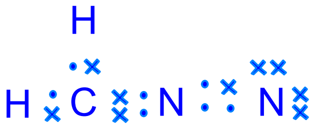
(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

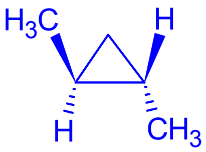
Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2.~~Formation of methylene, CH_2, and N_2 from diazomethane, CH_2N_2.~~

Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, d~~D~~raw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule. [1]



(ii) Draw the structure of the cyclic molecule formed in s~~S~~tep 2, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]



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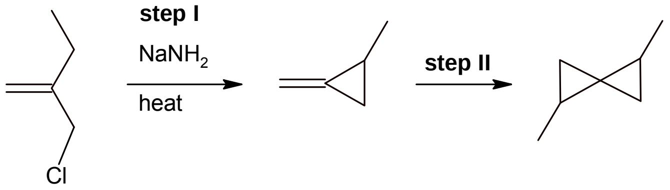
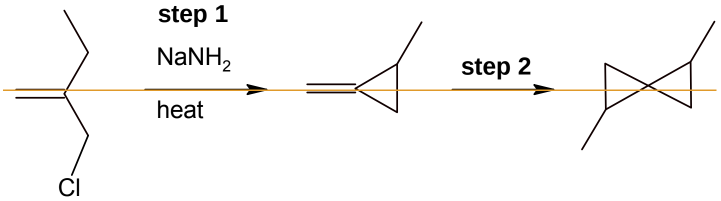
Yes, the molecule contains two chiral centres and does not have an internal plane of symmetry.

~~(h)~~ Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.

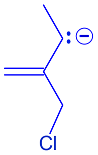




A **B**

(iii~~i~~) **Step I~~1~~** involves the reaction of molecule **A** with $NaNH_2$ to form NH_3 and a negatively-charged~~n~~ organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I~~1~~** and draw the organic intermediate that was formed. [2]

- Molecule A reacted with $NaNH_2$ in an acid base reaction
- 

- (Intramolecular) nucleophilic substitution

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(iv~~i~~) By considering the reactivity of the Cl atom, explain why~~if~~ molecule **C** cannot be used to replace molecule **A** in the synthesis above.

[1~~2~~]

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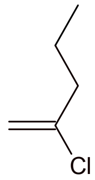


C

The chloro group is directly bonded to the double bond.

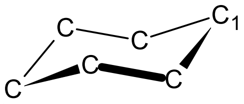
- The p orbital of Cl overlaps with the π orbital of the C=C bond,
- hence lone pair on Cl delocalises into the C=C bond,
- strengthening the C – Cl bond.

Hence, the Cl atom is resistant to nucleophilic substitution.

(v) Using the above information, s~~S~~uggest a suitable reagent for **step** **II**~~**2**~~. [1]

$CH(CH_3)N_2$

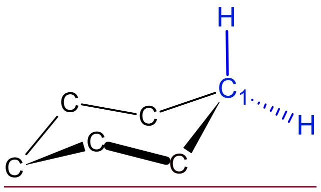
(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the “chair shape” arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing ~~in~~ the 3-D arrangement of hydrogen atoms bonded to~~for~~ C_1, explain why cyclohexane does not experience ring strain.

[2~~2~~]



- Cyclohexane does not experience ring strain as cyclohexane bond angles are close to 109.5° due to the chair shape formation.

~~**(i)** Explain the reaction with $NaNH_2$. [1]~~

~~**(ii)** Hence, explain the formation of compound **C**. [1]~~

~~**(iii)** Suggest skeletal structures for compounds **B** and **C**. [2]~~

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~~When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH{=}CHCO_2K$) for 15 minutes, it was found that 110 cm^3 H_2, measured at r.t.p, was collected at the cathode. The following reaction took place.~~

~~$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$~~

~~**(d)** State the relationship between the Faraday constant, *F* and the Avogadro's constant, *L*. [1]~~

~~**(e)** Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]~~

~~**(f)** Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:~~

- ~~mass of NaOH before experiment = 10.501 g~~
- ~~mass of NaOH after experiment = 10.904 g~~
- ~~initial reading on syringe = 10.0 cm^3~~
- ~~final reading on syringe = 120.0 cm^3~~

~~**(i)** State the oxidation state of carbon in ethyne. [1]~~

~~**(ii)** With the help of an equation, explain the purpose of passing the anode gas through NaOH. [1]~~

~~**(iii)** Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]~~

~~**(iv)** Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]~~

~~**(g)** When aqueous potassium maleate was acidified, maleic acid, $HO_2CCH{=}CHCO_2H$ (pK_{a1} = 1.90 and pK_{a2} = 6.07) was liberated. Fumaric acid (pK_{a1} = 3.03 and pK_{a2} = 4.44) is a stereoisomer of maleic acid.~~
~~With a suitable illustration, suggest a reason why maleic acid has a lower pK_{a1} but higher pK_{a2} than fumaric acid.~~
~~[2]~~

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5(a) ~~Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.~~

The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail ~~for~~ this difference. [1]

Fluorine and chlorine are gases but bromine is a liquid and iodine is a solid at room temperature. The enthalpy change of atomisation includes the energy required to change $Br_2(l) \rightarrow Br_2(g)$ and $I_2(s) \rightarrow I_2(g)$ [to vapourise bromine and iodine to the gaseous state].

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is –24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

$$\Delta H_r = \sum \text{Bonds broken} - \sum \text{Bonds formed}$$

$-24.0 = \frac{1}{2}$ BE(Cl–Cl) + $\frac{1}{2}$ BE(I–I) – BE(I–Cl)

BE(I–Cl) = +220.5

= +221 kJmol^{-1}

~~Below is a synthetic route involving L-DOPA and dopamine:~~

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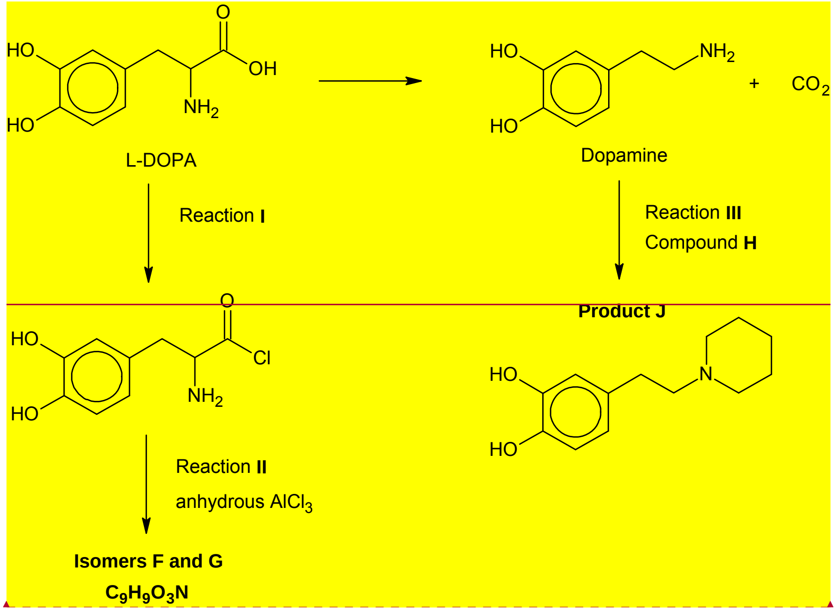
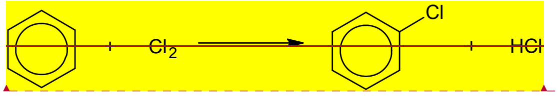


~~(i) State the reagents and conditions and any observations in Reaction I. [1]~~

~~(ii) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.~~



~~The reaction occurs in several steps.~~

~~• The first step is the reaction between Cl_2 and $AlCl_3$.~~

~~$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$~~

~~• The benzene ring is then attacked by the Cl^+ cation in the second step.~~

~~$AlCl_3$ reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.~~

~~Predict the structures of isomers **F** and **G** in Reaction **II**. [2]~~

~~**(iii)** In Reaction **III**, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]~~

(iii) Explain why your answer in **(ii)** ~~does not correspond~~is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

I–Cl is polar while I–I and Cl–Cl are non-polar molecules. There is additional electrostatic attraction between $I^{\delta+}$ and $Cl^{\delta-}$. Hence, the actual bond energy of I–Cl is greater than the average bond energies of I–I and Cl–Cl.

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(b) ICl reacts with pure water to form HCl and HI:

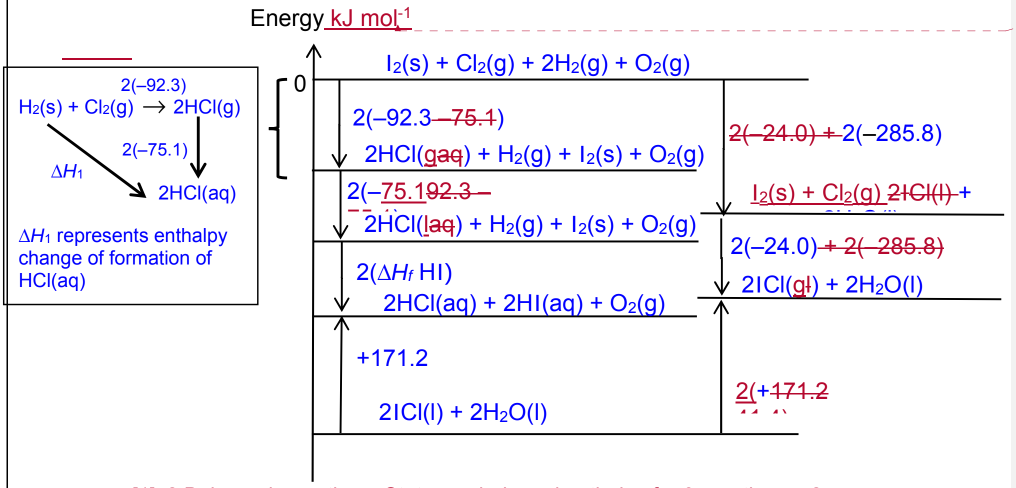
$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g)$ ΔH_r = +171.2 kJ mol^{-1}

Using ΔH_r, the following data, as well as relevant data from **a(ii)**, draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram ~~,~~ and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]



[1]x2 Balanced equations, State symbols and enthalpy for 3 reactions x 2

[1] ~~Label energy terms on diagram, arrows correctly~~

~~[1] Recognise the enthalpy change of formation~~ Energy level diagram (energy axis, ‘0’ at elements level, correct direction of arrows)

By Hess’ Law:

2(–24.0) + 2(–285.8) + (+171.2) = 2(41.4) + 2(–92.3) + 2(–75.1~~167.4~~) + 2ΔH_f(HI(aq))

2ΔH_f(HI(aq)) = – 2(–75.1) – 2(–92.3) + 2(–285.8) + 2(–24.0) – 2(41.4) + (+171.2)

~~–48.0 –571.6 + 171.2 + 334.8~~

ΔH_f(HI(aq)) = – 98~~56~~.2~~8~~ kJ mol^{-1} [1]

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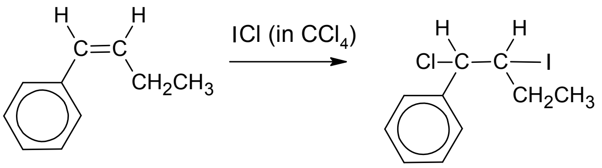
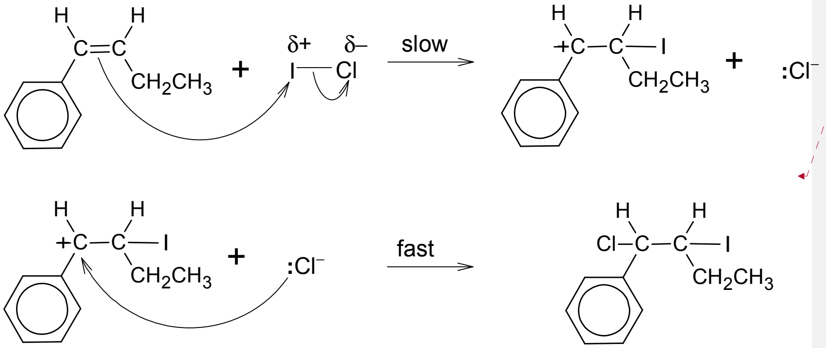
(~~b~~c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.



E

(i) Describe the mechanism for the formation of **E**. [3]

Electrophilic Addition



- Name of mechanism
- Correct arrows indicated
- Correct carbocation drawn
- Balanced equations
- Slow/ fast steps
- Charges on the atoms, lone pairs of electrons on Cl^-

Every 2 points – 1 mark

~~**(ii)** Dopamine is a bidentate ligand. When different volumes of 0.0030 mol dm⁻³ of aqueous Cr(III) and 0.0020 mol dm⁻³ of alkaline dopamine solution were mixed, a complex R is formed. Analysis of R shows that its formula is~~ ~~$[Cr(C_8H_9NO_2)_x(H_2O)_y]^{z}$~~~~, where x, y and z are integers.~~

~~To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.~~

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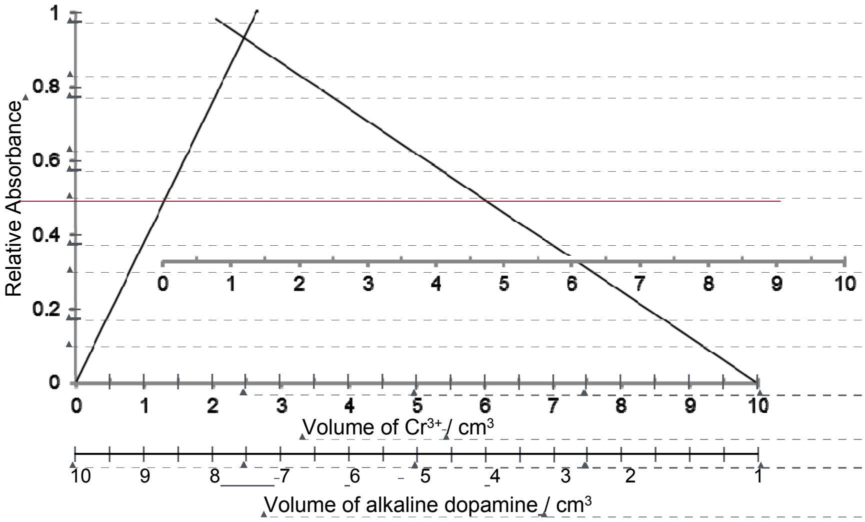
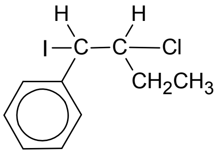


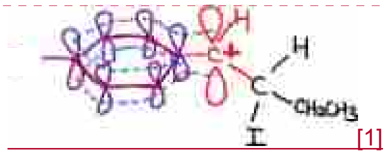
~~**(i)** Use the graph and the information given to determine the formula of complex R. Show your workings clearly.~~ ~~[3]~~

With the aid of a diagram, explain why **E** is formed and not **F**. [2]



F

The carbocation and the C atoms in benzene ring are sp^2 hybridised. The (+) charge on carbocation is dispersed over the neighbouring benzene ring. Due to the effective overlap between the unhybridised p-orbitals of benzene and the empty p-orbital on the carbocation, the delocalised electrons makes the (+) charge on the carbocation less (+). [1]



[1]

(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

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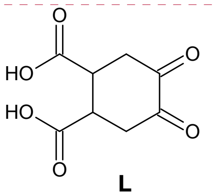
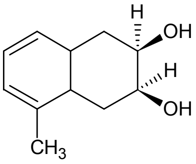
K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.

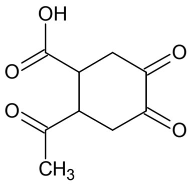


L

Suggest structures for **J** and **K** and explain the reactions described. [5]



J



K

Observations	Deductions
J,$C_{11}H_{16}O_2$ decolourises bromine water	**J** could be alkene or phenol. An alkene undergoes electrophilic addition reaction with Br_2(aq) to form halogenoalkane.
22.7 dm^3 of hydrogen is formed at s.t.p when **J** is reacted with sodium metal	$n(H_2) = \frac{22.7}{22.7}$ = 1 mol of H_2 is formed. $ROH + Na \rightarrow RO^-Na^+ + ½H_2$ Since 1 FG produces ½ mole of H_2, there must be 2 –OH groups present. –COOH group is absent as it will only produce only ½ mole of H_2 and 2 –COOH groups or 1 –OH & 1 –COOH groups cannot be present as it will not correspond to the molecular formula of **J**.
On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed	Secondary alcohol and the alkene in **J** undergoes oxidation with $KMnO_4$ to form ketones and carboxylic acid. There is a decrease in 2C atoms – which suggest that ethane-1,2-dioc acid was oxidised to form CO_2. From the given structure of **L**, it can be seen that **K** is unlikely a phenol and should not contain benzene as there will not be oxidation that leads to a reduction of 2 C atoms.
K reacts with sodium carbonate and 2,4 DNPH	**K** undergoes acid-base with Na_2CO_3 → –$COCH_3$ present. **K** undergoes condensation with 2,4 DNPH → –confirms presence of ketones.
K reacts with alkaline aqueous iodine to form **L**	**K** undergoes mild oxidation with alkaline I_2(aq) → –$COCH_3$ present. **K** undergoes acid-base reaction with alkali to form salt → –COOH present.

1 mark for each correct structure
3 marks for explanation
5 points – 3 marks
3 to 4 points – 2 marks
2 points – 1 mark

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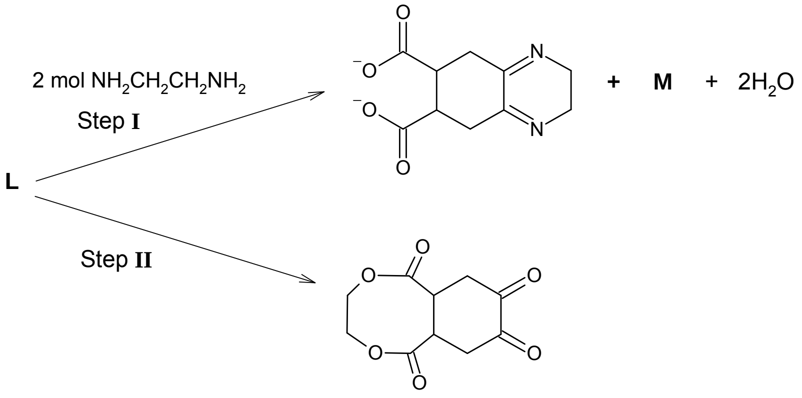
(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



N

(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

$^+NH_3CH_2CH_2NH_3^+$ [1] Types of reaction: Condensation, Acid – Base [1]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

~~**(ii)** The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o. The relationship between Δ_o and colours of complexes can be described in the equation below:~~

$$\Delta_o = \frac{hc}{\lambda}$$

~~where h is Planck's constant, c is the speed of light and λ is the wavelength of light absorbed~~

~~colour~~	~~absorbed λ / nm~~
~~violet~~	~~410~~
~~indigo~~	~~430~~
~~blue~~	~~480~~
~~blue-green~~	~~500~~
~~green~~	~~530~~
~~yellow~~	~~580~~
~~orange~~	~~610~~
~~red~~	~~680~~

$CH_2(OH)CH_2(OH)$, concentrated H_2SO_4 heat under reflux.

OR
1) PCl_5 at rtp 2) $CH_2(OH)CH_2(OH)$, rtp

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~~Given that Δ_o for complex **R** is 4.125 x 10^{-22} kJ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**. [2]~~

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~~**(c)** Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:~~

~~$I^-(aq) + I_2(s)$ — $I_3^-(aq)$~~

~~**(i)** Draw a fully labelled experimental set-up for a voltaic cell made up of a $Cr_2O_7^{2-}$/ Cr^{3+} half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [3]~~

~~**(ii)** By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to the I_2/I^- half-cell. [3]~~

~~**(d)** Explain the following statements.~~

~~**(i)** BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity. [2]~~

~~**(ii)** $SiCl_4$ reacts violently in water but CCl_4 has no reaction with water. [1]~~

~~**(iii)** Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist. [1]~~

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NANYANG JUNIOR COLLEGE
JC2 PRACTICAL PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	Mark Scheme

CLASS 1 7 | REG NO. | TUTOR

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018

2 hour 30 minutes

Candidates answer on the Question Paper

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 22 and 23.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 28
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This document consists of **23** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 To determine the concentrations of aqueous sodium hydroxide and aqueous ethanedioic acid and hence the percentage by mass of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

You are provided with the following reagents.

- **FB 1** is a mixture of approximately 0.01 mol dm^{-3} aqueous sodium ethanedioate, $C_2O_4Na_2$, and approximately 0.1 mol dm^{-3} ethanedioic acid, $C_2O_4H_2$
- **FB 2** is a dilute solution of sodium hydroxide, NaOH
- **FB 3** is 0.0755 mol dm^{-3} aqueous sodium carbonate
- thymolphthalein indicator

Both sodium hydroxide and sodium carbonate are bases which will neutralise ethanedioic acid as shown in **reactions 1** and **2**.

$2NaOH + C_2O_4H_2 \rightarrow C_2O_4Na_2 + 2H_2O$ **reaction 1**

$Na_2CO_3 + C_2O_4H_2 \rightarrow C_2O_4Na_2 + CO_2 + H_2O$ **reaction 2**

In this experiment, you will add different volumes of **FB 3** to identical samples of the mixture of aqueous sodium ethanedioate, $C_2O_4Na_2$, and ethanedioic acid, $C_2O_4H_2$, **FB 1**. You will then complete the neutralisation of $C_2O_4H_2$ in each mixture by titration with dilute sodium hydroxide, **FB 2**.

Each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end-points.

Graphical analysis of your results will enable you to determine the concentrations of the ethanedioic acid in the mixture of aqueous $C_2O_4Na_2$, and $C_2O_4H_2$ and of the sodium hydroxide.

Read through the whole method of conducting the experiment before starting any practical work.

The experiment

(a) Titrations

Experiment 1

1. Fill a burette with **FB 3**.
2. Pipette 25.0 cm^3 of **FB 1** into a 250 cm^3 conical flask.
3. Run 5.00 cm^3 of **FB 3** into the flask.
4. Add 10 – 15 drops of thymolphthalein indicator to the flask.
5. Fill a second burette with **FB 2**.
6. Titrate the mixture in the conical flask against **FB 2** until the first permanent pale blue colour remains in the solution.
7. Rinse the conical flask thoroughly before it is used for the next experiment.

The end-point should be found after the addition of approximately 14 cm^3 of **FB 2**.

One titration, performed accurately, will be sufficient.

Experiment 5

1. Repeat **Experiment 1** but run 30.00 cm^3 of **FB 3** into the flask containing 25.0 cm^3 of **FB 1**.

Experiments 2 – 4

Select **three** other suitable volumes of **FB 3** for use in **Experiments 2 – 4**. Your selected volumes must be between the volumes used in **Experiments 1 and 5**.

Do not use volumes of FB 3 outside the range of 5 – 30 cm^3.

Repeat the procedures used in **Experiment 1** but, in each case, add 25.0 cm^3 of **FB 1** and your chosen volume of **FB 3** into the conical flask. You should perform your titrations in order of **increasing** volume of **FB 3**.

Rinse this conical flask thoroughly between each titration.

Prepare a table in the space below and use it to record the titration results for each volume of **FB 3** added. You should record your titration results in order of **increasing** volume of **FB 3** added.

Experiment	1	2	3	4	5
Volume of **FB 3** added / cm^3	5.00	11.00	18.00	24.00	30.00
Initial burette reading / cm^3	0.00	20.00	0.00	11.70	21.60
Final burette reading / cm^3	15.80	34.00	11.70	21.60	29.80
Volume of **FB 2** added / cm^3	15.80	14.00	11.70	9.90	8.20

[1]: Correct column or row headings and units for titration recordings
Acceptable forms of units:
Use of solidus, e.g. / cm^3
Unit in brackets, e.g. (cm^3)
In words, e.g. volume in cubic centimetres
AND
All burette readings and/or volumes/titres recorded to 2 dp or to nearest 0.05 cm^3)

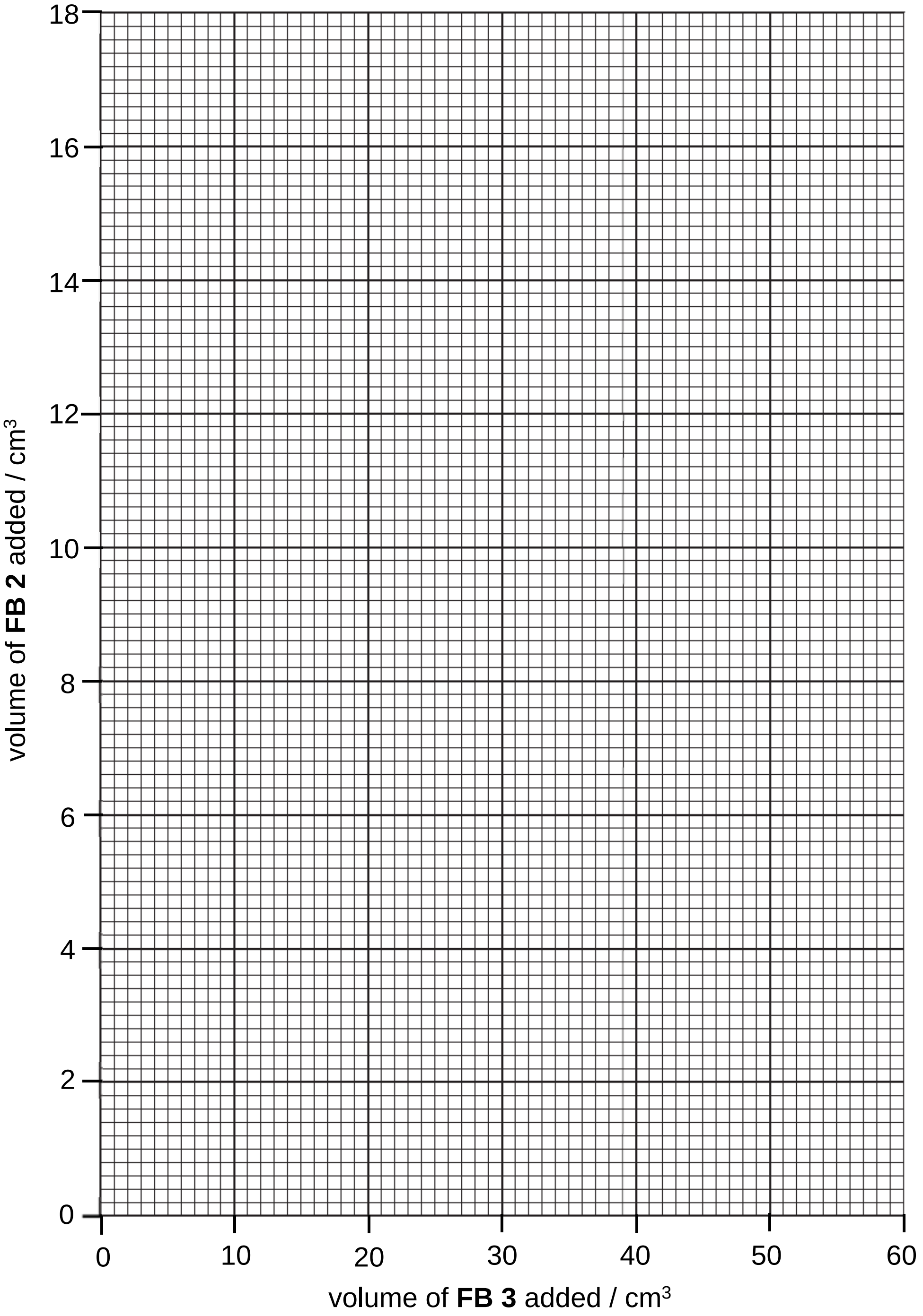
[1]: Follows instructions.
Selects three additional volumes of **FB 3** which are within the range 5 – 30 cm^3 for experiments 2, 3, and 4.
AND All gaps between adjacent **FB 3** volumes should be ≥ 5 cm^3 and ≤ 10 cm^3
AND Completes a total of 5 experiments.

[2]

(b) **(i)** Plot, on the grid below, your values for the **FB 2** titre (*y-axis*) against the volume of **FB 3** added (*x-axis*).

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for

- the volume of **FB 3** required, V_{max}**(FB 3)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 2** is added;
- the volume of **FB 2** required, V_{max}**(FB 2)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 3** is added.



Teacher's V_{max}**(FB 3)**	
diff.	
Teacher's V_{max}**(FB 2)**	
diff.	
I	
II	
III	
IV	
V	

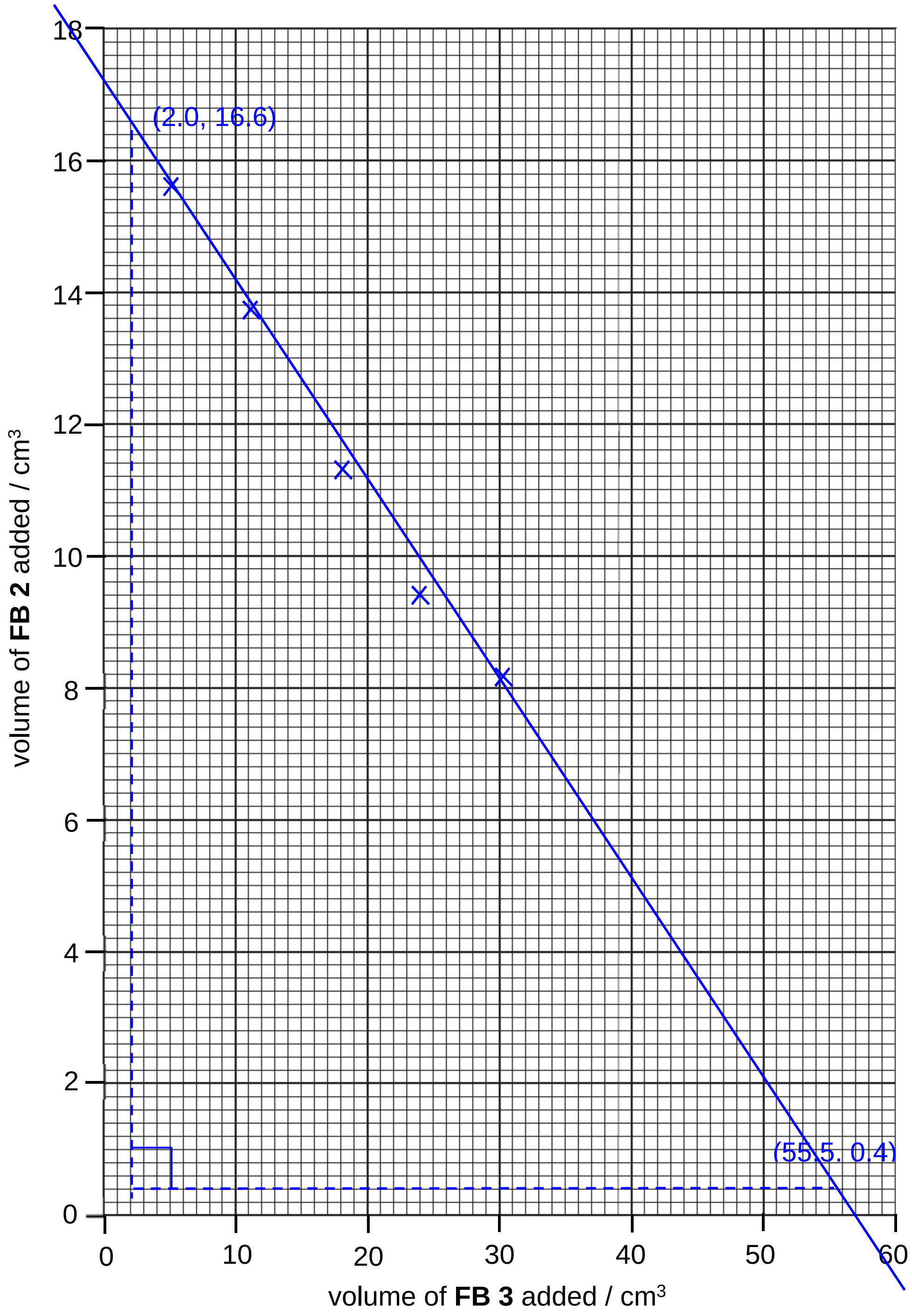
V_{max}**(FB 3)** = ……………….. V_{max}**(FB 2)** = ………………..

[5]

(b) **(i)** Plot, on the grid below, your values for the **FB 2** titre (*y-axis*) against the volume of **FB 3** added (*x-axis*).

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for

- the volume of **FB 3** required, **V_{max}(FB 3)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 2** is added;
- the volume of **FB 2** required, **V_{max}(FB 2)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 3** is added.



Teacher's **V_{max}(FB 3)**	
diff.	
Teacher's **V_{max}(FB 2)**	
diff.	
I	
II	
III	
IV	
V	

V_{max}(FB 3) = 57.00 cm^3…… **V_{max}(FB 2)** = 17.20 cm^3……

[5]

[1]: All points plotted to within ½ small square in either direction and in the correct square.

[1]: The graph line is the straight best-fit line
AND
Line is correctly extrapolated to intersect both axes. i.e. one continuous straight line
AND
no point is further than 1 cm^3 away from the line in either direction

[2]: Accuracy for V_{max}(FB 3) and V_{max}(FB 2)

[1] Reads correctly, to ±½ small square, the value for **V_{max}(FB 3)** and the value for **V_{max}(FB 2)**
If the student has not shown the extrapolation on the graph, the student may still earn this mark if the values quoted correspond to correct extrapolation of the student's graph line.

(ii) Calculate the gradient of your graph line, showing clearly how you did this.

$$\text{gradient} = \frac{16.6 - 0.4}{2 - 55.5} = -0.3028 \approx -0.303$$

gradient = –0.303………………… [1]

To earn this mark, students must

- Use clearly stated co-ordinates from graph **or** correct values of *Δtitre* and of *Δ(volume of **FB 3** used)* obtained from a clearly drawn triangle *(allow measurements to ± ½ small square). Coordinates could be from **V_{max}** values*.
- Use a triangle (or equivalent coordinates/Δ values) which covers at least 3 large squares in each direction
- Correctly calculate gradient. (ignore sig figs for this mark)

Do not award this mark if the graph line is not straight.
For this mark, ignore missing working and incorrect/missing units.

(iii) Explain, in terms of the chemistry involved, the direction of the slope of your graph.

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

……………………………………………………………………………… [1]

[1]: Negative gradient because the more Na_2CO_3 added, the less NaOH is needed for neutralisation (or words to that effect)

Calculations
Show your working and appropriate significant figures in **all** of your calculations.

(c) **(i)** Using appropriate data from your graph, calculate the concentration of ethanedioic acid, $C_2O_4H_2$ in **FB 1**.

1 mol of Na_2CO_3 will completely neutralise 1 mol of $C_2O_4H_2$

V_{max}(**FB 3**) = 57.00 cm^3

$$[C_2O_4H_2] = \frac{\frac{57.00}{1000} \times 0.0755}{\frac{25.0}{1000}} = 0.1721 \approx 0.172 \text{ mol dm}^{-3}$$

concentration of $C_2O_4H_2$ in **FB 1** = 0.172 mol dm^{-3} ……….. [1]

(ii) Using your answer to **(c)(i)** and appropriate data from your graph, calculate the concentration of sodium hydroxide in **FB 2**.

2 mol of NaOH will completely neutralise 1 mol of $C_2O_4H_2$

V_{max}(**FB 2**) = 17.20 cm^3

$$[NaOH] = \frac{\frac{57.00}{1000} \times 0.0755 \times 2}{\frac{17.20}{1000}} = 0.5004 \approx 0.500 \text{ mol dm}^{-3}$$

concentration of sodium hydroxide in **FB 2** = 0.500 mol dm^{-3} … [1]

(d) Use the expression below to calculate the concentration of sodium hydroxide in **FB 2**. Give your answer to three significant figures.

$$[NaOH] = \frac{2[Na_2CO_3]}{|\,gradient\,|}$$

$$[NaOH] = \frac{2(0.0755)}{0.3028} = 0.4986 \approx 0.499 \text{ mol dm}^{-3}$$

concentration of sodium hydroxide in **FB 2** = 0.499 mol dm^{-3}…………………… [1]

[1 mark]
Correctly calculates [NaOH] using the given expression
Show working in **(c)(ii)**, **(d)** and **(e)**
3 significant figures in final section answers to **(c)(ii)**, **(d)** and **(e)**
Show appropriate units in answers in **(c)(i)**, **(c)(ii)**, **(d)(ii)**, **(d)(iii)** and **(e)**

(e) Student **B** repeats the experiment described in **(a)**. However, student **A** had used up **FB 3**. As such student **B** has to prepare another 250 cm^3 of **FB 3**. Unknowingly, he weighs a sample of solid sodium carbonate which is slightly damp for the preparation of **FB 3**.

Suggest and explain what effect this will have on the value of **V_{max}(FB 3)** he obtains.

effect on **V_{max}(FB 3)** ……………………………………………………………………..
value of **V_{max}(FB 3)** too high

explanation ………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………. [1]

presence of water means mass of Na_2CO_3 weighed out is lower than expected, so $[Na_2CO_3]$ in **FB 3** is lower than expected, so more **FB 3** is needed to neutralise the ethanedioic acid in **FB 1**.

(f) A student performs the original experiment using solutions of different concentration to those you have used. He determines the gradient of his line using a small triangle.

He calculates the concentration of NaOH in **FB 2**. In part **(c)(ii)** he obtains a value of 0.589 mol dm^{-3}. In part **(d)** he obtains a value of 0.581 mol dm^{-3}.

Suggest which of these two values is likely to be more accurate. Explain your answer.

the more accurate value is 0.589 ……………………………………………..

explanation …………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………. [1]

because it is based on larger/the maximum/the intercept volumes.

AND

so the effect of a reading error will be less significant.

(g) Plan an experiment to determine the percentage by mass of sodium ethanedioate, $C_2O_4Na_2$ in **FB 1**.

Acidified potassium manganate(VII) oxidises ethanedioate ions, $C_2O_4^{2-}$ ions, as shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

However, the reaction takes place slowly at first. The rate of the reaction increases as more products are produced. This is because one of the products acts as a catalyst for the reaction. Hence this reaction is an example of 'autocatalysis'.

(i) Identify the product that acts as the catalyst in the reaction.

……………………………………………………………………………… [1]

(ii) Using the information given above, complete the procedures for this additional experiment which is written partially as shown below.

*Do **NOT** carry out this experiment.*

1. Fill a burette with 0.020 mol dm^{-3} of an aqueous solution of potassium manganate(VII).
2. Pipette 10.0 cm^3 of **FB 1** into a 250 cm^3 conical flask.
3. Using a 10 cm^3 measuring cylinder, add in 10 cm^3 of sulfuric acid into the same conical flask.
4. ………………………………………………………………………………

   ………………………………………………………………………………

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   Heat the mixture in the conical flask to about 60/70/80 °C.
5. Titrate the mixture in the conical flask against potassium manganate(VII) until the first permanent pale pink……………….. colour remains in the solution.
6. Repeat the titration ……………………………………………………………

   ………………………………………………………………………………

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   ………………………………………………………………………………
   Repeat the titration as many times necessary to achieve two consistent readings (to be within ±0.10 cm^3. The average of the two consistent readings will be the volume of potassium manganate(VII) added to achieve endpoint.)

[2]

(h) **Planning**

The volume of aqueous sodium hydroxide needed to completely neutralise all the ethanedioic acid, $C_2O_4H_2$ present in **FB 1** can also be obtained by carrying out a thermometric titration.

The reaction between an acid and an alkali is exothermic. It is possible to make use of this fact to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration* and can be used to calculate the concentration of an acid solution and the value of the enthalpy change of neutralisation, ΔH_n.

The concentration of an acid solution can be determined by adding various volumes of acid and alkali and measure the change in temperature. A series of about six experiments were conducted, where different volumes of alkali were added to a fixed volume (for example 25.0 cm^3) of acid while keeping the total volume of the solution constant by adding appropriate volumes of water.

The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated (extended) until they cross.

(i) Using the information given above, you are required to write a plan for a thermometric titration in which a known concentration of an aqueous solution of sodium hydroxide is added to **FB 1**.

You are to determine the volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in **FB 1**.

You may also assume that you are provided with:

- **FB 1** which is a mixture of approximately 0.01 mol dm^{-3} aqueous sodium ethanedioate, $C_2O_4Na_2$, and approximately 0.1 mol dm^{-3} ethanedioic acid, $C_2O_4H_2$.
- 0.35 mol dm^{-3} sodium hydroxide, NaOH
- graph paper;
- the equipment normally found in a school or college laboratory.

Your plan should include:

- calculation of the approximate volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in **FB 1**;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a table containing the volumes of each reagent to be added
- how you would recognise that the equivalence-point had been passed;
- on the grid provided, a sketch of the graph you would expect to obtain;
- an explanation of the shape of your graph;

……………………………………………………………………………………………………

…………………………………………………………………………………………..………………. [8]

[1] Calculation:

Given approx. $[C_2O_4H_2] = 0.1$ mol dm^{-3} and [NaOH] = 0.35 mol dm^{-3}

Given fix acid volume at 25.0 cm^3

$$n(C_2O_4H_2) = \frac{25.0}{1000} \times 0.1 = 0.0025 \text{ mol}$$

$n(NaOH) = 2n(C_2O_4H_2) = 0.0025 \times 2 = 0.005$ mol

approximate **V_{max}(FB 2)** = 0.005 / 0.35 × 1000 = 14.29 cm^3 (ignore the precision when presenting this answer)

Procedure:

1. Use a burette to transfer 25.00 cm^3 of **FB 1** into a styrofoam cup. (Place the cup in a 250 cm^3 beaker to prevent it tipping over.) Record the initial temperature of **FB 1** using a thermometer graduated in 0.2 °C.
2. From a second burette, measure the required volume of water as shown in the table below and add to the **FB 1** in the styrofoam cup. (Use the thermometer to stir the mixture gently.)
3. From a third burette, measure the required volume of NaOH as shown in the table below into a 100 cm^3 beaker and add to **FB 1** in the styrofoam cup. Use the thermometer to stir the mixture gently.
4. Record the highest temperature reached.
5. Repeat steps **1** to **4** by varying the volume of water and NaOH added to **FB 1** as shown in the table below.
6. The temperature change, $\Delta T = T_{final} - T_{initial}$, where T_{final} is the highest temperature measured and $T_{initial}$ is the initial temperature of **FB 1**.
7. Plot a graph of the ΔT against the volume of NaOH added.
8. The equivalence-point is reached once the temperature is observed to stop rising.

Experiment	Volume of NaOH / cm^3	Volume of **FB 1** / cm^3	Volume of water / cm^3	Initial temperature of **FB 1** / °C	Highest temperature / °C	ΔT / °C
1	8.00	25.00	22.00			
2	12.00	25.00	18.00			
3	14.00	25.00	16.00			
4	16.00	25.00	14.00			
5	18.00	25.00	12.00			
6	20.00	25.00	10.00			

Marking Scheme

1 mark for describing the followings in the procedure:

- state the use of burette to measure the volumes of water, NaOH and **FB 1**
- state the precision of the thermometer to be used
- use styrofoam cup as the container for the solution mixture

1 mark for describing the followings in the procedure:

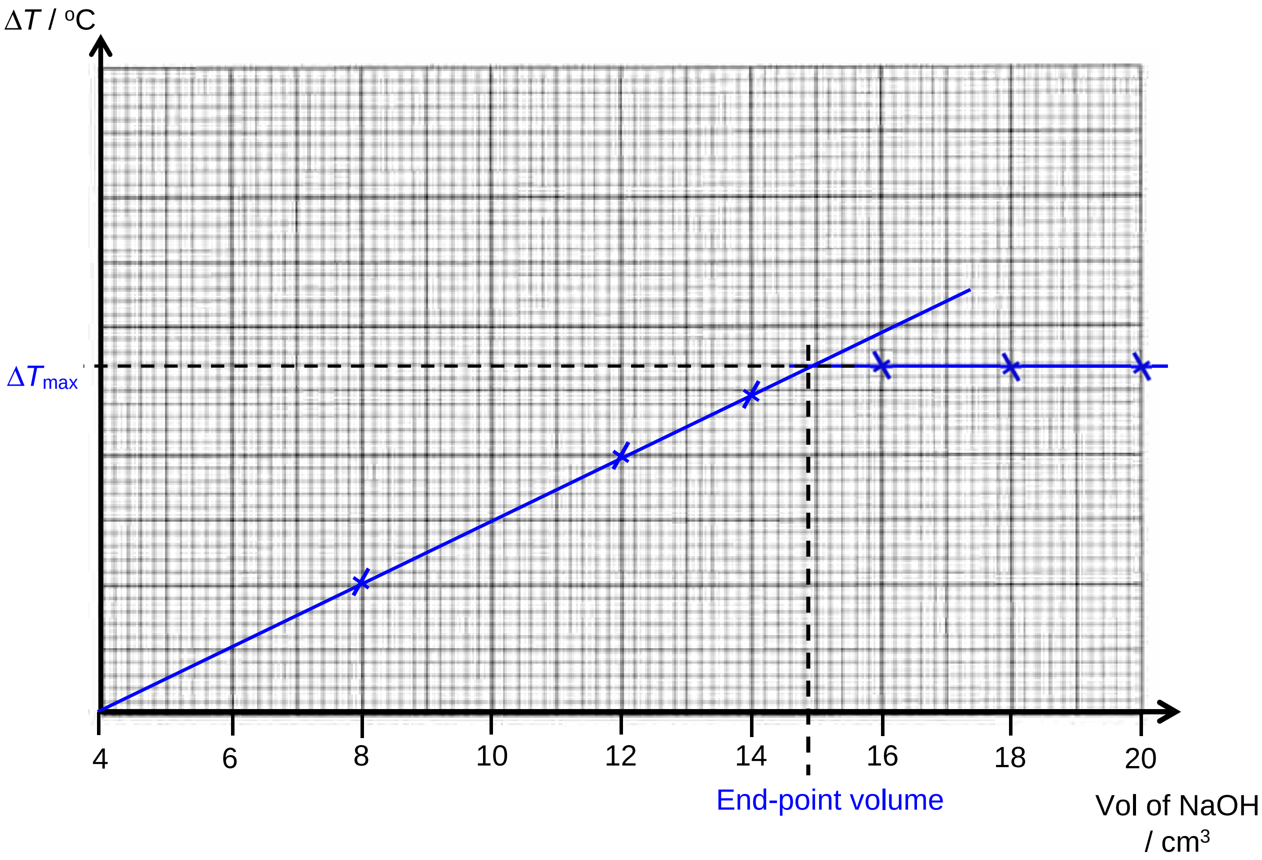
- measure out a fixed volume of **FB 1** and determine its initial temperature
- mix **FB 1**, NaOH and water (either **FB 1** or NaOH should be the last reagent to be added) and record the highest temperature obtained
- repeat the experiment by varying the volumes of NaOH and water to be added and ensuring that the total volume of the reaction mixture remains constant

1 mark for selecting an appropriate fixed volume of **FB 1** and range of volume of water and NaOH taking into account the followings:

- The minimum fixed volume of reaction mixture is 25.00 cm^3 so that the bulb of the thermometer is completely immersed into the solution when measuring the initial temperature
- Using the approximate $\mathbf{V_{max}}$**(FB 2)** calculated to select the appropriate range of the volume of NaOH to be added, i.e. 3 volumes less than 14 cm^3 and 3 volumes greater than 14 cm^3
- Adding appropriate volumes of water to ensure that the total volume of the reaction mixture is fixed and preferably be less than 100 cm^3 taking into account the maximum volume of the polystyrene cup used and to prevent spillage upon mixing

1 mark for writing step **8** in the above procedure

Sketch of graph expected to be obtained:



Marking Scheme
1 mark for

- labelling the axes correctly and indicating the scales on the x axis
- indicating the end-point volume of NaOH

1 mark for drawing a linear, increasing line and a linear, horizontal line. These lines are then extrapolated until they cross. The point of intersection is the equivalence point.

Explanation of the shape of the graph:

Before equivalence point, the limiting reagent is NaOH, hence both the number of moles of water and the total volume of the solution are increasing. According to $\Delta H_n = -\frac{m \times {}^{c}\!/_{1000} \times \Delta T}{n_{H_2O}}$, ΔT is directly proportional to the number of moles of water. Since the number of moles of water increases with increasing volume of NaOH so ΔT increases.

After the equivalence point, the limiting reagent is **FB 3**. The number of moles of water which depend on **FB 3** remain constant as a fixed volume of **FB 3** is used. Hence ΔT remains unchanged.

1 mark for sensible explanation

(ii) In another experiment, hydrochloric acid is used instead of **FB 1**.
If the hydrochloric acid has the same concentration as the ethanedioic acid present in **FB 1**, draw on your graph in **(i)** another pair of lines to show the results you would expect to obtain.

Explain your answer.

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

……………………………………………………………………………………… [3]

[1]: Line rises more steeply and intersects second line at a higher temperature rise
[1]: Maximum is reached at ½V(NaOH) needed to completely neutralised the ethanedioic acid in **FB 1**
[1]: Some of the heat that would have been released is used to ionise the ethanedioic acid and the reacting mole ratio between hydrochloric acid and sodium hydroxide is 1 : 1.

[Total: 28]

2 You are required to determine the enthalpy change of combustion of ethanol.

When an exothermic reaction takes place in a container such as a metal calorimeter, some of the evolved heat energy is absorbed by the metal calorimeter.

When an endothermic reaction takes place some of the required heat energy is supplied by the metal calorimeter.

The amount of heat energy evolved or supplied for a 1 °C change in temperature is known as the heat capacity of the metal calorimeter.

In preparation for your experiment to determine the enthalpy change of combustion of ethanol, you will first need to determine the approximate heat capacity of a 100 cm^3 metal calorimeter.

Before starting any practical work read through the instructions in (a) and draw up a table to record your results.

(a) Determining the approximate heat capacity of the 100 cm^3 metal calorimeter

When samples of hot and cold water are mixed in the 100 cm^3 metal calorimeter, some heat is lost to the metal calorimeter in raising its temperature. To determine the approximate heat capacity of your 100 cm^3 metal calorimeter, you will determine the maximum temperature rise when a sample of hot water is added to cold water in the metal calorimeter.

- Use a 50 cm^3 measuring cylinder to transfer 50 cm^3 of cold water into the 100 cm^3 metal calorimeter.
- Use the 50 cm^3 measuring cylinder to transfer 50 cm^3 of cold water into a 100 cm^3 beaker.
- Note the temperature of the water in this 100 cm^3 beaker and heat it **carefully and gently** until the temperature of the water in it has increased by 45–50 °C then stop heating, *e.g. if the water is at 20.0 °C you should warm it to 65–70 °C.*
- Stir the cold water in the 100 cm^3 metal calorimeter with the thermometer.
- Record the temperature of the cold water (this is the temperature at t = 0 min).
- Record the temperature each minute for 3 minutes.
- After you have taken the reading at t = 3 min, use the thermometer to stir the hot water in the 100 cm^3 beaker.
- At t = 4 min, measure the temperature of the hot water and record this value in the box below.
- **Immediately** add the hot water from the 100 cm^3 beaker to the cold water in the 100 cm^3 metal calorimeter.
- Stir with the thermometer but do not record the temperature.
- Continue to stir the water throughout the experiment.
- Record the temperature at t = 5 min, and then every ½ minute until t = 8 min.
- Record all measurements of time and temperature obtained.

The temperature, T_1, of the hot water at t = 4 min is 72.0………… °C.

Table of results

time / s	0	1	2	3	5	5.5	6	6.5
temperature / °C	31.5	31.5	31.5	31.5	49.0	49.0	48.5	48.0

time / s	7	7.5	8
temperature / °C	48.0	47.5	47.0

[3]

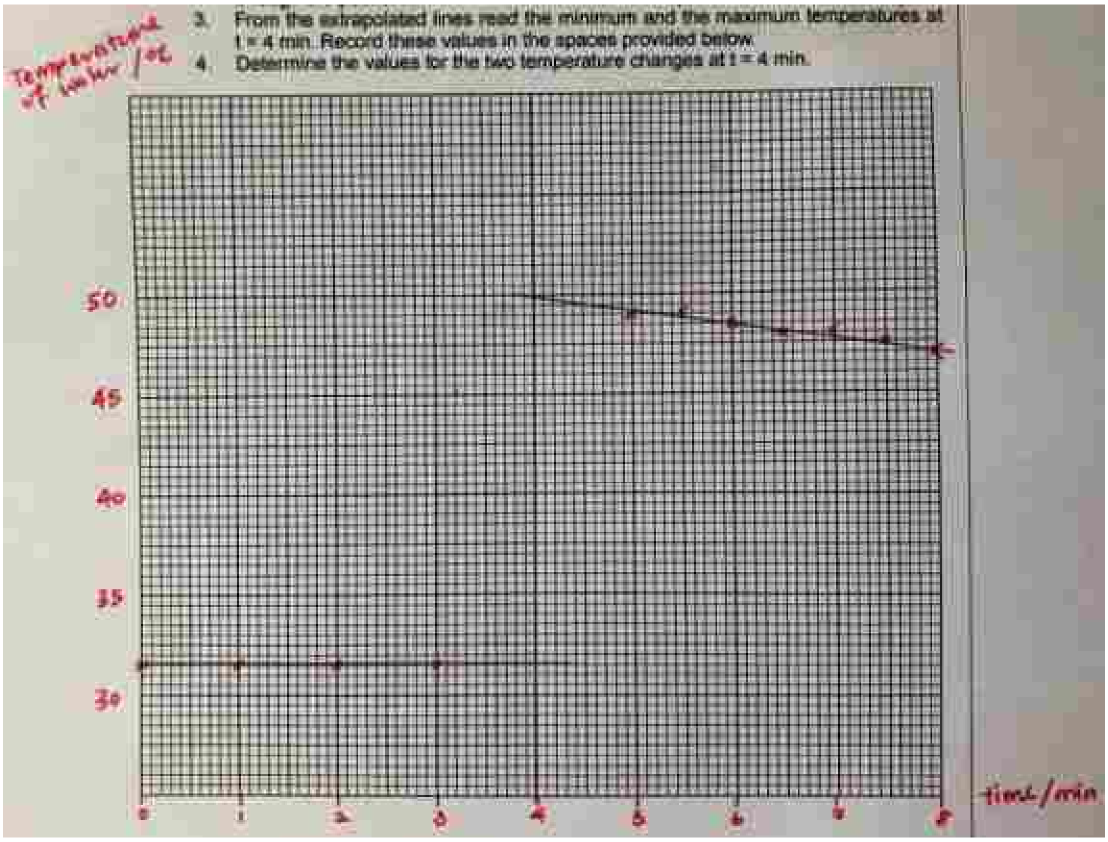
[1]: Follows instructions with regard to times and temperature readings 0-3 minutes at 1 minute intervals; 5-8 minutes at ½ minute intervals, **and T_1** recorded in box. (Ignore if also in table)

[1]: All columns correctly labelled with appropriate unit shown.
Must use solidus, brackets or describe fully in words.
If units not included in column headings every entry must have correct unit shown
Accept min, mins, minutes

[1]: All **thermometer readings** (table and box) recorded to nearest 0.5 °C.
Ignore the precision for the recording of time.

(b) Graph plotting

1. Plot a graph of the temperature of the water in the 100 cm^3 metal calorimeter (y-axis) against time (x-axis) on the grid below. Do not plot the temperature, T_1, of the hot water at t = 4 min.
2. Draw two straight lines of best fit; one through the points up to t = 3 min; the second through the points from t = 5 min to t = 8 min. Extrapolate both lines to t = 4 min.
3. From the extrapolated lines read the minimum and the maximum temperatures at t = 4 min. Record these values in the spaces provided below.
4. Determine the values for the two temperature changes at t = 4 min.



3. From the extrapolated lines read the minimum and the maximum temperatures at t = 4 min. Record these values in the spaces provided below.
4. Determine the values for the two temperature changes at t = 4 min.

Minimum temperature, $\boldsymbol{T_2}$, at t = 4 min is 31.5............... °C.
Maximum temperature, $\boldsymbol{T_3}$, at t = 4 min is 50.0............... °C.
Temperature rise for 50 cm^3 of cold water in the 100 cm^3 metal calorimeter, ($\boldsymbol{T_3 – T_2}$) is 18.5............. °C.
Temperature fall for 50 cm^3 of hot water from the 100 cm^3 beaker, ($\boldsymbol{T_1 – T_3}$) is 22.0........... °C.
[4]

[1]: Temperature of water in the metal calorimeter plotted on y-axis against time on x-axis.
NYJC mark scheme: Clearly labelled axes. Units required. Allow ECF from how headers are labelled in table in **(a)**.
*CIE mark scheme and FYI only: Clearly labelled axes (ignore units) [temp/time are minimum acceptable labels] but accept **T / °C** and **t / min** as labels. The unit is necessary in this case*

[1]: Uniform and sensible scales for candidate's choice of graph.
Plotted points must be in at least 4 large squares on the temperature axis and 5 large squares on the time axis.
Do **not** include any plotted value of $\mathbf{T_1}$.

[1]: There should be a minimum of 5 plotted points between 5 and 8 minutes.
Examiner then checks plotting of points at t_0 min, t_5 min and t_8 min and the plotting of any suspect point.
If any of the t_0 min, t_5 min and t_8 min points is missing check the adjacent point.
Points should be within ½ of a small square of the correct position and in the correct small square

[1]: Acceptable straight lines drawn – an acceptable straight line is one passing through the majority of points or has balanced points on either side of the line
and
correct values of $\mathbf{T_2}$ and $\mathbf{T_3}$ read (to within ½ small square) from the graph.

Extrapolation need not be drawn on the graph

(c) **Calculations**
Working should be shown in all calculations.
[**4.2 J** are absorbed or released when the temperature of 1.0 cm^3 of **water** changes by 1.0 °C.]

(i) Calculate the heat energy gained by the 50 cm^3 of cold water in the 100 cm^3 metal calorimeter.

heat energy gained by cold water = $50 \times 4.2 \times 18.5 = 3885 \approx 3890$ J

The heat energy gained by the cold water = 3890………… J.

(ii) Calculate the heat energy lost by the 50 cm^3 of hot water from the 100 cm^3 beaker.

heat energy lost by hot water = $50 \times 4.2 \times 22.0 = 4620$ J

The heat energy lost by the hot water = 4620………… J.

(iii) The difference between the values calculated in **(i)** and **(ii)** is an approximate value for the total heat energy absorbed by the 100 cm^3 metal calorimeter during the experiment. The heat capacity of the metal calorimeter is the amount of heat energy absorbed for a 1 °C change in temperature.

$$\begin{array}{c}\textit{approximate heat capacity}\\ \textit{of the } 100\ cm^3 \textit{metal calorimeter}\end{array} = \frac{(\textit{heat energy lost}) - (\textit{heat energy gained})}{(T_3 - T_2)}\ \text{J °C}^{-1}$$

Use your answers to **(i)** and **(ii)** and the temperature rise from **(b)** to calculate the approximate heat capacity of the 100 cm^3 metal calorimeter.

approximate heat capacity of the 100 cm^3 metal calorimeter

$$= \frac{4620 - 3885}{18.5}$$

$= 39.72$

≈ 39.7 J $°C^{-1}$

The approximate heat capacity of the 100 cm^3 metal calorimeter = 39.7………… J $°C^{-1}$.
[1]

(i) and **(ii)**
Award one mark if both of the following expressions are correctly evaluated.
heat gained = 210 × candidate value of ($T_3 - T_2$)
heat lost = 210 × candidate value of ($T_1 - T_3$)
Units should be consistent. Ignore any sign given.
(iii) no mark.

(d) Determining the enthalpy change of combustion of ethanol, C_2H_5OH

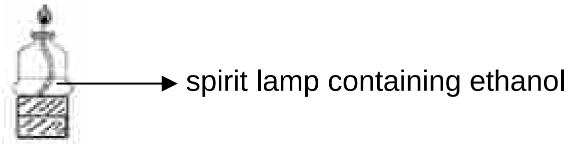
An experiment was carried out as follows to determine the enthalpy change of combustion of ethanol.

The 100 cm^3 metal calorimeter used in **(a)** was used to contain some water. The water was heated using ethanol placed in a spirit lamp. The temperature rise was recorded. The spirit lamp was weighed before and after the experiment to determine the mass of ethanol used. The following results were obtained.

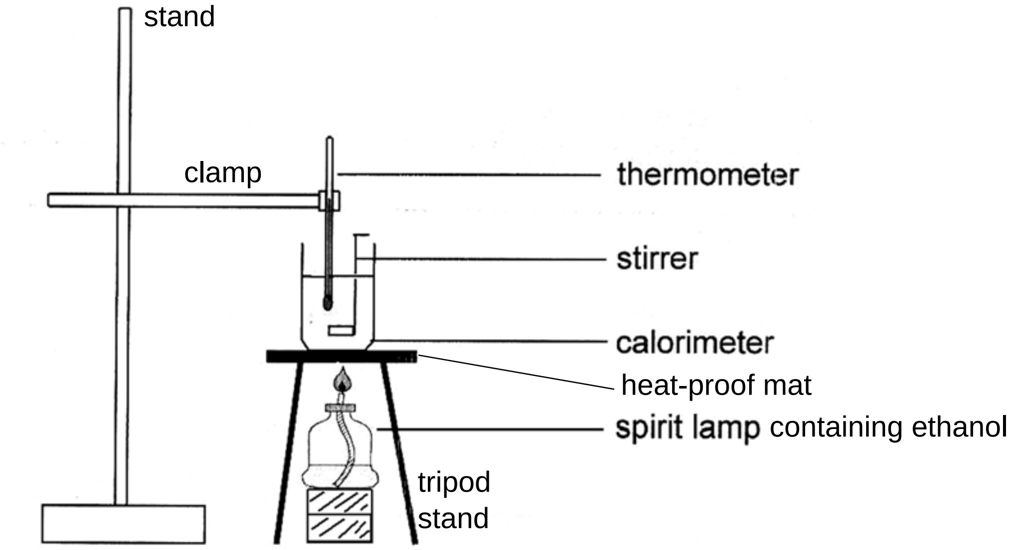
mass of ethanol burned = 0.391 g
mass of water heated = 40.0 g
temperature rise = 19.5 ^{o}C

(i) Complete the following diagram to show the experimental set-up needed to carry out the experiment to determine the enthalpy change of combustion of ethanol.
You are to use the following apparatus to complete the diagram:

- stand and clamp
- 100 cm^3 metal calorimeter
- thermometer
- tripod stand and heat-proof mat



[1]



(ii) Use your answer in **(c)(iii)** and the results obtained to calculate the enthalpy change of combustion of ethanol.
[*A*r: O, 16.0; C, 12.0; H, 1.0]
[specific heat capacity of water = 4.2 J °C^{-1} cm^{-3}]
(If you were unable to answer **(c)(iii)**, you may assume that the heat capacity of the 100 cm^3 metal calorimeter is 50 J °C^{-1}.)

ΔH_c(ethanol)

$$= -\frac{(40.0\times4.2\times10^{-3}\times19.5)+(39.72\times10^{-3}\times19.5)}{0.391/46.0}$$

$= -477$ kJ mol^{-1}

enthalpy change of combustion of ethanol = –477 kJ mol^{-1}……………[1]

(iii) Calculate the maximum percentage error in the measurement of each mass used in the experiment.

mass measured	maximum error in a single reading	maximum percentage error / %
0.391 g of ethanol burned	0.0005 g	(0.0005×2)/0.391*100 = 0.256 %
40.0 g of water	0.05 g	0.05/40.0*100 = 0.125 %

[1]

[Total: 11]

3 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

FB 4 is a solution containing **one** cation and **one** anion from the Qualitative Analysis Notes in pages 22 and 23.
Solid **FB 5** contains the sodium ion, and **one** anion from the Qualitative Analysis Notes in pages 22 and 23.

(a) Carry out the following tests on **FB 4** and state the observations you make.

(i)	To 1 cm depth of aqueous **FB 4** in a test-tube, add aqueous ammonia the	White ppt soluble in excess NH_3(aq) [M1]
	add sulfuric acid dropwise until there is no further observations.	White ppt reforms, soluble in excess [M2]
(ii)	To 1 cm depth of aqueous **FB 4** in a test-tube, add silver nitrate,	White ppt formed, soluble in excess NH_3(aq) [M3]
	followed by aqueous ammonia.	

For Examiner's Use			
Obs points	9-11 pts 6 mks 7-8 pts 5 mks 5-6 pts 4 mks 4 pts 3mks 3 pts 2 mks 1-2 pts 1 mk	*marks*	

(b) Carry out the following tests on **FB 5** and state the observations you make.

	test	*observations*
(i)	Place half of the solid **FB 5** in a boiling tube. Heat strongly until the solid melts and a gas is given off. Test and identify the gas. Continue the strong heating for 2 – 3 min, then leave the tube to cool and retain the residue for the test in **(iv)**.	White solid melts to give colourless liquid. [M4] Colourless, odourless gas relights a glowing splint. Gas is O_2. [M5] White residue obtained on cooling [M6]
(ii)	To the remaining half of **FB 5** is the boiling tube, add 3 cm depth of aqueous sodium hydroxide. Warm gently and retain for the test in **(iii)**.	No NH_3 gas given off. [M7]
(iii)	To the solution from the test in **(ii)**, add a piece of aluminium foil and warm gently.	Pungent colourless gas turns moist red litmus blue. (Gas is NH_3.) [M8]
(iv)	Dissolve the residue from test in **(i)** in distilled water and divide the solution into **three** parts. Use these for the tests in **(v)** to **(vii)**.	
(v)	To one part of the solution from **(iv)**, add aqueous potassium iodide followed by dilute sulfuric acid.	Solution turns yellow/brown/black solid formed [M9]
(vi)	To the second part of the solution from **(iv)**, add aqueous potassium manganate (VII) followed by dilute sulfuric acid.	Purple MnO_4^- solution decolourised [M10]
(vii)	To the third part of the solution **(iv)**, add aqueous sodium hydroxide and a piece of aluminium foil. Warm gently.	Pungent colourless gas turns moist red litmus blue. (Gas is NH_3.) [M11]

[6]

(c) **(i)** Suggest the identities of the cation and anion present in **FB 4** from your observations from the tests in **(a).**

cation: …………………… **anion:** …………………… [1]

Zn^{2+} & Cl^- [1]

(ii) Write equations, with state symbols to explain your observations for test in **a(i).**

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

………………………………………………………………………………

……………………………………………………………………………… [3]

When aq NH_3 is added, a white ppt of $Zn(OH)_2$ is formed.

- $Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2$ ……. (1)

- When excess aqueous NH_3 is added, ligand exchange takes place. NH_3 ligand replaces water ligand from $[Zn(H_2O)_6]^{2+}$ to form $[Zn(NH_3)_4]^{2+}$ which is a colourless solution.

- $[Zn(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+} + 6H_2O$ ……. (2)

Accept $[Zn(NH_3)_6]^{2+}$ and $[Zn(NH_3)_4(H_2O]_2]^{2+}$ and pls mark equation (2) accordingly.

- This causes $[Zn(H_2O)_6]^{2+}$ to drop, hence equilibrium (1) shifts to the left, and the precipitate, $Zn(OH)_2$ dissolves.

  (The drop in $[Zn(H_2O)_6]^{2+}$ also causes the ionic product of $Zn(OH)_2$ to decrease to the extent that IP of $Zn(OH)_2$ < Ksp of $Zn(OH)_2$. Hence the precipitate, $Zn(OH)_2$ dissolves.)

- When $H_2SO_4(aq)$ was added, $[NH_3]$ decreases, hence equilibrium (1) shifts to the left, and the precipitate, $Zn(OH)_2$ reforms.

- precipitate dissolves due to further removal of OH^- by the excess $H_2SO_4(aq)$, causing the POE of reaction (2) to shift to the left.

3 marks for 6 bullets correct
2 marks for 3, 4-5 bullets correct
1 mark for 1-2 bullets correct

(d) **(i)** Suggest the identity of the other anion present in **FB5** ***before*** it was heated.

……………………………………………………………………………… [1]
NO_3^- [1]

(ii) Suggest the identity of the anion present in **FB5** ***after*** it was heated.

……………………………………………………………………………… [1]
NO_2^- [1]

(iii) In **(b)(v)**, the anion is behaving as ………………………….. [1]
an oxidising agent [1]

(iv) In **(b)(vi)**, the anion is behaving as …………………………. [1]
a reducing agent [1]

(v) Suggest the purpose of carrying out test **(b)(ii)**.

…………………………………………………………………………………

…………………………………………………………………………………

……………………………………………………………………………… [1]

- To remove any NH_4^+ ions that is present as NH_3, as the presence of NH_4^+ will interfere with the results of **(b)(iii)**.

OR

- to confirm that there is no NH_4^+ ions present in the sample, so that there will be no interference of the results of **(b)(iii)**.

1 mark

(c) Student **C** carried out the following experiment on **FB 5**, predict the observations that will be observed and write your answer in the blanks.

Experiment	Observation
To solid **FB 5** in a boiling tube. Heat heat strongly for 4 min. Let the residue cool. Add dilute sulfuric acid to it.	Brown pungent gas formed (Gas is NO_2.)

[1]

[Total: 16]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^{-}(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^{-}(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^{-}(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^{-}(aq)	NH_3 liberated on heating with OH^{-}(aq) and Al foil
nitrite, NO_2^{-}(aq)	NH_3 liberated on heating with OH^{-}(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I	black solid / purple gas	brown	purple

Nanyang JC 2018 H2 Chemistry Prelim Practical Exam

Apparatus
2 × 50 cm^3 burettes
1 × burette clamp
1 × stand
2 × funnel for filling burettes
1 × 250 cm^3 conical flask
1 × 25 cm^3 pipette
1 × pipette filler
1 × white tile
1 × 250 cm^3 beaker, labelled “for waste”
1 × 100 cm^3 beaker
1 × metal calorimeter
1 × stopwatch
1 × –10 ^oC to +110 ^oC at 1 ^oC thermometer
50 cm^3 measuring cylinder
1 × glass rod
1 × Bunsen burner
1 × lighter
1 × tripod
1 × heatproof mat
1 × test-tube rack
1 × test-tube holder
1 × metal spatula
4 × test-tubes
2 × boiling tubes
3 × droppers
1 × wash bottle containing distilled water
Access to paper towels
Access to gas supply
Access to delivery tubes
Access to a clear plastic bag containing 3 × red and 3 × blue litmus paper, 2 × strips of filter paper, splints

Chemicals

label	per candidate	identity	notes
FB 1	200	solution containing a mixture of 0.119 mol dm^{-3} of ethanedioic acid and 0.0149 mol dm^{-3} of sodium ethanedioate	Dissolve 15.00 g of $C_2O_4H_2.2H_2O$ & 2.00 g of $C_2O_4Na_2$ in each dm^3 of solution
FB 2	100	0.35 mol dm^{-3} sodium hydroxide	Dissolve 14.00 g of NaOH in each dm^3 of solution
FB 3	250 cm^3	aqueous sodium carbonate	Dissolve 8.00 g of aqueous sodium carbonate in each dm^3 of solution
thymolphthalein indicator	5 cm^3	thymolphthalein indicator	freshly-prepared
FB 4	5 cm^3	0.1 mol dm^{-3} of aqueous zinc chloride solution	Dissolve 13.64 g of $ZnCl_2$ in each dm^3 of solution
FB 5	~ 3 g	sodium nitrate	Weigh about 3 g of $NaNO_3$ in a boiling tube and seal the boiling tube

Bench Reagents

- aluminium foil
- aqueous potassium iodide
- aqueous silver nitrate
- aqueous potassium manganate(VII)
- dilute sulfuric acid
- aqueous sodium hydroxide
- aqueous ammonia
- limewater

NANYANG JUNIOR COLLEGE
JC2 PRACTICAL PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

CLASS	1	7			REG NO.			TUTOR	

CHEMISTRY 9729/04

Paper 4 Practical

28 August 2018

2 hour 30 minutes

Candidates answer on the Question Paper

Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory, where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 22 and 23.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 28
2	/ 11
3	/16
Total	/55

This document consists of **23** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

1 **To determine the concentrations of aqueous sodium hydroxide and aqueous ethanedioic acid and hence the percentage by mass of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.**

You are provided with the following reagents.

- **FB 1** is a mixture of approximately 0.01 mol dm^{-3} aqueous sodium ethanedioate, $C_2O_4Na_2$, and approximately 0.1 mol dm^{-3} ethanedioic acid, $C_2O_4H_2$
- **FB 2** is aqueous sodium hydroxide, NaOH
- **FB 3** is 0.0755 mol dm^{-3} aqueous sodium carbonate
- thymolphthalein indicator

Both sodium hydroxide and sodium carbonate are bases which will neutralise ethanedioic acid as shown in **reactions 1** and **2**.

$2NaOH + C_2O_4H_2 \rightarrow C_2O_4Na_2 + 2H_2O$ **reaction 1**

$Na_2CO_3 + C_2O_4H_2 \rightarrow C_2O_4Na_2 + CO_2 + H_2O$ **reaction 2**

In this experiment, you will add different volumes of **FB 3** to identical samples of the mixture of aqueous sodium ethanedioate, $C_2O_4Na_2$, and ethanedioic acid, $C_2O_4H_2$, **FB 1**. You will then complete the neutralisation of $C_2O_4H_2$ in each mixture by titrating with dilute sodium hydroxide, **FB 2**.

Each titration is to be performed **once only**, so great care should be taken that you do not exceed the end-points.

Graphical analysis of your results will enable you to determine the concentrations of the ethanedioic acid in the mixture of aqueous $C_2O_4Na_2$, and $C_2O_4H_2$, **FB 1** and of the sodium hydroxide, **FB 2**.

Read through the whole method of conducting the experiment before starting any practical work.

The experiment

(a) Titrations

Experiment 1

1. Fill a burette with **FB 3**.
2. Pipette 25.0 cm^3 of **FB 1** into a 250 cm^3 conical flask.
3. Run 5.00 cm^3 of **FB 3** into the flask.
4. Add 10 – 15 drops of thymolphthalein indicator to the flask.
5. Fill a second burette with **FB 2**.
6. Titrate the mixture in the conical flask against **FB 2** until the first permanent pale blue colour remains in the solution.
7. Rinse the conical flask thoroughly before it is used for the next experiment.

The end-point should be found after the addition of approximately 14 cm^3 of **FB 2**.

One titration, performed accurately, will be sufficient.

Experiment 5

1. Repeat **Experiment 1** but run 30.00 cm^3 of **FB 3** into the flask containing 25.0 cm^3 of **FB 1**.

Experiments 2 – 4

Select **three** other suitable volumes of **FB 3** for use in **Experiments 2 – 4**. Your selected volumes must be between the volumes used in **Experiments 1 and 5**.

Do not use volumes of FB 3 outside the range of 5 – 30 cm^3.

Repeat the procedures used in **Experiment 1** but, in each case, add 25.0 cm^3 of **FB 1** and your chosen volume of **FB 3** into the conical flask. You should perform your titrations in order of **increasing** volume of **FB 3**.

Rinse this conical flask thoroughly between each titration.

Prepare a table in the space below and use it to record the titration results for each volume of **FB 3** added. You should record your titration results in order of **increasing** volume of **FB 3** added.

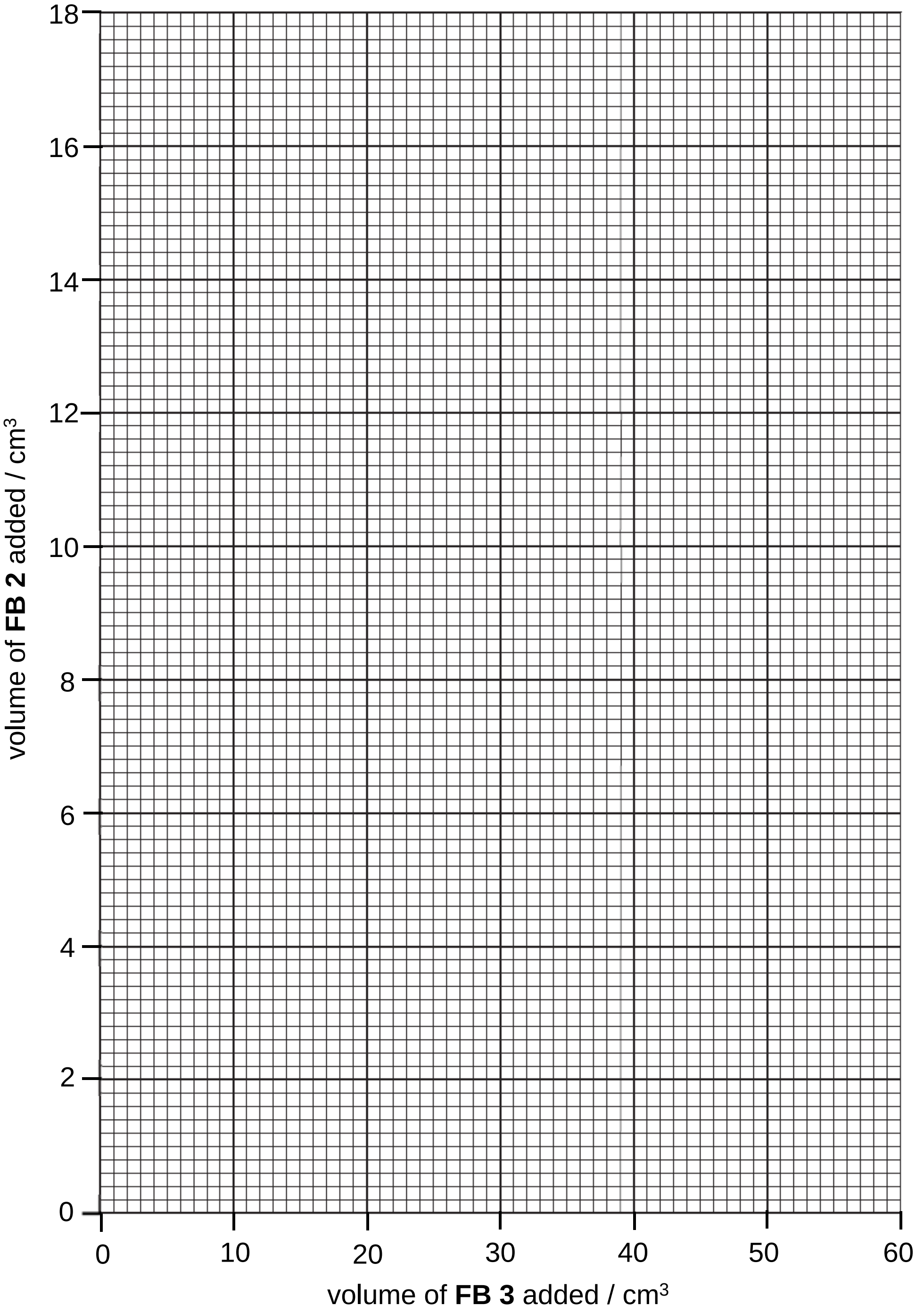
I	
II	

[2]

(b) **(i)** Plot, on the grid below, your values for the **FB 2** titre (*y-axis*) against the volume of **FB 3** added (*x-axis*).

Draw the line of best fit, taking into account all of your plotted points. Hence obtain values for

- the volume of **FB 3** required, $\mathbf{V_{max}}$**(FB 3)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 2** is added;
- the volume of **FB 2** required, $\mathbf{V_{max}}$**(FB 2)**, to react completely with 25.0 cm^3 of **FB 1** if no **FB 3** is added.



Teacher's *V_{max}***(FB 3)**	
diff.	
Teacher's *V_{max}***(FB 2)**	
diff.	
I	
II	
III	
IV	
V	

$\mathbf{V_{max}}$**(FB 3)** = ……………….. $\mathbf{V_{max}}$**(FB 2)** = ………………..

[5]

(ii) Calculate the gradient of your graph line, showing clearly how you did this.

gradient = ...………………… [1]

(iii) Explain, in terms of the chemistry involved, the direction of the slope of your graph.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………… [1]

Calculations
Show your working and appropriate significant figures in **all** of your calculations.

(c) **(i)** Using appropriate data from your graph, calculate the concentration of ethanedioic acid, $C_2O_4H_2$ in **FB 1**.

concentration of $C_2O_4H_2$ in **FB 1** = …………………. [1]

(ii) Using your answer to **(c)(i)** and appropriate data from your graph, calculate the concentration of sodium hydroxide in **FB 2**.

concentration of sodium hydroxide in **FB 2** = ……………… [1]

(d) Use the expression below to calculate the concentration of sodium hydroxide in **FB 2**.

$$[NaOH] = \frac{2[Na_2CO_3]}{|\,gradient\,|}$$

concentration of sodium hydroxide in **FB 2** = ………………………… [1]

(e) Student **B** repeats the experiment described in **(a)**. However, student **A** had used up **FB 3**. As such student **B** has to prepare another 250 cm^3 of **FB 3**. Unknowingly, he weighs a sample of solid sodium carbonate which is slightly damp for the preparation of **FB 3**.

Suggest and explain what effect this will have on the value of **V_{max}(FB 3)** he obtains.

effect on **V_{max}(FB 3)** …………………………………………………………………..

explanation ……………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………… [1]

(f) A student performs the original experiment using solutions of different concentration to those you have used. He determines the gradient of his line using a small triangle.

He calculates the concentration of NaOH in **FB 2**. In part **(c)(ii)** he obtains a value of 0.589 mol dm^{-3}. In part **(d)** he obtains a value of 0.581 mol dm^{-3}.

Suggest which of these two values is likely to be more accurate. Explain your answer.

the more accurate value is …………………………………………………………..

explanation ……………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………… [1]

(g) Plan an experiment to determine the percentage by mass of sodium ethanedioate, $C_2O_4Na_2$ in **FB 1**.

Acidified potassium manganate(VII) oxidises ethanedioate ions, $C_2O_4^{2-}$ ions, as shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

However, the reaction takes place slowly at first. The rate of the reaction increases as more products are produced. This is because one of the products acts as a catalyst for the reaction. Hence this reaction is an example of 'autocatalysis'.

(i) Identify the product that acts as the catalyst in the reaction.

……………………………………………………………………………… [1]

(ii) Using the information given above, complete the procedures for this additional experiment which is written partially as shown below.

*Do **NOT** carry out this experiment.*

1. Fill a burette with 0.020 mol dm^{-3} of an aqueous solution of potassium manganate(VII).
2. Pipette 10.0 cm^3 of **FB 1** into a 250 cm^3 conical flask.
3. Using a 10 cm^3 measuring cylinder, add in 10 cm^3 of sulfuric acid into the same conical flask.
4. ……………………………………………………………………………….....

   ……………………………………………………………………………….....

   ……………………………………………………………………………….....

   ……………………………………………………………………………….....
5. Titrate the mixture in the conical flask against potassium manganate(VII) until the first permanent ……..……………….. colour remains in the solution.
6. Repeat the titration …..…………………………………………………….....

   ……………………………………………………………………………….....

   ……………………………………………………………………………….....

   ……………………………………………………………………………….....

[2]

(h) Planning

The volume of aqueous sodium hydroxide needed to completely neutralise all the ethanedioic acid, $C_2O_4H_2$ present in **FB 1** can also be obtained by carrying out a thermometric titration.

The reaction between an acid and an alkali is exothermic. It is possible to make use of this fact to determine the equivalence-point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration* and can be used to calculate the concentration of an acid solution and the value of the enthalpy change of neutralisation, ΔH_n.

The concentration of an acid solution can be determined by adding various volumes of acid and alkali and measuring the change in temperature. A series of about six experiments were conducted, where different volumes of alkali were added to a fixed volume (for example 25.0 cm^3) of acid while keeping the total volume of the solution constant by adding appropriate volumes of water.

The data obtained is plotted and two best-fit graph lines are drawn. One line is drawn using data before the equivalence-point and the second line using the remaining data. These lines are then extrapolated (extended) until they cross.

(i) Using the information given above, you are required to write a plan for a thermometric titration in which a known concentration of an aqueous solution of sodium hydroxide is added to **FB 1**.

You are to determine the volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in **FB 1**.

You may also assume that you are provided with:

- **FB 1** which is a mixture of approximately 0.01 mol dm^{-3} aqueous sodium ethanedioate, $C_2O_4Na_2$, and approximately 0.1 mol dm^{-3} ethanedioic acid, $C_2O_4H_2$.
- 0.35 mol dm^{-3} aqueous sodium hydroxide, NaOH
- graph paper;
- the equipment normally found in a school or college laboratory.

Your plan should include:

- calculation of the approximate volume of aqueous sodium hydroxide required to completely neutralise the ethanedioic acid present in 25.0 cm^3 of **FB 1**;
- brief, but specific, details of the apparatus you would use, bearing in mind the levels of precision they offer;
- an outline of how the results would be obtained;
- a table containing the volumes of each reagent to be added
- how you would recognise that the equivalence-point had been passed;
- on the grid provided, a sketch of the graph you would expect to obtain;
- an explanation of the shape of your graph;

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Explanation of the shape of the graph:

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

……………………………………………………………………………………………………..

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……………………………………………………………………………………..……………… [8]

(ii) In another experiment, hydrochloric acid is used instead of **FB 1**.
If the hydrochloric acid has the same concentration as the ethanedioic acid present in **FB 1**, draw on your graph in **(i)** another pair of lines to show the results you would expect to obtain.

Explain your answer.

…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………. [3]

[Total: 28]

2 You are required to determine the enthalpy change of combustion of ethanol.

When an exothermic reaction takes place in a container such as a metal calorimeter, some of the evolved heat energy is absorbed by the metal calorimeter.

When an endothermic reaction takes place some of the required heat energy is supplied by the metal calorimeter.

The amount of heat energy evolved or supplied for a 1 °C change in temperature is known as the heat capacity of the metal calorimeter.

In preparation for your experiment to determine the enthalpy change of combustion of ethanol, you will first need to determine the approximate heat capacity of a 100 cm^3 metal calorimeter.

Before starting any practical work read through the instructions in (a) and draw up a table to record your results.

(a) Determining the approximate heat capacity of the 100 cm^3 metal calorimeter

When samples of hot and cold water are mixed in the 100 cm^3 metal calorimeter, some heat is lost to the metal calorimeter in raising its temperature. To determine the approximate heat capacity of your 100 cm^3 metal calorimeter, you will determine the maximum temperature rise when a sample of hot water is added to cold water in the metal calorimeter.

- Use a 50 cm^3 measuring cylinder to transfer 50 cm^3 of cold water into the 100 cm^3 metal calorimeter.
- Use the 50 cm^3 measuring cylinder to transfer 50 cm^3 of cold water into a 100 cm^3 beaker.
- Note the temperature of the water in this 100 cm^3 beaker and heat it **carefully and gently** until the temperature of the water in it has increased by 45–50 °C then stop heating, *e.g. if the water is at 20.0 °C you should warm it to 65–70 °C.*
- Stir the cold water in the 100 cm^3 metal calorimeter with the thermometer.
- Record the temperature of the cold water (this is the temperature at t = 0 min).
- Record the temperature each minute for 3 minutes.
- After you have taken the reading at t = 3 min, use the thermometer to stir the hot water in the 100 cm^3 beaker.
- At t = 4 min, measure the temperature of the hot water and record this value in the box below.
- **Immediately** add the hot water from the 100 cm^3 beaker to the cold water in the 100 cm^3 metal calorimeter.
- Stir with the thermometer but do not record the temperature.
- Continue to stir the water throughout the experiment.
- Record the temperature at t = 5 min, and then every ½ minute until t = 8 min.
- Record all measurements of time and temperature obtained on page 13.

The temperature, $\boldsymbol{T_1}$, of the hot water at t = 4 min is ………………… °C.

Table of results

I	
II	
III	

[3]

(b) **Graph plotting**

1. Plot a graph of the temperature of the water in the 100 cm^3 metal calorimeter (y-axis) against time (x-axis) on the grid below. Do not plot the temperature, $\boldsymbol{T_1}$, of the hot water at t = 4 min.
2. Draw two straight lines of best fit; one through the points up to t = 3 min; the second through the points from t = 5 min to t = 8 min. Extrapolate both lines to t = 4 min.
3. From the extrapolated lines read the minimum and the maximum temperatures at t = 4 min. Record these values in the spaces provided below.
4. Determine the values for the two temperature changes at t = 4 min.

I	
II	
III	
IV	

Minimum temperature, $\boldsymbol{T_2}$, at t = 4 min is ……….............. °C.

Maximum temperature, $\boldsymbol{T_3}$, at t = 4 min is ……….............. °C.

Temperature rise for 50 cm^3 of cold water in the 100 cm^3 metal calorimeter, ($\boldsymbol{T_3} - \boldsymbol{T_2}$) is …………...... °C.

Temperature fall for 50 cm^3 of hot water from the 100 cm^3 beaker, ($\boldsymbol{T_1} - \boldsymbol{T_3}$) is …………...... °C.

[4]

(c) **Calculations**
Working should be shown in all calculations.
[**4.2 J** are absorbed or released when the temperature of 1.0 cm^3 of **water** changes by 1.0 °C.]

(i) Calculate the heat energy gained by the 50 cm^3 of cold water in the 100 cm^3 metal calorimeter.

The heat energy gained by the cold water = ………………… J.

(ii) Calculate the heat energy lost by the 50 cm^3 of hot water from the 100 cm^3 beaker.

The heat energy lost by the hot water = ………………… J.

(iii) The difference between the values calculated in **(i)** and **(ii)** is an approximate value for the total heat energy absorbed by the 100 cm^3 metal calorimeter during the experiment. The heat capacity of the metal calorimeter is the amount of heat energy absorbed for a 1 °C change in temperature.

$$\begin{matrix}\textit{approximate heat capacity}\\ \textit{of the } 100 \textit{ cm}^3 \textit{metal calorimeter}\end{matrix} = \frac{(\textit{heat energy lost}) - (\textit{heat energy gained})}{(T_3 - T_2)} \text{ J °C}^{-1}$$

Use your answers to **(i)** and **(ii)** and the temperature rise from **(b)** to calculate the approximate heat capacity of the 100 cm^3 metal calorimeter.

The approximate heat capacity of the 100 cm^3 metal calorimeter = ………………… J $°C^{-1}$.
[1]

(d) Determining the enthalpy change of combustion of ethanol, C_2H_5OH

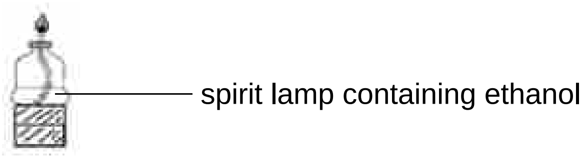
An experiment was carried out as follows to determine the enthalpy change of combustion of ethanol.

The 100 cm^3 metal calorimeter used in **(a)** was used to contain some water. The water was heated using ethanol placed in a spirit lamp. The temperature rise was recorded. The spirit lamp was weighed before and after the experiment to determine the mass of ethanol used. The following results were obtained.

mass of ethanol burned = 0.391 g
mass of water heated = 40.0 g
temperature rise = 19.5 ^{o}C

(i) Complete the following diagram to show the experimental set-up needed to carry out the experiment to determine the enthalpy change of combustion of ethanol.
You are to use the following apparatus to complete the diagram:

- stand and clamp
- 100 cm^3 metal calorimeter
- thermometer
- tripod stand and heat-proof mat



[1]

(ii) Use your answer in **(c)(iii)** and the results obtained to calculate the enthalpy change of combustion of ethanol.
[*A*r: O, 16.0; C, 12.0; H, 1.0]
[specific heat capacity of water = 4.2 J $^{o}C^{-1}$ cm^{-3}]
(If you were unable to answer **(c)(iii)**, you may assume that the heat capacity of the 100 cm^3 metal calorimeter is 50 J $^{o}C^{-1}$.)

enthalpy change of combustion of ethanol = ……………………..[1]

(iii) Calculate the maximum percentage error in the measurement of each mass used in the experiment.

mass measured	maximum error in a single reading	maximum percentage error / %
0.391 g of ethanol burned	0.0005 g	
40.0 g of water	0.05 g	

[1]

[Total: 11]

[Turn over

3 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

FB 4 is a solution containing **one** cation and **one** anion from the Qualitative Analysis Notes in pages 22 and 23.
Solid **FB 5** contains the sodium ion and **one** anion from the Qualitative Analysis Notes in pages 22 and 23.

(a) Carry out the following tests on **FB 4** and state the observations you make.

	Test	*Observations*
(i)	To 1 cm depth of aqueous **FB 4** in a test-tube, add aqueous ammonia, then	
	add sulfuric acid dropwise until there is no further observations.	
(ii)	To 1 cm depth of aqueous **FB 4** in a test-tube, add silver nitrate,	
	followed by aqueous ammonia.	

For Examiner's Use			
Obs points		*marks*	

(b) Carry out the following tests on **FB 5** and state the observations you make.

	Test	*Observations*
(i)	Place half of the solid **FB 5** in a boiling tube. Heat strongly until the solid melts and a gas is given off. Test and identify the gas. Continue the strong heating for 2-3 min, then leave the tube to cool and retain the residue for the test in **(iv)**.	
(ii)	To the remaining half of **FB 5** in the boiling tube, add 3 cm depth of aqueous sodium hydroxide. Warm gently and retain for the test in **(iii)**.	
(iii)	To the solution from the test in **(ii)**, add a piece of aluminium foil and warm gently.	
(iv)	Dissolve the residue from test in **(i)** in distilled water and divide the solution into **three** parts. Use these for the tests in **(v)** to **(vii)**.	☒
(v)	To one part of the solution from **(iv)**, add aqueous potassium iodide followed by dilute sulfuric acid.	
(vi)	To the second part of the solution from **(iv)**, add aqueous potassium manganate (VII) followed by dilute sulfuric acid.	
(vii)	To the third part of the solution **(iv)**, add aqueous sodium hydroxide and a piece of aluminium foil. Warm gently.	

[6]

(c) **(i)** Suggest the identities of the cation and anion present in **FB 4** from your observations from the tests in **(a).**

cation: …………………… **anion:** …………………… [1]

(ii) Write equations, with state symbols to explain your observations for test in **a(i).**

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………………………………………………………………………………………

……………………………………………………………………………………… [3]

(d) **(i)** Suggest the identity of the anion present in **FB5** ***before*** it was heated.

……………………………………………………………………………………… [1]

(ii) Suggest the identity of the anion present in **FB5** ***after*** it was heated.

……………………………………………………………………………………… [1]

(iii) In **(b)(v)**, the anion is behaving as ………………………….. [1]

(iv) In **(b)(vi)**, the anion is behaving as …………………………. [1]

(v) Suggest the purpose of carrying out test **(b)(ii)**.

………………………………………………………………………………………

………………………………………………………………………………………

……………………………………………………………………………………… [1]

(e) Student **C** carried out the following experiment on **FB 5**, predict the observations that will be observed and write your answer in the blanks.

Test	*Observations*
To solid **FB 5** in a boiling tube. Heat heat strongly for 4 min. Let the residue cool. Add dilute sulfuric acid to it.	

[1]

[Total: 16]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl (aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br (aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I (aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3 (aq)	NH_3 liberated on heating with OH (aq) and A*l* foil
nitrite, NO_2 (aq)	NH_3 liberated on heating with OH (aq) and A*l* foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I	black solid / purple gas	brown	purple

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME ☐

CT GROUP	1	7	S			INDEX NUMBER		

CHEMISTRY **9729/01**

Paper 1 Multiple Choice **21 September 2018**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

1 In an experiment, 25.0 cm^3 of 0.02 mol dm^{-3} of vanadium(II) ions was found to react with 15.00 cm^3 of 0.02 mol dm^{-3} of acidified $KMnO_4$. The half equation for the reduction of MnO_4^- is:

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

What is the final oxidation state of vanadium?

A +3

B +4

C +5

D +6

2 Sulfur dichloride dioxide, SO_2Cl_2, reacts with water to give a mixture of sulfuric acid and hydrochloric acid.

How many moles of calcium hydroxide, $Ca(OH)_2$, would be needed to neutralise the solution formed by adding one mole of SO_2Cl_2 to an excess of water?

A 1

B 2

C 3

D 4

3 *The use of Data Booklet is relevant to this question.*

An ion **E^{2+}** contains 24 protons.

Which of the following statements about **E^{2+}** is **incorrect**?

A The enthalpy change for the reaction **E**(g) → **E^{2+}**(g) + 2e is +2243 kJ mol^{-1}.

B The removal of the two electrons from **E** to form **E^{2+}** is from the 4s subshell.

C The angle of deflection of **E^{2+}** in an electric field is smaller than that of **E^{3+}**.

D **E^{2+}** is isoelectronic with Mn^{3+}.

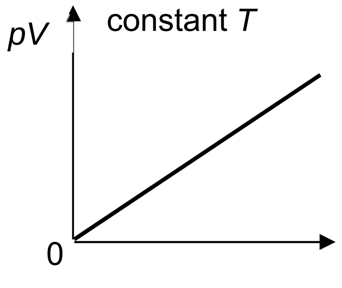
4 Which of the following statements explain why aluminium chloride, $\mathrm{A}l_2\mathrm{C}l_6$, sublime at a relatively low temperature?

1 Intermolecular forces between the $\mathrm{A}l_2\mathrm{C}l_6$ molecules are weak.
2 The dative bonds between $\mathrm{A}l$ and $\mathrm{C}l$ atoms are weak.
3 The covalent bonds between $\mathrm{A}l$ and $\mathrm{C}l$ atoms are weak.

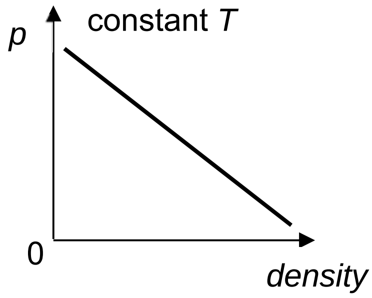
A 1 only
B 1 and 2 only
C 2 and 3 only
D 3 only

5 Which of the following diagrams correctly describes the behavior of a fixed mass of an ideal gas? (T is measured in K)

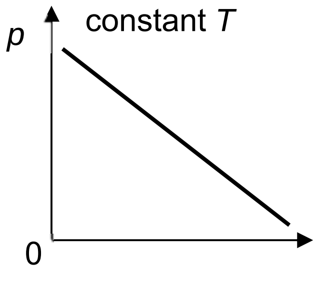
A



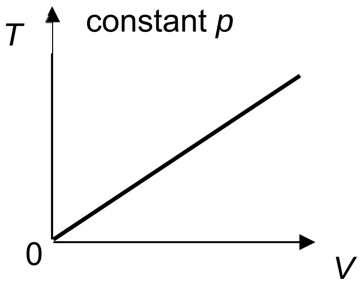
B



C



D



6 The enthalpy change of reaction between hydrogen sulfide and oxygen is ΔH_1.

$$H_2S(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s) \qquad \Delta H_1$$

What information is **not** needed to calculate ΔH_1?

A enthalpy change of vaporisation of $H_2O(l)$
B enthalpy change of formation of $H_2S(g)$
C enthalpy change of formation of $H_2O(l)$
D enthalpy change of combustion of $S(s)$

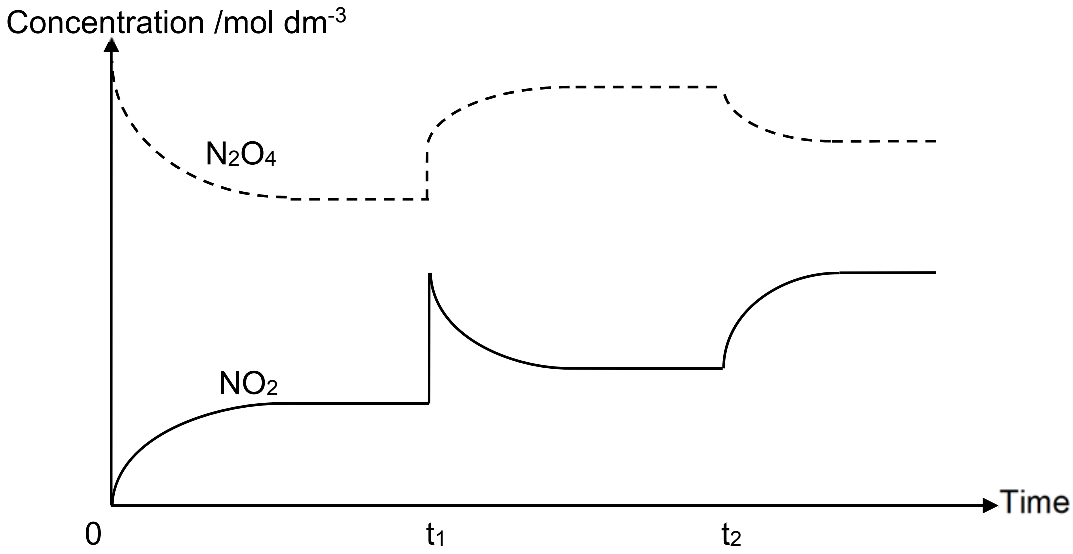
7 Which suggested mechanism is consistent with the experimentally determined rate equations?

	Rate equation	**Suggested mechanism**	
A	Rate = $k[NO]^2[O_2]$	$2NO(g) \rightarrow N_2O_2(g)$ $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$	(fast) (slow)
B	Rate = $k[H_2][I_2]$	$H_2(g) \rightarrow 2H(g)$ $2H(g) + I_2(g) \rightarrow 2HI(g)$	(slow) (fast)
C	Rate = $k[HBr][O_2]$	$2HBr(g) + O_2(g) \rightarrow 2HBrO(g)$ $HBrO(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$	(slow) (fast)
D	Rate = $k[H_2O_2][I^-]$	$2H^+(aq) + 2I^-(aq) \rightarrow 2HI(aq)$ $2HI(aq) + H_2O_2(aq) \rightarrow I_2(aq) + 2H_2O(l)$	(fast) (slow)

8 An amount of N_2O_4 was placed in a closed vessel and allowed to reach equilibrium as shown below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

Two changes were made to the equilibrium system at t_1 and t_2.



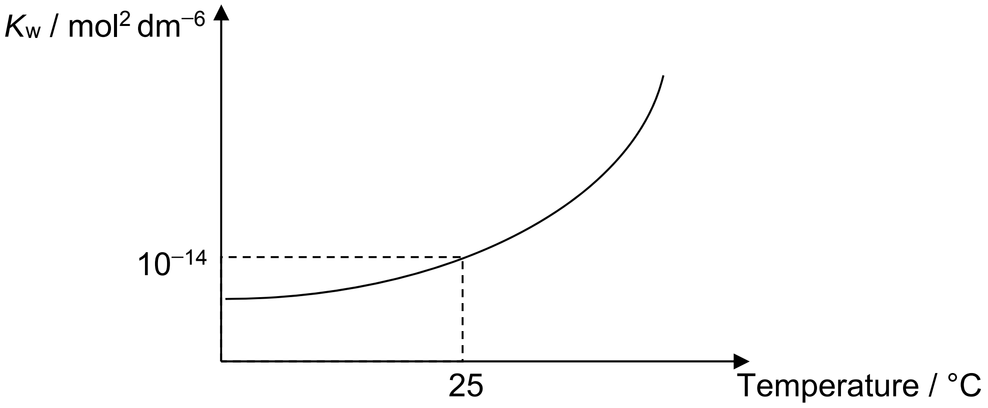
Which are the changes made at t_1 and t_2?

	t_1	t_2
A	More NO_2 was added	Temperature was increased
B	An inert gas was added at constant volume	Temperature was decreased
C	Volume of the system was decreased	Temperature was increased
D	Volume of the system was increased	Temperature was decreased

9 Water dissociates as shown:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, varies with temperature as shown in the graph below.



Which statements about the above equilibrium system are correct?

1 The pH of water decreases as temperature increases.

2 The concentrations of H^+ and OH^- are equal at all temperatures.

3 The dissociation of water is exothermic.

A 2 only

B 3 only

C 1 and 2 only

D 2 and 3 only

10 The pH range and colour changes for two acid-base indicators are given below:

Indicator	Colour in acidic solution	pH range	Colour in basic solution
P	Violet	3.0-5.0	red
Q	Yellow	5.7-7.6	blue

Which solution will appear red in **P** and yellow in **Q**?

A 0.1 mol dm^{-3} of HCl

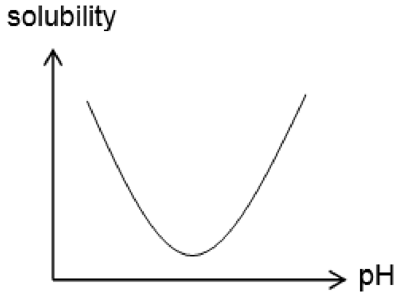
B 0.1 mol dm^{-3} of NaOH

C 0.1 mol dm^{-3} of CH_3CO_2H (K_a = 1.8 x 10^{-5} mol dm^{-3})

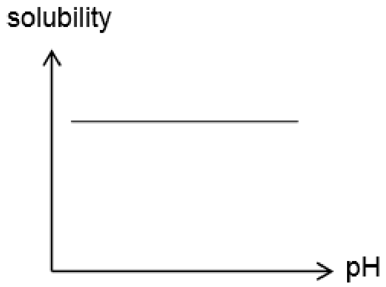
D 0.1 mol dm^{-3} of HX (K_a= 2.5 x 10^{-10} mol dm^{-3})

11 The solubility product of calcium carbonate, $CaCO_3$, is 4.81 x 10^{-9} mol^2 dm^{-6}. Which of the following graphs shows how the solubility of $CaCO_3$ will vary with pH at constant temperature?

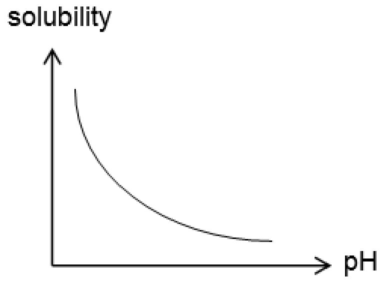
A



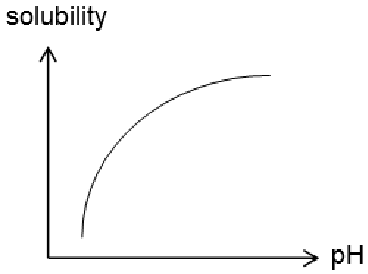
B



C



D



12 The equilibrium between Ag_2CO_3, a sparingly soluble salt, and its saturated solution is as shown below.

$$Ag_2CO_3(s) + aq \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

K_{sp} of Ag_2CO_3 = 8.2 × 10^{-12} mol^3 dm^{-9}

Which one of the following is correct?

1 Adding NaC*l*(aq) will cause more Ag_2CO_3 solid to dissolve.

2 Upon the addition of sodium carbonate, solubility of Ag_2CO_3 increases.

3 K_{sp} of Ag_2CO_3 decreases as $AgNO_3$ solution is added to it.

A 1 only

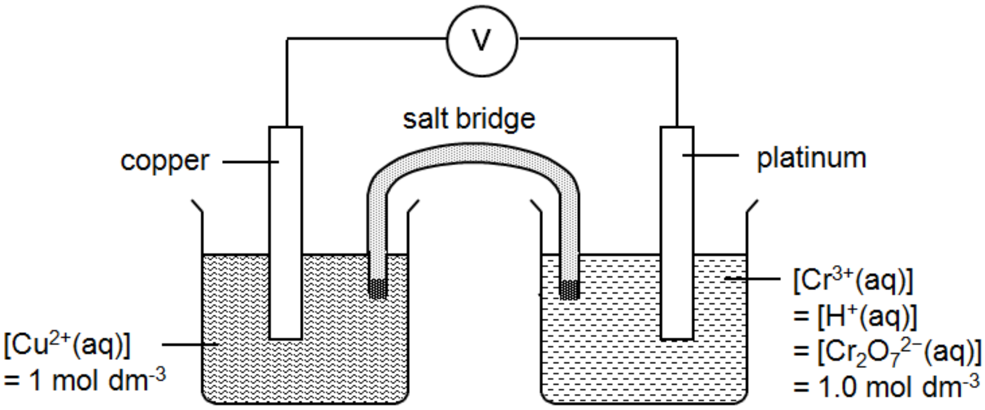
B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

13 *Use of the Data Booklet is relevant to this question.*

A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified $Cr_2O_7^{2-}/Cr^{3+}$ half-cell under standard conditions.

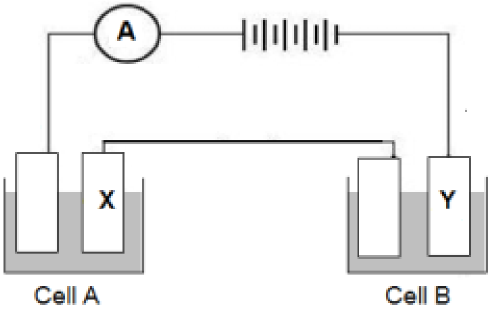


Which of the following correctly describes the effect on the e.m.f of the cell when the respective change is made?

	change	**effect on e.m.f of cell**
A	using a larger copper electrode	increases
B	addition of concentrated H_2SO_4 into reduction half-cell	decreases
C	addition of dilute NaOH into oxidation half-cell	decreases
D	addition of water into oxidation half-cell	increases

14 *Use of the Data Booklet is relevant to this question.*

A student carried out an experiment involving the electrolysis of aqueous copper(II) sulfate in cell **A** and aqueous chromium(III) sulfate in cell **B**.



Given that 6.35 g of copper was deposited at electrode **X** at the end of the experiment, what is the mass of chromium deposited at electrode **Y**?

A	0.87 g	**B**	1.74 g
C	3.47 g	**D**	10.4 g

15 ***P*, *Q*** and ***R*** are elements of the third period of the Periodic Table. The oxide of ***P*** is amphoteric, the oxide of ***Q*** is basic and oxide of ***R*** is acidic.

What is the order of increasing ionic radius?

A ***RQP***

B ***QPR***

C ***PRQ***

D ***PQR***

16 Which of the following statements about Group 2 elements and their compounds is correct?

1 Magnesium hydroxide decomposes on heating to give magnesium oxide and steam.

2 1 mole of strontium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate

3 Magnesium has a higher melting point than strontium.

A 1 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

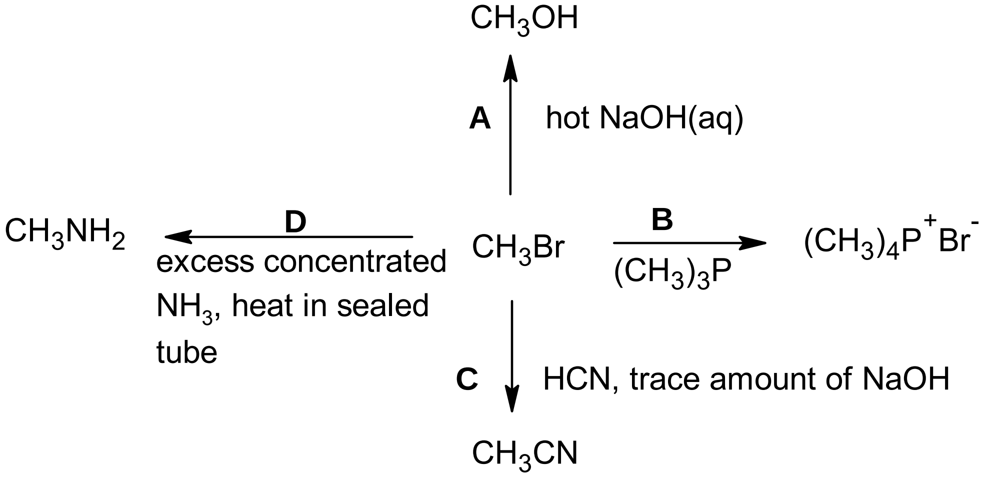
17 Adding KSCN (aq) to $FeNO_3$(aq) causes the colour of the solution to change from yellow to blood red.

Which of the following row correctly shows the number of d-electrons and the energy gap between the d-orbitals, before and after the reaction?

	number of d-electrons	energy gap between the d-orbitals
A	changes	changes
B	changes	remains the same
C	remains the same	changes
D	remains the same	remains the same

18 A reaction scheme involving bromomethane is given below.

Which of the reactions does **not** take place?



19 3-ethylpentane can react with bromine in the presence of sunlight to give two monosubstituted halogenoalkanes:

1-bromo-3-ethylpentane and 3-bromo-3-ethylpentane.

Given the relative rates of abstracting H atoms are:

Type of H atom	primary	secondary	Tertiary
Relative rate of abstraction	1	4	6

What is the expected ratio of 1-bromo-3-ethylpentane to 3-bromo-3-ethylpentane formed?

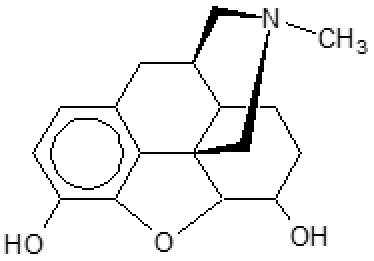
A 9 : 1

B 6 : 1

C 3 : 2

D 1 : 6

20 Morphine is an effective pain killer.



morphine

Which of the following statements about morphine is correct?

A It contains 10 chiral centers.

B It does not decolourise Br_2(aq).

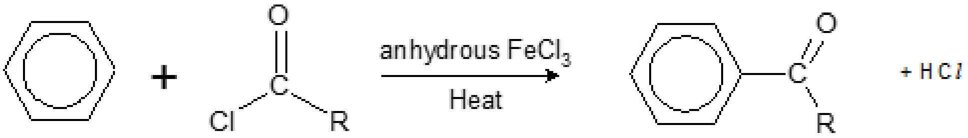
C It turns cold alkaline $KMnO_4$ from purple to colourless.

D One mole of morphine reacts with excess sodium to give 1 mole of H_2 gas.

21 Under suitable conditions, ethene may undergo a reaction with an interhalogen compound, I*Cl*. Which of the following shows the structure of the intermediate formed?

A $[CH_3CH_2]^+$ **B** $[CH_3CHI]^+$ **C** $[CH_2CH_2I]^+$ **D** $[CH_2CH_2Cl]^+$

22 Anhydrous iron(III) chloride is made by passing chlorine gas over heated iron. It can be used as a catalyst in the acylation of benzene, a process called Friedel-Crafts acylation, to produce carbonyl compounds.



The mechanism of the above reaction is similar to that of chlorination of benzene. Which of the following statements is **not** correct about the mechanism?

A The organic intermediate has a ring with one *sp*^{3} hybridised carbon.

B The overall order of reaction is 1.

C The mechanism involves RCO^+ as an electrophile.

D $FeCl_3$ is a homogeneous catalyst.

23 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

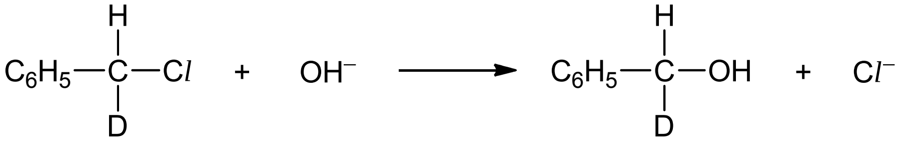
A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

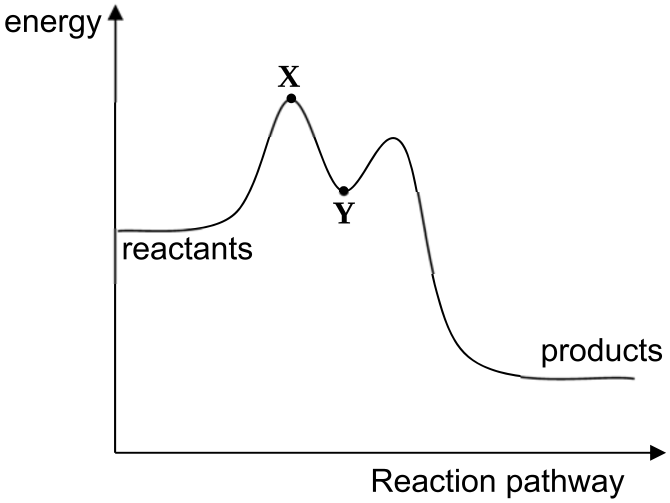
C $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

D $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

24 The energy profile for the following reaction is shown below. [D = ^2H]



$$C_6H_5-C(H)(D)-Cl + OH^- \longrightarrow C_6H_5-C(H)(D)-OH + Cl^-$$

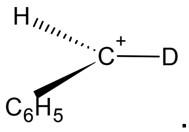


Which of the following conclusions can be drawn?

A The product has no effect on the rotation of plane polarised light.

B The rate of reaction can be increased by increasing concentration of OH^-.

C The structure of the species at point **X** is



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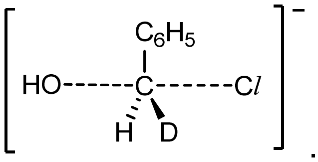
D The structure of the species at point **Y** is



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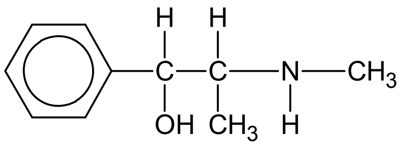
25 Ephedrine is a drug that is widely used in cold and allergy medications.

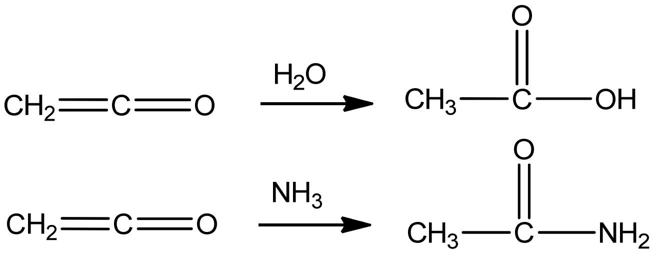


Ephedrine

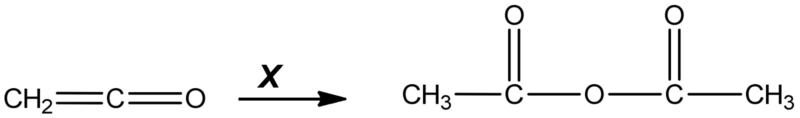
Which of the following pairs of reagents consists of one which reacts with ephedrine and one which does **not** react with ephedrine?

A	CH_3CO_2H	CH_3COCl
B	$HCl(aq)$	$SOCl_2$
C	CH_3Br	$NaOH(aq)$
D	$[Ag(NH_3)_2]^+$	2,4-dinitrophenylhydrazine

26 Ketene ($CH_2{=}C{=}O$) can combine with nucleophiles such as H_2O or NH_3 to make ethanoic acid and ethanamide respectively, as shown below.



Which of the following is the correct nucleophile ***X*** for the reaction below?



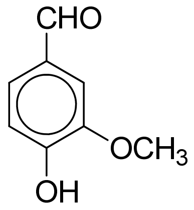
A HCO_2CH_3

B CH_3CHO

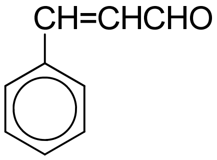
C CH_3COCH_3

D CH_3CO_2H

27 Vanillin and cinnamaldehyde are found in natural products and have very pleasant fragrances.



vanillin



cinnamaldehyde

Which of the following reagents could be used to distinguish between the two compounds? You may assume that the $–OCH_3$ group in vanillin is inert.

1 Fehling's solution

2 hot acidified aqueous $KMnO_4$

3 2, 4-dinitrophenylhydrazine

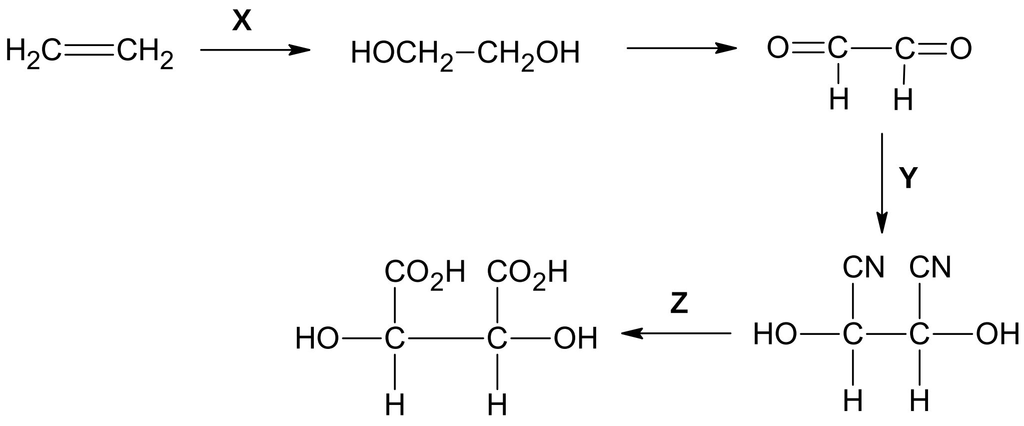
A 1 only

B 2 only

C 1 and 2 only

D 1, 2 and 3

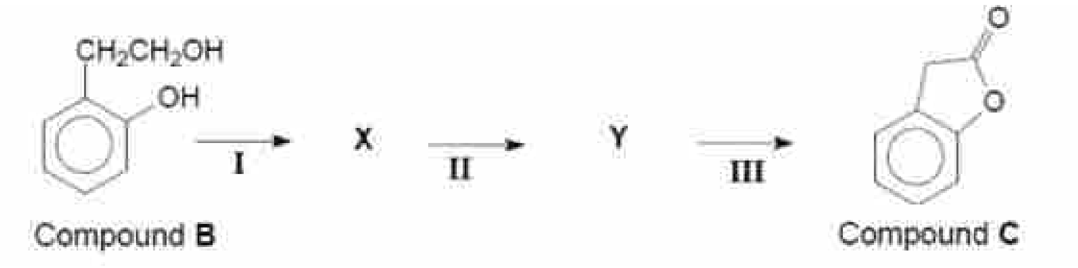
28 The following is a method of synthesising tartaric acid, a compound found in wine.



Which set of reagents and conditions can be used for the synthesis?

	stage **X**	stage **Y**	stage **Z**
A	cold $KMnO_4$, NaOH(aq)	cold HCN, trace KCN(aq)	hot $K_2Cr_2O_7$, H_2SO_4(aq)
B	cold $KMnO_4$, NaOH(aq)	ethanolic KCN, heat	HC*l*(aq), heat
C	cold $KMnO_4$, H_2SO_4(aq)	ethanolic KCN, heat	hot $K_2Cr_2O_7$, H_2SO_4(aq)
D	cold $KMnO_4$, H_2SO_4(aq)	cold HCN, trace KCN(aq)	HC*l*(aq), heat

29 Compound **B** can be converted to compound **C** as shown below.



Which of the following statements regarding the reaction scheme is correct?

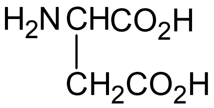
A Step **I** may involve the use of PCl_5.

B Step **I** may involve the use of hot acidified $KMnO_4$.

C Step **III** may involve the use of aqueous NaOH.

D Step **III** may involve the use of hot concentrated H_2SO_4.

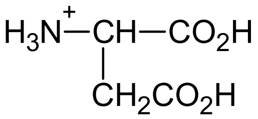
30 Which structure will be present when the amino acid aspartic acid,



$$H_2N\underset{\displaystyle CH_2CO_2H}{\underset{|}{CH}}CO_2H$$

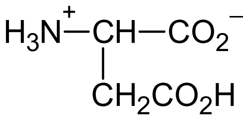
is in aqueous solution at pH 10?

A



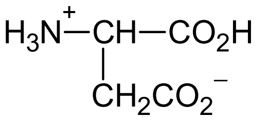
$$H_3\overset{+}{N}-\underset{\displaystyle CH_2CO_2H}{\underset{|}{CH}}-CO_2H$$

B



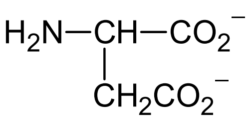
$$H_3\overset{+}{N}-\underset{\displaystyle CH_2CO_2H}{\underset{|}{CH}}-CO_2^-$$

C



$$H_3\overset{+}{N}-\underset{\displaystyle CH_2CO_2^-}{\underset{|}{CH}}-CO_2H$$

D



$$H_2N-\underset{\displaystyle CH_2CO_2^-}{\underset{|}{CH}}-CO_2^-$$

End of paper

2018 P1 Prelim answers

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
C	B	B	A	D	D	A	C	C	D	C	A	D	C	D
16	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
B	C	C	C	D	**C**	B	B	A	C	D	C	**D**	C	D

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME			
CT GROUP	1 7 S	INDEX NUMBER	

CHEMISTRY **9729/02**

Paper 2 Structured **11 September 2018**

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 9	4	/12
2	/ 8	5	/ 10
3	/ 18	6	/ 18
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

This document consists of **21** printed pages.

Answer **all** questions in the spaces provided.

1 (a) Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include Ca^{2+} and Mg^{2+}. Lime softening is a type of water treatment where aqueous Na_2CO_3 is added to remove Ca^{2+} ion as $CaCO_3$ is precipitated. These precipitates are then removed by sedimentation and filtration, where X^{2+} can be Ca^{2+} and Mg^{2+}.

$$X^{2+}(aq) + Na_2CO_3(aq) \rightarrow XCO_3(s) + 2Na^{+}(aq)$$

In the laboratory, 1 cm^3 of 0.50 mol dm^{-3} Na_2CO_3 is added to 10 cm^3 of a raw water sample. What is the minimum concentration of Ca^{2+} in the original raw water sample, which would cause a white precipitate to be observed?

The value of K_{sp} for $CaCO_3$ is 4.81×10^{-9} mol^2 dm^{-6}.

[2]

(b) A saturated solution of raw water containing both CaF_2 and $Ca(OH)_2$ has a pH of 12 at 25°C.

calcium compound	numerical value of K_{sp}
CaF_2	3.2×10^{-11}
$Ca(OH)_2$	6.4×10^{-6}

(i) Calculate the concentration of hydroxide ions in the solution.

[1]

(ii) Hence, calculate the solubility of CaF_2 in the raw water sample. Show your working clearly.

[2]

(c) Using the following data, construct an energy cycle to calculate the enthalpy change for the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	ΔH / kJ mol^{-1}
$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	−57.1
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$	−63.7
$H_2SO_4(aq) + CaCO_3(s) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$	−151.5

[4]

[Total: 9]

2 The reaction of ethanal with iodine occurs in the presence of acid catalyst, HC*l*. . The reaction is given below.

$$I_2 + CH_3CHO \xrightarrow{HCl} CH_2ICHO + HI \qquad \text{Reaction 1}$$

The table shows the results obtained when the concentrations of I_2, CH_3CHO and HC*l* were varied.

Experiment	Initial [HC*l*] / mol dm^{-3}	Initial [I_2] / mol dm^{-3}	Initial [CH_3CHO] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.20	0.20	1.6×10^{-6}
2	0.10	0.40	0.30	2.4×10^{-6}
3	0.40	0.40	0.20	6.4×10^{-6}
4	0.10	0.20	2.00	1.6×10^{-5}

(a) **(i)** Deduce the orders of reaction with respect to I_2, CH_3CHO and HC*l*. Hence, determine the rate equation.

[3]

(ii) The half-life of ethanal in experiment 1 was 60 seconds. Predict the half-life of ethanal in experiments 2 and 3. Explain your answer.

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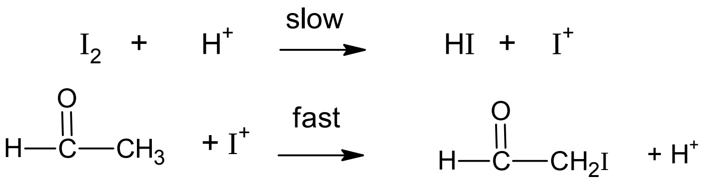
(iii) Sketch the graph of concentration of iodine against time for experiment 4.

Experiment	Initial [HC*l*] / mol dm^{-3}	Initial [I_2] / mol dm^{-3}	Initial [CH_3CHO] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
4	0.10	0.20	2.00	1.6 x 10^{-5}

[1]

(b) The following mechanisms **A** and **B** are proposed for the reaction of ethanal, iodine and acid catalyst in Reaction 1.

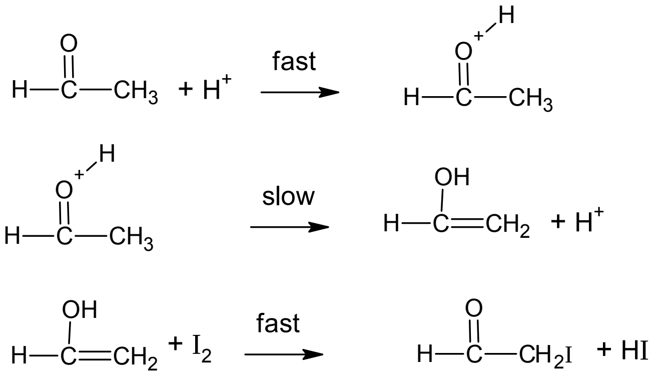
Mechanism A



$$I_2 + H^+ \xrightarrow{\text{slow}} HI + I^+$$

$$H{-}C({=}O){-}CH_3 + I^+ \xrightarrow{\text{fast}} H{-}C({=}O){-}CH_2I + H^+$$

Mechanism B



$$H{-}C({=}O){-}CH_3 + H^+ \xrightarrow{\text{fast}} H{-}C({=}O^+{-}H){-}CH_3$$

$$H{-}C({=}O^+{-}H){-}CH_3 \xrightarrow{\text{slow}} H{-}C(OH){=}CH_2 + H^+$$

$$H{-}C(OH){=}CH_2 + I_2 \xrightarrow{\text{fast}} H{-}C({=}O){-}CH_2I + HI$$

Which of the above mechanisms best agrees with the experimentally determined rate equation in **(a)(i)**? Explain your answer.

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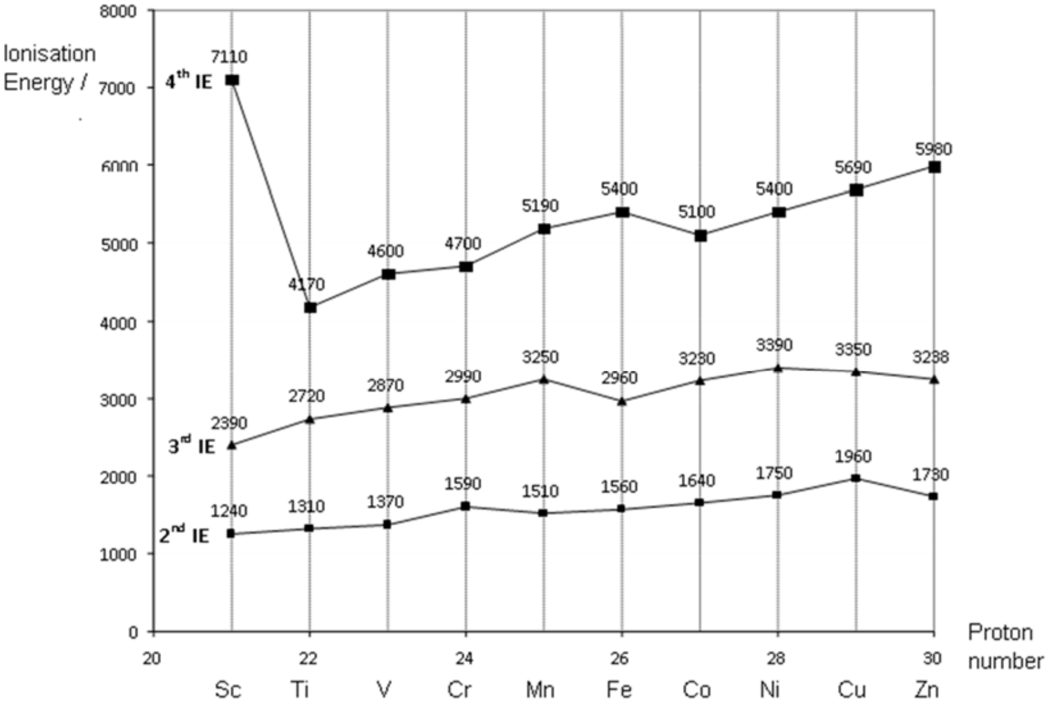
[Total: 8]

3 Transition metal is "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incompletely filled d sub-shell". Chromium and vanadium, both transition metals, have found a number of industrial uses due to their toughness and resistance to heat and corrosion.

The table below shows some information of a Group 2 metal calcium, vanadium and chromium.

	Vanadium	**Chromium**	**Calcium**
Melting point/ ^{o}C	1910	1875	843
Atomic radius/ nm	0.135	0.129	0.197
Common Oxidation Number	+2, +3, +4, +5	+2, +3, +6	+2

The graph below shows the second to fourth ionisation energies for the first row d block elements scandium to zinc.



(a) **(i)** Although the vanadium atom has more electrons than the calcium atom, the atomic radius of vanadium is smaller than that of calcium. Suggest an explanation for this.

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…………………………………………………………………………………………….........[2]

(ii) Explain why the second ionisation energies of transition elements from Ti to Cu are relatively invariant.

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………………………………………………………………………………………… [2]

(iii) Explain why the second ionisation energy of chromium is higher than that of manganese.

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………………………………………………………………………………………… [2]

(b) **(i)** State the **full** electronic configuration of Cr^{3+} ion.

………………………………………………………………………………………… [1]

(ii) The complex ion $[Cr(H_2O)_6]^{3+}$ is green, and it is an octahedral complex. On the Cartesian axes shown in Fig. 2.1, draw **fully-labelled** diagrams of the following:

- One of the d orbitals at the lower energy level in an octahedral complex- Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram 'upper'.

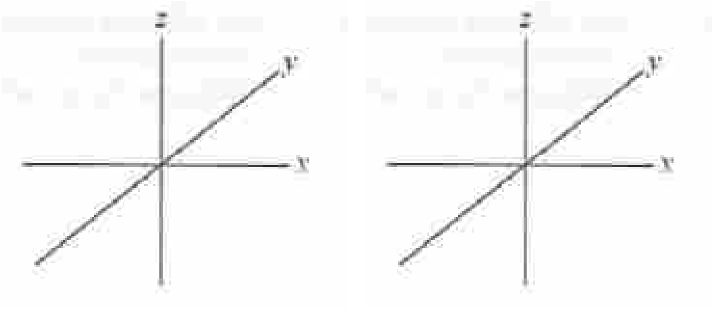

Fig. 3.1

[2]

(iii) Suggest which of the two compounds chromium(III) oxide, Cr_2O_3, and chromium(III) carbonate, $Cr_2(CO_3)_3$, would have a more exothermic lattice energy. Explain your answer.

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……………………………………………………………………………………………......... [2]

(iv) The compound K_3CrO_4 is a green solid. When mixed with dilute H_2SO_4, it undergoes disproportionation to yield Cr^{3+}(aq) and $Cr_2O_7^{2-}$(aq) ions.

By writing appropriate half-equations, write an overall balanced equation for the disproportionation of CrO_4^{3-} in acid.

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……………………………………………………………………………………………......... [2]

(v) Purification of chromium can be achieved by electro-refining chromium from an impure chromium anode onto a pure chromium cathode in an electrolytic cell. How many hours will it take to plate 130 g of chromium onto the cathode if the current passed through the cell is held constant at 34.0 A?

Assume the chromium in the electrolytic solution is present as Cr^{3+}.

[2]

(c) The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

If a small amount of aqueous manganese(II) ions, Mn^{2+}, is added to the mixture, the rate of reaction increases rapidly.

State the property, typical of transition metals, which allow manganese (II) ions to behave as a homogeneous catalyst in this reaction.

By considering the data given below, write relevant chemical equations to support your answer.

$$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$$

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………………………………………………………………………………………………… [3]

[Total:18]

4 (a) Citric acid is commonly found in citrus fruits such as lemons. Mixtures of citric acid and its salt, sodium citrate, are often used as "acidity regulators". These are food additives that have a buffering action on the pH of foodstuffs.

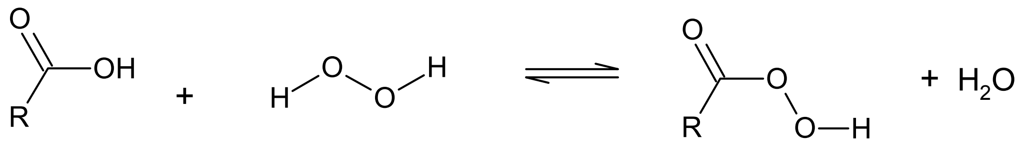
$$\underset{\text{citric acid}}{C_5H_7O_4CO_2H} \rightleftharpoons \underset{\text{citrate}}{C_5H_7O_4CO_2^-} + H^+$$

K_a of citric acid = 7.4×10^{-4} mol dm^{-3}

A typical citric acid / sodium citrate buffer mixture is prepared by mixing 0.100 mol dm^{-3} citric acid and 0.200 mol dm^{-3} sodium citrate in a volume ratio 2:3 respectively. Calculate the pH of the buffer solution.

[2]

(b) The reaction between carboxylic acids and hydrogen peroxides produce peroxyacids.



The p*K*a values of four compounds are listed in the table below.

name	**formula**	***pK*a**
Water	H_2O	14.0
Hydrogen peroxide	H_2O_2	11.7
Methanoic acid	HCO_2H	3.7
Peroxymethanoic acid	HCO_3H	7.1

Suggest an explanation for why

(i) The p*K*a of H_2O_2 is less than that for water

....

.... [1]

(ii) the p*K*a of HCO_3H is more than that for HCO_2H

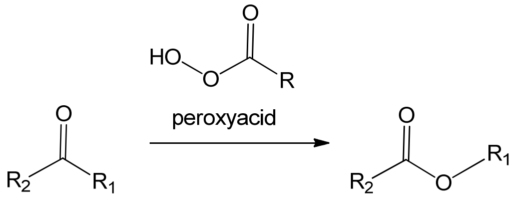
…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………… [2]

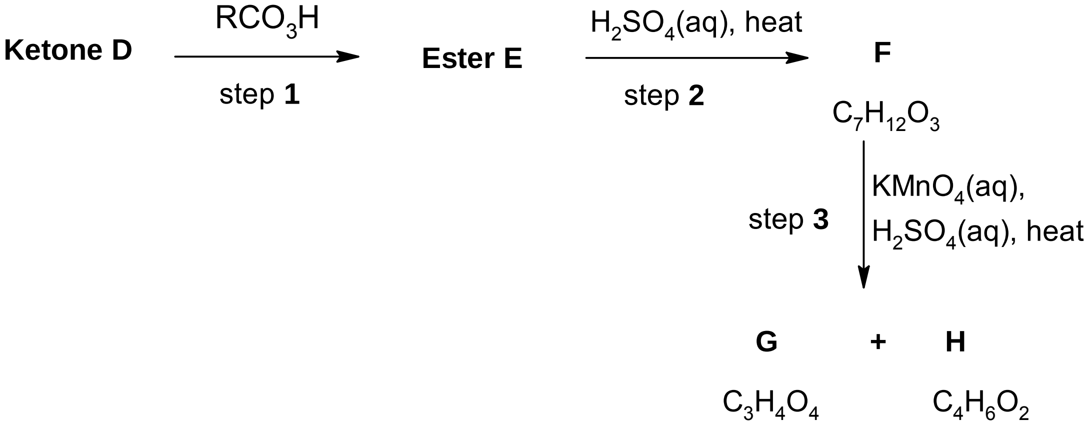
(c) The Baeyer-Villiger oxidation is an organic reaction in which peroxyacids react with ketones to give esters, as shown in the equation below.



In the following scheme, ketone **D** ($C_7H_{10}O$) undergoes Baeyer-Villiger oxidation in step **1** to form ester **E**. Ketone **D** also decolourises orange aqueous Br_2.

F is the **only** product formed, from treating ester **E** with hot $H_2SO_4(aq)$.

Hot acidified $KMnO_4$ oxidises several classes of organic compounds to ketones, carboxylic acids and carbon dioxide. By this means, the structures of compounds can be determined. The scheme below shows the oxidation products of **F**.



(i) State the type of reaction Ester **E** undergoes with hot $H_2SO_4(aq)$ in step 2.

Type of reaction: ……………………………………………………………… [1]

(ii) 1 mole **H** reacted with alkaline aqueous iodine to form 2 moles of CHI_3 yellow ppt. Suggest the structure of **H**.
Give the product of the reaction of **H** with alkaline aqueous iodine.
Structure of **H:**

Product**:**

[2]

(iii) **G** ($C_3H_4O_4$) was found to react with Na_2CO_3(aq). Suggest the structure of **G**.

[1]

(iv) From your answer in **(ii)** and **(iii)**, deduce and suggest the structure of **F**.

[1]

(v) Hence, suggest the structures of ketone **D** and ester **E**.

[2]
[Total: 12]

5 **(a)** **(i)** Oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$ is a fatty acid found in oils and fats, which has C=C double bond in the cis configuration.

The trans isomer of oleic acid is known as *elaidic acid*, which is found in partially hydrogenated vegetable oils.

Draw the skeletal formula for the ***trans*** isomer of oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$, which is also known as *elaidic acid*.

[1]

(ii) Suggest a brief explanation for the differences in melting points between oleic acid and its *trans* isomer, elaidic acid.

Compound	***Mr***	**Melting point / °C**
oleic acid (cis-isomer)	282	4.0
elaidic acid (trans-isomer)	282	45.0

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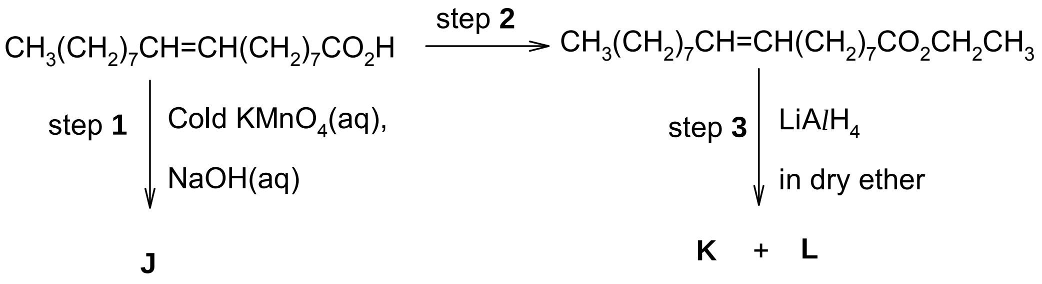
……………………………………………………………………………………………....... [1]

(iii) Below outlines a reaction scheme involving oleic acid.



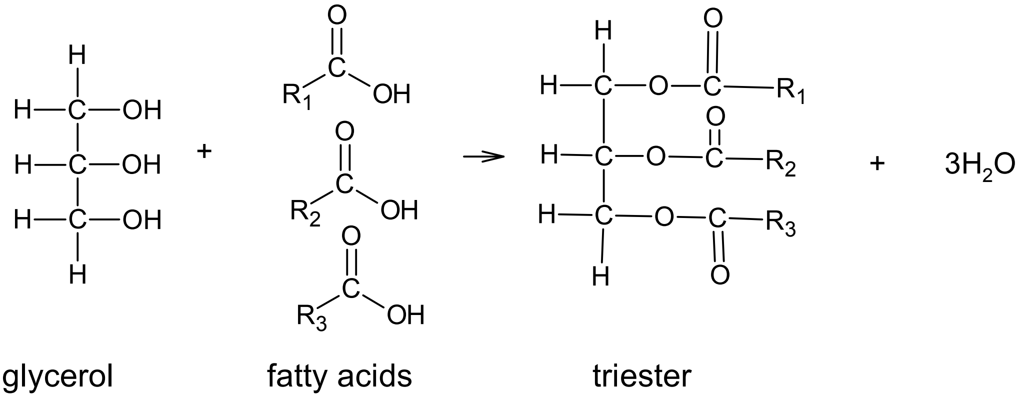
Give the reagents and conditions for step 2, and draw the structures of compounds **J**, **K** and **L** in the boxes provided below.

Step **2:** ....

J	**K**	**L**

[4]

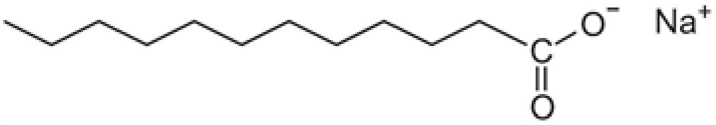
(b) Avocado oil consists mainly of triesters formed from glycerol (propane-1,2,3-triol) and long-chain carboxylic acids (fatty acids) as shown by the general equation.



The major component of avocado oil is triolein, the triester formed from glycerol and three units of oleic acid (fatty acid).

(i) A student tried to flush his cup with water to wash away the avocado oil, but was not successful. The student then tried using soap to wash away the avocado oil in the cup, and was successful.

The following compound, sodium stearate is a typical soap for washing.



By reference to the type of intermolecular forces formed between the soap, avocado oil and water, explain why sodium stearate is able to wash away the avocado oil in the cup.

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……………………………………………………………………………………………[2]

(ii) Below shows the nutrition content of fats, carbohydrates and protein present in one serving of avocado milkshake.

	Mass present in 1 serving of milkshake	Fuel value/ kJ g^{-1}
Total Fat	30 g	
Saturated fat (tristearin)	6 g	42.4
Unsaturated fat (triolein)	24 g	x
Trans fat	0 g	-
Carbohydrates	18g	17
Protein	2g	17
Dietary Fiber	16g	8
Potassium	850 mg	-

Fats constitute the bulk of the milkshake, and are metabolised into carbon dioxide and water when subjected to combustion in a bomb calorimeter. There are two types of fats in the milkshake, saturated versus unsaturated fat.

You may assume that the unsaturated fat and saturated fat in the milkshake are triolein and tristearin respectively.

The combustion of triolein, $C_{57}H_{104}O_6$, the unsaturated fat is as follows:

$$C_{57}H_{104}O_6 + 80O_2 \rightarrow 57\ CO_2 + 52\ H_2O \quad \Delta H_c^{\ominus} = -35100\ \text{kJ mol}^{-1}$$

The **fuel value** of a substance is defined as the heat energy released, when **one gram** of the substance undergoes combustion.

Calculate x, the fuel value of triolein, the unsaturated fat, and hence deduce if triolein or tristearin is a better source of energy (M_r of triolein = 884).

[2]
[Total: 10]

6 Aluminium oxide is frequently used in organic reactions and is also a common component in cosmetics. It is primarily used in the production of aluminium.

(a) Aluminium oxide reacts with aqueous sodium hydroxide to give a homogeneous solution. Similarly, aluminium reacts with aqueous sodium hydroxide to give the same homogeneous solution and a gas that pops with a lighted splint.

(i) Write a balanced equation for the reaction of a piece of aluminium foil when it is placed into aqueous sodium hydroxide.

………………………………………………………………………………………....... [1]

(ii) In reaction **(a)(i)**, a white solid layer was first seen on the aluminium foil before the homogeneous solution was formed. Identify the solid and write an equation to explain how the homogeneous solution was formed from the solid.

Solid: ………………………………

……………………………………………………………………………………..

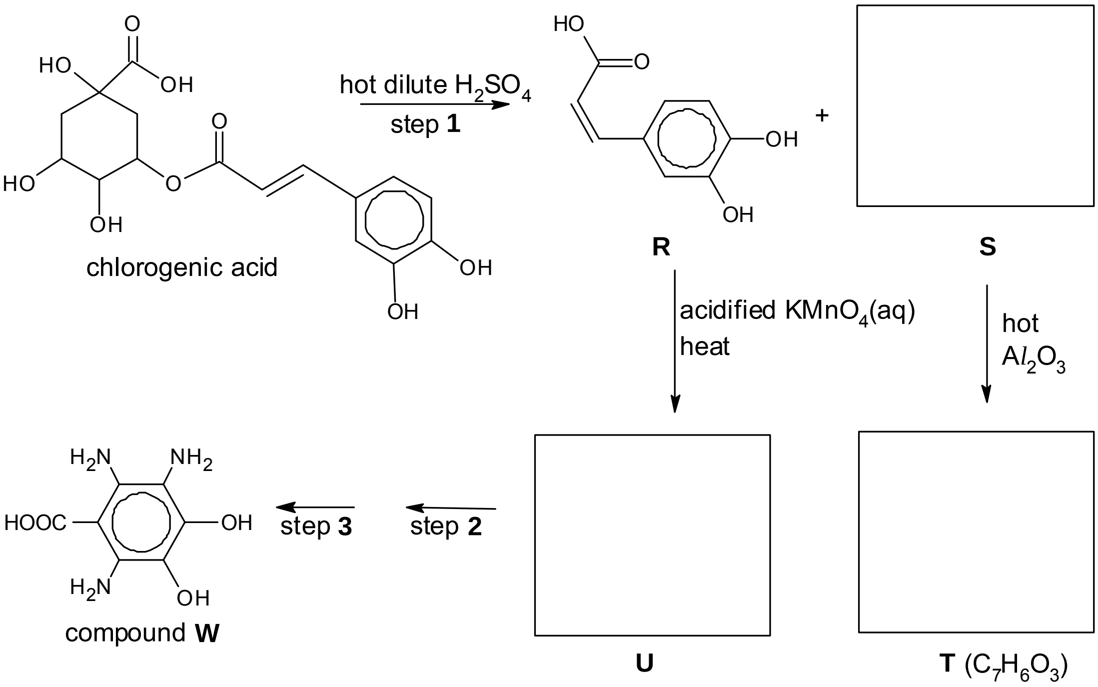
……………………………………………………………………………………..

…………………………………………………………………………………… [2]

(b) Polyphenols are often reducing agents known as antioxidants.

An example of a polyphenol is chlorogenic acid.

The structure of chlorogenic acid and its reaction scheme is shown below. In the reaction scheme, compound **T**, $C_7H_6O_3$, is formed from compound **S** and heated Al_2O_3. Compound **T** reacts with neutral aqueous iron(III) chloride to form a violet solution.



(i) Draw the structures of organic compounds **S**, **T** and **U** in the boxes provided in the scheme above. [3]

(ii) Compound **U** can be converted to compound **W** in two steps.

Suggest reagents and conditions for steps **2** and **3**.

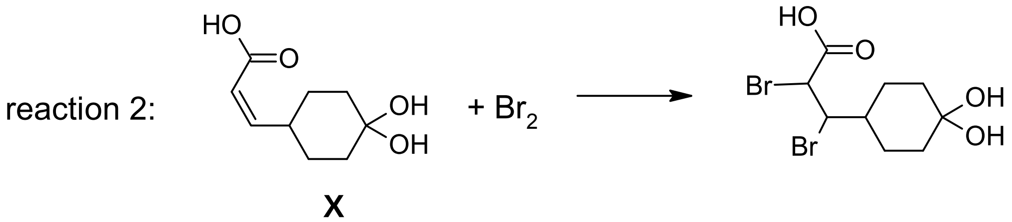
Step 2: .... [1]

Step 3: .... [1]

(iii) If hot dilute sodium hydroxide was used to react with chlorogenic acid, state the number of moles of NaOH that would be required to react with one mole of chlorogenic acid.

Number of mol of NaOH: ………........... [1]

(iv) Compound **X** shown below is an analog of compound **R** in the scheme. When compound **X** is added to bromine in CC*l*4 in the dark, there is a rapid reaction 2, that decolourises the bromine.



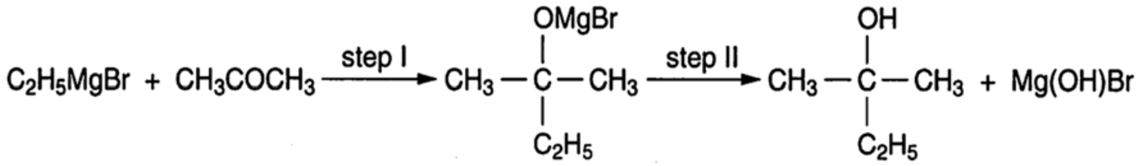
X

The product of this reaction 2, exists as a mixture of four stereoisomers. State the type of isomerism exhibited and draw all the stereoisomers.

[3]

(c) In a Grignard reaction, the Grignard reagent, RMgBr (alkyl or aryl magnesium halide), may be added to a carbonyl compound for the formation of an alcohol.

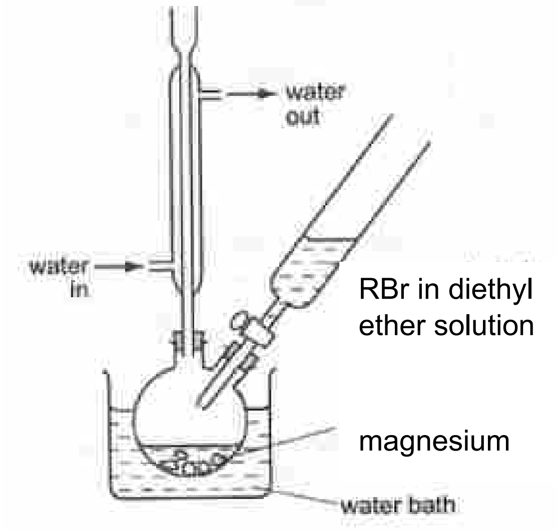
A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} CH_3-\underset{C_2H_5}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{\text{step II}} CH_3-\underset{C_2H_5}{\overset{OH}{C}}-CH_3 + Mg(OH)Br$$

(i) Draw the structural formula of the Grignard reagent that will react with propanone to form 2–methylhexan–2–ol in a similar two–step reaction. [1]

(ii) To prepare 2–methylhexan–2–ol, the following set-up and procedure was used.



<u>Preparation of the Grignard reagent:</u>

1. Several small pieces of Mg was placed in a round-bottomed flask.
2. 9.6 g of an appropriate bromoalkane, RBr, was dissolved in anhydrous diethyl ether. It is important to exclude water as Grignard reagent undergoes acid-base reaction with water rapidly to form an alkane, destroying the Grignard reagent.
3. To initiate the reaction, add just enough RBr/ ether solution from the dropping funnel to cover the magnesium. Start stirring with a magnetic stir bar and use a water bath to heat the reaction flask as the RBr/ ether solution is slowly added dropwise into the metal.
4. The mixture was heated under reflux for about 15 minutes and cooled in an ice-bath.

Reaction of Grignard reagent with propanone:

5. Add 1.2 g of anhydrous propanone in the dropping funnel and add propanone dropwise to the Grignard reagent.
6. Allow the reaction mixture to stand at room temperature for 30 minutes.
7. The mixture was then slowly poured with vigorous stirring into an ice-cold substance **Z** in a beaker. Almost immediately, a solid precipitate is seen.
8. Filter the mixture and collect the ethereal solution in a clean and dry conical flask.
9. Add anhydrous magnesium sulfate to the ethereal solution, cork the flask tightly and leave the mixture to stand for a while.
10. Filter and collect the filtrate in a round-bottom flask which is then placed on a rotary dryer to evaporate all the solvent diethyl ether away.

I. Assuming that 1.9 g of 2–methylhexan–2–ol was prepared using the procedure, calculate the percentage yield for this synthesis. [2]

II. During the preparation of the Grignard reagent, anhydrous diethyl ether was used as the solvent in step 2, as the Grignard reagent can be destroyed in the presence of water.

Write an equation to show the reaction of the Grignard reagent with water.

…………………………………………………………………………………………....... [1]

III. Identify substance **Z** in step 7, in the beaker.

…………………………………………………………………………………………....... [1]

IV. Suggest what is removed when anhydrous magnesium sulfate is added to the ethereal solution in step 9.

…………………………………………………………………………………………....... [1]

[Total: 18]

End of paper

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME			
CT GROUP	1 | 7 | S | |	INDEX NUMBER	| | |

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your class, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

FOR EXAMINER'S USE			
Paper 1			**/ 30**
Paper 2			
1	/ 9	4	/12
2	/ 8	5	/ 10
3	/ 18	6	/ 18
Penalty		sf	unit
Paper 2			**/ 75**
Paper 3			**/ 80**
Paper 4			**/ 55**
Total			

Answer **all** questions in the spaces provided.

1 **(a)** Water hardness is determined by the concentration of multivalent cations in the water. Common cations found in hard water include Ca^{2+} and Mg^{2+}. Lime softening is a type of water treatment where aqueous Na_2CO_3 is added to remove Ca^{2+} ion as $CaCO_3$ is precipitated. These precipitates are then removed by sedimentation and filtration, where X^{2+} can be Ca^{2+} and Mg^{2+}.

$$X^{2+}(aq) + Na_2CO_3(aq) \rightarrow XCO_3(s) + 2Na^+(aq)$$

In the laboratory, 1 cm^3 of 0.50 mol dm^{-3} Na_2CO_3 is added to 10 cm^3 of a raw water sample. What is the minimum concentration of Ca^{2+} in the original raw water sample, which would cause a white precipitate to be observed?

The value of K_{sp} for $CaCO_3$ is 4.81×10^{-9} $mol^2\ dm^{-6}$.

[2]

$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$

Let original concentration of Ca^{2+} be y mol dm^{-3}

Upon mixing

$[Ca^{2+}] = \dfrac{10\times10^{-3}\times y}{11\times10^{-3}} = 0.9091y$ mol dm^{-3}

$[CO_3^{2-}] = \dfrac{1\times10^{-3}\times0.5}{11\times10^{-3}} = 0.04545$ mol dm^{-3}

Both $[Ca^{2+}]$ and $[CO_3^{2-}]$ correct

$IP = [Ca^{2+}][CO_3^{2-}] \geq K_{sp}$

$(0.9091y)(0.04545) = 4.81 \times 10^{-9}$

$y = 1.16 \times 10^{-7}$ mol dm^{-3}

(b) A saturated solution of raw water containing both CaF_2 and $Ca(OH)_2$ has a pH of 12 at 25°C.

calcium compound	numerical value of K_{sp}
CaF_2	3.2×10^{-11}
$Ca(OH)_2$	6.4×10^{-6}

(i) Calculate the concentration of hydroxide ions in the solution. [1]

pH = 12

pOH = 2

$[OH^-] = 10^{-2} = 1.00 \times 10^{-2}$ mol dm^{-3}

(ii) Hence, calculate the solubility of CaF_2 in the raw water sample. Show your working clearly. [2]

K_{sp} of $Ca(OH)_2 = [Ca^{2+}]_{total}[OH^-]^2$

$6.4 \times 10^{-6} = [Ca^{2+}]_{total}(1.00 \times 10^{-2})^2$

$[Ca^{2+}]_{total} = 0.0640$ mol dm^{-3}

$[Ca^{2+}]_{total}[F^-]^2 = 3.2 \times 10^{-11}$

$(0.0640)[F^-]^2 = 3.2 \times 10^{-11}$

$[F^-] = 2.24 \times 10^{-5}$ mol dm^{-3}

Solubility of $CaF_2 = (2.24 \times 10^{-5})/2 = 1.12 \times 10^{-5}$ mol dm^{-3}

[2]

(c) Using the following data, construct an energy cycle to calculate the enthalpy change for the thermal decomposition of calcium carbonate.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

	ΔH / kJ mol^{-1}
$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	−57.1
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$	−63.7
$H_2SO_4(aq) + CaCO_3(s) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$	−151.5

$$\begin{tikzcd}
H_2O(l) + H_2SO_4(aq) + CaCO_3(s) \arrow[rr, "\Delta H_r"] \arrow[ddr, "-151.5"'] & & CaO(s) + H_2O(l) + CO_2(g) + H_2SO_4(aq) \arrow[d, "-63.7"] \\
& & Ca(OH)_2(aq) + CO_2(g) + H_2SO_4(aq) \arrow[dl, "2(-57.1)"] \\
& CaSO_4(aq) + CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

By Hess' Law,

$\Delta H_r = -151.5 - (2)(-57.1) - (-63.7)$

$\Delta H_r = +26.4$ kJ mol^{-1}

[Total: 9]

2 The reaction of ethanal with iodine occurs in the presence of acid catalyst, HC*l*. . The reaction is given below.

$$I_2 + CH_3CHO \xrightarrow{HCl} CH_2ICHO + HI \qquad \text{Reaction 1}$$

The table shows the results obtained when the concentrations of I_2, CH_3CHO and HC*l* were varied.

Experiment	Initial [HC*l*] / mol dm^{-3}	Initial [I_2] / mol dm^{-3}	Initial [CH_3CHO] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}

1	0.10	0.20	0.20	1.6×10^{-6}
2	0.10	0.40	0.30	2.4×10^{-6}
3	0.40	0.40	0.20	6.4×10^{-6}
4	0.10	0.20	2.00	1.6×10^{-5}

(a) **(i)** Deduce the orders of reaction with respect to I_2, CH_3CHO and HC*l*. Hence, determine the rate equation.

[3]

Comparing expt 1 and 4

[HC*l*] and [I_2] are kept constant, when [CH_3CHO] is 10 times, initial rate is 10 times.

Hence reaction is first order wrt CH_3CHO.

Let rate = $k\,[HCl]^m\,[I_2]^n\,[CH_3CHO]$

Comparing expt 1 and 2

When $\frac{(2)}{(1)}$, $\frac{(rate)_2}{(rate)_1} = \frac{2.4 \times 10^{-6}}{1.6 \times 10^{-6}} = \frac{k\,(0.10)^m\,(0.40)^n\,(0.3)}{k\,(0.10)^m\,(0.20)^n\,(0.2)}$

n = 0

Hence reaction is zero order wrt I_2.

Comparing expt 2 and 3

When $\frac{(2)}{(3)}$, $\frac{(rate)_2}{(rate)_3} = \frac{2.4 \times 10^{-6}}{6.4 \times 10^{-6}} = \frac{k\,(0.10)^m\,(0.3)}{k\,(0.40)^m\,(0.2)}$

m = 1

Hence reaction is first order wrt HC*l*.

Hence rate = $k\,[HCl]\,[CH_3CHO]$

(ii) The half-life of ethanal in experiment 1 was 60 seconds. Predict the half-life of ethanal in experiments 2 and 3. Explain your answer.

HC*l* functions as a catalyst. Hence, [HC*l*] remains constant in each expt. Therefore, for each experiment, the reaction becomes a pseudo-first order reaction.

Rate = k [ethanal] [HC*l*]

= k^* [ethanal] where $k^* = k\,[HCl]$

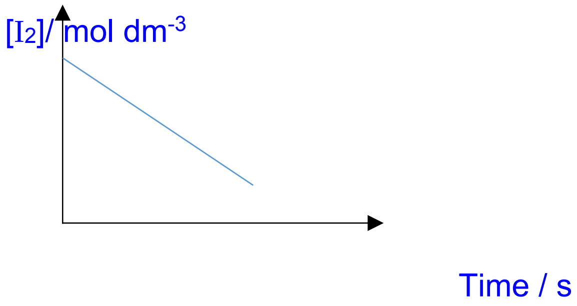
For a first order reaction, $t_{1/2} = \ln 2 / k^* = \ln 2 / k\,[HCl]$

In expt 2, when [HC*l*] is the same as in expt 1, $t_{1/2}$ = 60 s

In expt 3, when [HC*l*] is four times compared to expt 1**, $t_{1/2}$ = 60/4 = 15 s**

(iii) Sketch the graph of concentration of iodine against time for experiment 4.

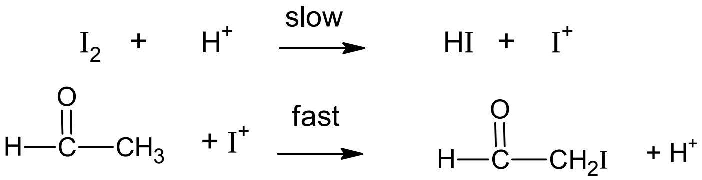
Experiment	Initial [HC*l*] / mol dm^{-3}	Initial [I_2] / mol dm^{-3}	Initial [CH_3CHO] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
4	0.10	0.20	2.00	1.6 x 10^{-5}



[1]

(b) The following mechanisms **A** and **B** are proposed for the reaction of ethanal, iodine and acid catalyst in Reaction 1.

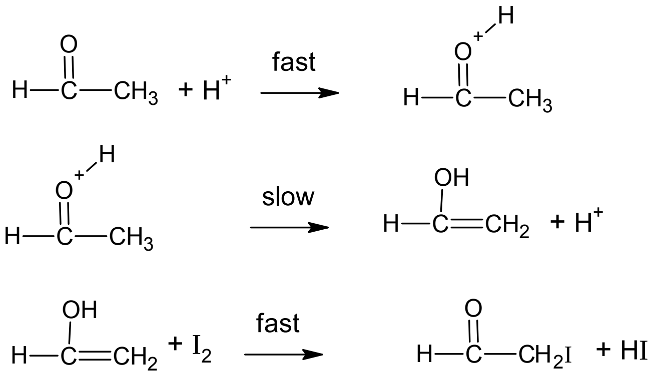
Mechanism A



$$I_2 + H^+ \xrightarrow{\text{slow}} HI + I^+$$

$$H-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + I^+ \xrightarrow{\text{fast}} H-\overset{\overset{\displaystyle O}{||}}{C}-CH_2I + H^+$$

Mechanism B



$$H-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + H^+ \xrightarrow{\text{fast}} H-\overset{\overset{\displaystyle \overset{+}{O}-H}{||}}{C}-CH_3$$

$$H-\overset{\overset{\displaystyle \overset{+}{O}-H}{||}}{C}-CH_3 \xrightarrow{\text{slow}} H-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 + H^+$$

$$H-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 + I_2 \xrightarrow{\text{fast}} H-\overset{\overset{\displaystyle O}{||}}{C}-CH_2I + HI$$

Which of the above mechanisms best agrees with the experimentally determined rate equation in **(a)(i)**? Explain your answer.

Mechanism B

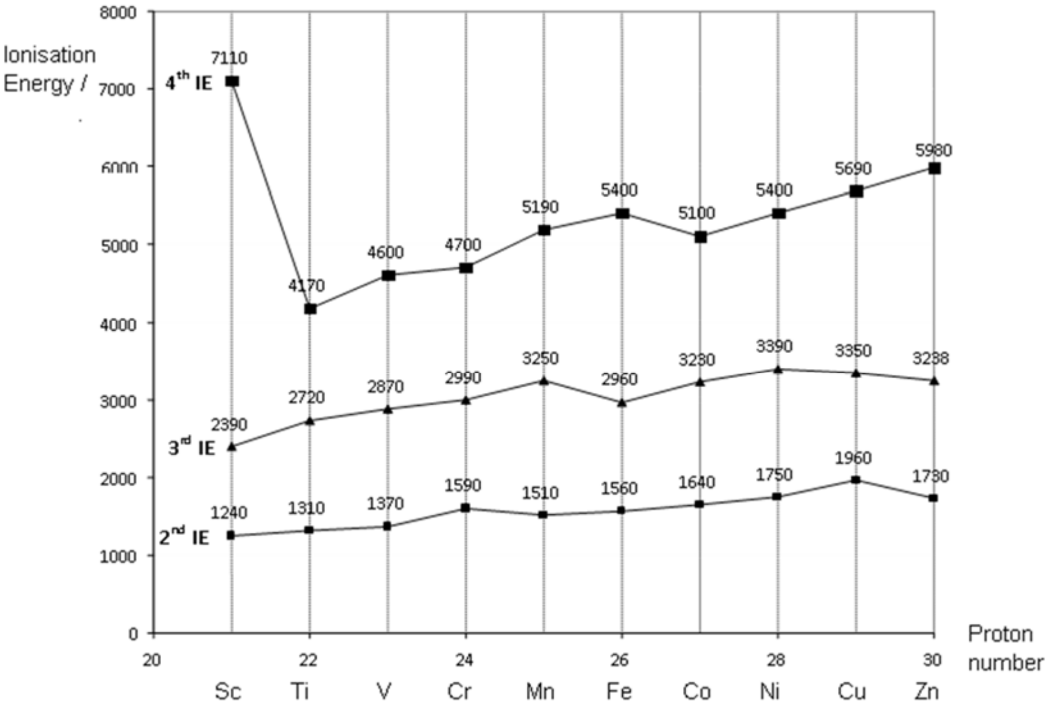
The slow (rate-determining) step involves one molecule of ethanal and colliding with one molecule of hydrochloric acid.

3 Transition metal is "an element whose atom has a partially filled d sub-shell, or which can give rise to cations with an incompletely filled d sub-shell". Chromium and vanadium, both transition metals, have found a number of industrial uses due to their toughness and resistance to heat and corrosion.

The table below shows some information of a Group 2 metal calcium, vanadium and chromium.

	Vanadium	**Chromium**	**Calcium**
Melting point/ °C	1910	1875	843
Atomic radius/ nm	0.135	0.129	0.197
Common Oxidation Number	+2, +3, +4, +5	+2, +3, +6	+2

The graph below shows the second to fourth ionisation energies for the first row d block elements scandium to zinc.



(a) **(i)** Although the vanadium atom has more electrons than the calcium atom, the atomic radius of vanadium is smaller than that of calcium. Suggest an explanation for this.

Atomic radius of vanadium is smaller than that of calcium because vanadium has higher nuclear charge and the 3d electrons shield the 4s electrons poorly.

These result in a greater effective nuclear charge attraction in Vanadium, for the valence electrons, than calcium.

(ii) Explain why the second ionisation energies of transition elements from Ti to Cu are relatively invariant.

Effective nuclear charge increase very slightly or almost constant invariant. There is increase in nuclear charge but shielding effect increases due to electrons added to the 3d penultimate (inner) shell.

(iii) Explain why the second ionisation energy of chromium is higher than that of manganese.
Cr^+ = [Ar]$3d^5$, Mn^+ = [Ar]$3d^5 4s^1$

The second electron removed from manganese is a 4s−electron while the second electron removed from chromium is a 3d−electron.

Since a 3d−electron is (is in inner shell) closer to the nucleus and has lower energy, more energy is required to remove it, causing second ionisation energy of Cr to be higher than that of Mn.

(b) **(i)** State the **full** electronic configuration of Cr^{3+} ion.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

(ii) The complex ion $[Cr(H_2O)_6]^{3+}$ is green, and it is an octahedral complex. On the Cartesian axes shown in Fig. 2.1, draw **fully-labelled** diagrams of the following:

- One of the d orbitals at the lower energy level in an octahedral complex- Label this diagram 'lower'.
- One of the d orbitals at the upper energy level in an octahedral complex. Label this diagram 'upper'. [2]

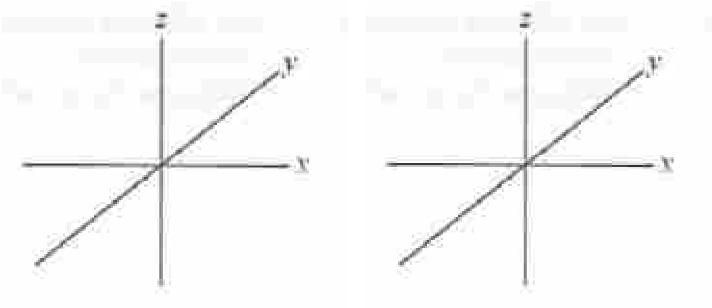
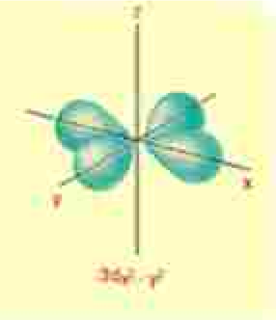
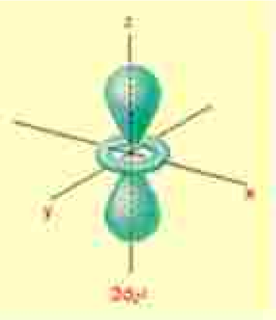


Fig. 3.1

Upper

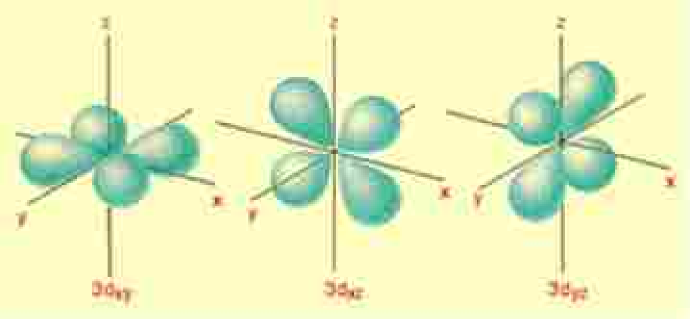


or



Lower

Any of the 3 orbitals (labelled) below



(iii) Suggest which of the two compounds chromium(III) oxide, Cr_2O_3, and chromium(III) carbonate, $Cr_2(CO_3)_3$, would have a more exothermic lattice energy. Explain your answer.

All ions have same charges. O^{2-} has smaller ionic radius than CO_3^{2-}, thus magnitude of lattice energy is bigger, Cr_2O_3 so more exothermic .

(iv) The compound K_3CrO_4 is a green solid. When mixed with dilute H_2SO_4, it undergoes disproportionation to yield Cr^{3+}(aq) and $Cr_2O_7^{2-}$(aq) ions.

By writing appropriate half-equations, write an overall balanced equation for the disproportionation of CrO_4^{3-} in acid.

$$\overset{(+5)}{CrO_4^{3-}} + 8H^+ + 2e^- \rightarrow \overset{(+3)}{Cr^{3+}} + 4H_2O$$

$$\overset{2(+5)}{2CrO_4^{3-}} + 2H^+ \rightarrow \overset{2(+6)}{Cr_2O_7^{2-}} + 2e^- + H_2O$$

Overall equation: $3CrO_4^{3-} + 10H^+ \rightarrow Cr^{3+} + Cr_2O_7^{2-} + 5H_2O$

(v) Purification of chromium can be achieved by electro-refining chromium from an impure chromium anode onto a pure chromium cathode in an electrolytic cell. How many hours will it take to plate 130 g of chromium onto the cathode if the current passed through the cell is held constant at 34.0 A?

Assume the chromium in the electrolytic solution is present as Cr^{3+}.

n(Cr) = 130/ 52.0 = 2.50 mol

n(e) = 2.50 x 3 = 7.50 mol

96500 C for 1 mol of e.

No of charges = 96500 x 7.50 = 7.238 x 10^5C

(96500 x 7.50) = 34 x t

t = 5.91 h

[2]

(c) The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow:

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

If a small amount of aqueous manganese(II) ions, Mn^{2+}, is added to the mixture, the rate of reaction increases rapidly.

State the property, typical of transition metals, which allow manganese (II) ions to behave as a homogeneous catalyst in this reaction.

By considering the data given below, write relevant chemical equations to support your answer.

$$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$$

Property: Mn^{2+}, a transition metal ion, can exist as variable oxidation states.

Step 1: Formation of intermediate (Mn^{2+} reacting with $S_2O_8^{2-}$)

$Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$ $E^\ominus_{oxd}$ = -1.54V

$S_2O_8^{2-} + 2e^- \rightleftharpoons SO_4^{2-}$ $E^\ominus_{red}$ = +2.01 V

$2Mn^{2+} + S_2O_8^{2-} \longrightarrow 2Mn^{3+} + SO_4^{2-}$

$E^\ominus_{cell}$ = $E^\ominus_{oxd}$ + $E^\ominus_{red}$ = +2.01 +-1.54 =+ 0.47V> 0, thus reaction is energetically feasible.

Step 2: Regeneration of catalyst

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\ominus_{red}$ = +1.54

$2I^- \rightleftharpoons I_2 + 2e^-$ $E^\ominus_{oxd}$ = –0.54 V

$2I^- + 2Mn^{3+} \longrightarrow I_2 + 2Mn^{2+}$

$E^\ominus_{cell}$ = $E^\ominus_{oxd}$ + $E^\ominus_{red}$ = + 1.00V >0, thus reaction is energetically feasible

[Total:18]

4 **(a)** Citric acid is commonly found in citrus fruits such as lemons.

Mixtures of citric acid and its salt, sodium citrate, are often used as “acidity regulators”. These are food additives that have a buffering action on the pH of foodstuffs.

$$\underset{\text{citric acid}}{C_5H_7O_4CO_2H} \rightleftharpoons \underset{\text{citrate}}{C_5H_7O_4CO_2^-} + H+$$

K_a of citric acid = 7.4×10^{-4} mol dm^{-3}

A typical citric acid / sodium citrate buffer mixture is prepared by mixing 0.100 mol dm^{-3} citric acid and 0.200 mol dm^{-3} sodium citrate in a volume ratio 2:3 respectively.

Calculate the pH of the buffer solution. [2]

$$[C_5H_7O_4CO_2H] = \frac{2}{5} \times 0.100$$

$$= 0.040 \text{ mol dm}^{-3}$$

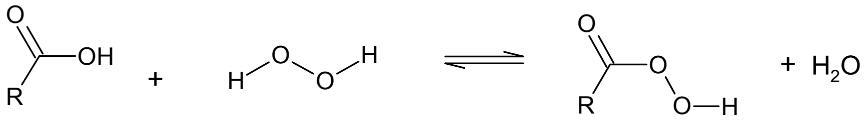
$$[C_5H_7O_4CO_2Na] = \frac{3}{5} \times 0.200$$

$$= 0.120 \text{ mol dm}^{-3}$$

$$\text{pH of the buffer} = -\lg\,(7.46 \times 10^{-4}) + \lg\left(\frac{0.120}{0.040}\right)$$

$$= 3.60$$

(b) The reaction between carboxylic acids and hydrogen peroxides produce peroxyacids.



The p*K*a values of four compounds are listed in the table below.

Name	**formula**	***pK*a**
Water	H_2O	14.0
Hydrogen peroxide	H_2O_2	11.7
Methanoic acid	HCO_2H	3.7

Peroxymethanoic acid	HCO_3H	7.1

Suggest an explanation for why

(i) The p*K*a of H_2O_2 is less than that for water [1]

Lower pK_a of H_2O_2 means H_2O_2 is stronger acid than H_2O.

Stability of anion: H-O-O^- > HO^-

H-O-O^- has additional O atom bonded to negatively charged O^-, this additional electronegative O helps to disperse the negative charge more (via inductive effect), stabilising H-O-O^- relative to HO^-

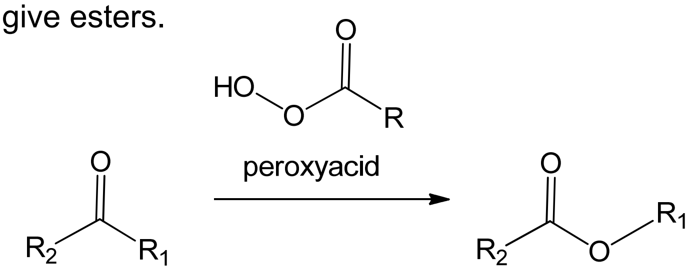
A **(ii)** The p*K*a of HCO_3H is more than that for HCO_2H [2]

Lower pK_a of HCO_2H means HCO_2H is stronger acid than HCO_3H

In HCO_2^-, the p orbitals of the 3 atoms of $-CO_2^-$ are all adjacent to each other, overlap sideways, allowing the delocalisation of the negative charge across the 3 atoms of $-COO^-$, thus HCO_2^- is much more stable than HCO_3^-.

In HCO_3^-, the negative charge cannot be delocalised thus HCO_3^- is less stable.

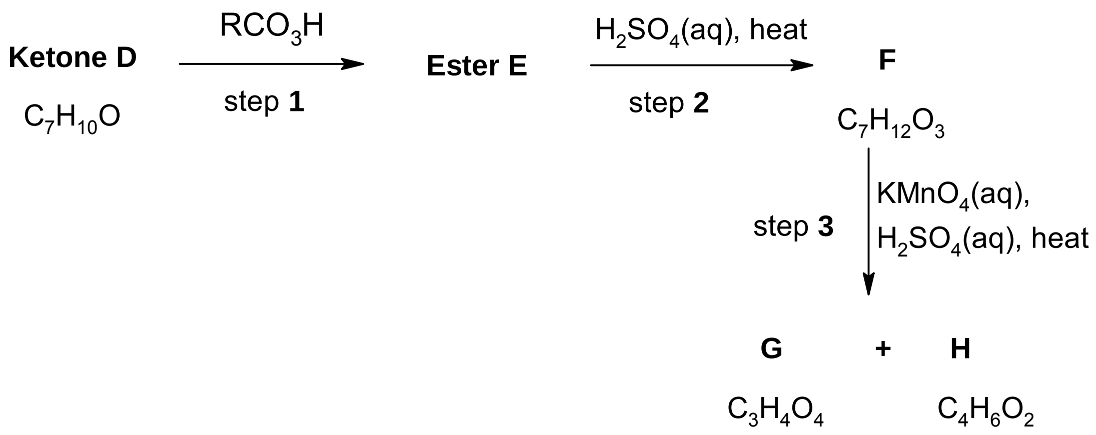
(c) The Baeyer-Villiger oxidation is an organic reaction in which peroxyacids react with ketones to give esters.



In the following scheme, ketone **D** ($C_7H_{10}O$) undergoes Baeyer-Villiger oxidation in step **1** to form ester **E**. Ketone **D** also decolourises orange aqueous Br_2.

F is the **only** product formed, from treating ester **E** with hot H_2SO_4(aq).

Hot acidified $KMnO_4$ oxidises several classes of organic compounds to ketones, carboxylic acids and carbon dioxide. By this means, the structures of compounds can be determined. The scheme below shows the oxidation products of **F**.



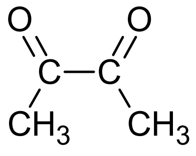
(i) State the type of reaction Ester **E** undergoes with hot H_2SO_4(aq) in step 2.

Hydrolysis

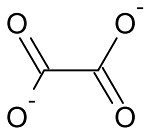
(ii) 1 mole **H** reacted with alkaline aqueous iodine to form 2 moles of CHI_3 yellow ppt. Draw the structure of **H**.

Give the product of the reaction of **H** with alkaline aqueous iodine. [2]

H:



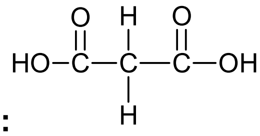
Product:



or $C_2O_4^{2-}$

K **(iii)** **G** ($C_3H_4O_4$) was found to react with Na_2CO_3(aq). Suggest the structure of **G**.

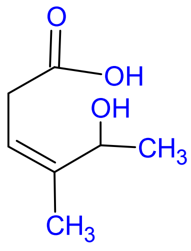
G:



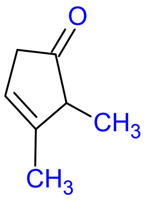
$HOOC{-}CH_2{-}COOH$

(iv) From your answer in **(ii)** and **(iii)**, deduce and suggest the structure of **F**. [1]

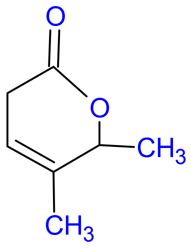
F:



(v) Hence, suggest the structures of ketone **D** and ester **E**.



D:$C_7H_{10}O$



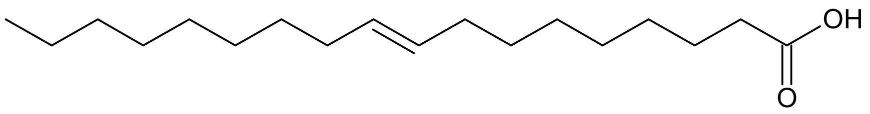
E: $C_7H_{10}O_2$

[Total: 12]

5 **(a)** **(i)** Oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$ is a fatty acid found in oils and fats, which has C=C double bond in the cis configuration.

The trans isomer of oleic acid is known as *elaidic acid*, which is found in partially hydrogenated vegetable oils.

Draw the skeletal formula for the ***trans*** isomer of oleic acid, $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$, which is also known as *elaidic acid*.



[1]

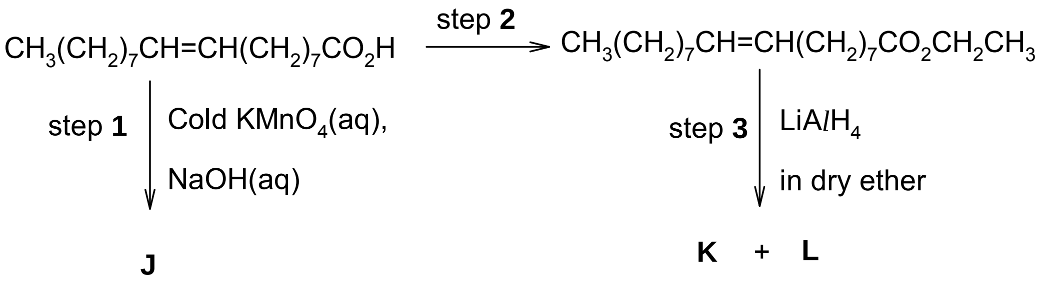
(ii) Suggest a brief explanation for the differences in melting points between oleic acid and its *trans* isomer, elaidic acid.

Compound	***Mr***	**Melting point / °C**
oleic acid (cis-isomer)	282	4.0
elaidic acid (trans-isomer)	282	45.0

[1]

The trans-double bond isomer of oleic acid, elaidic acid, has a more symmetrical shape and is thus able to pack more closely together, thus more energy to overcome the stronger instantaneous dipole-induced dipole forces of attraction which cause it to have a higher melting point.

(iii) Below outlines a reaction scheme involving oleic acid.

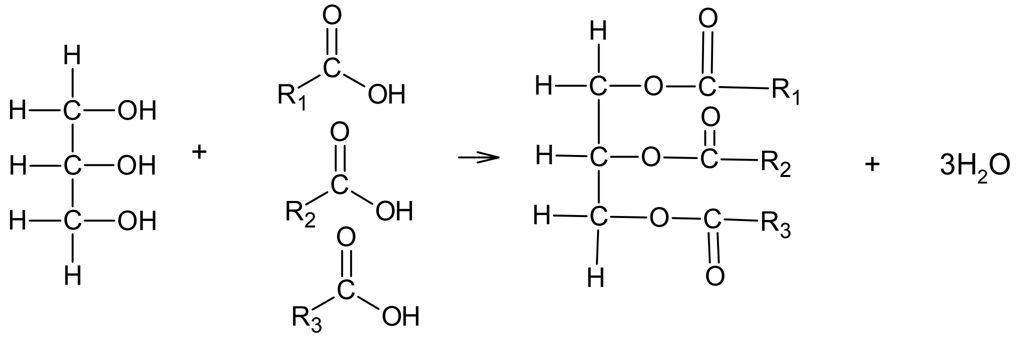


Give the reagents and conditions for step 2, and draw the structures of compounds **J**, **K** and **L** in the boxes provided below.

step **2**:	CH_3CH_2OH, concentrated H_2SO_4, heat
J:	$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7CO_2^- Na^+$ If student wrote $CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7COO^-$
K:	$CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$
L:	CH_3CH_2OH(K and L are inter-changeable)

[4]

(b) Avocado oil consists mainly of triesters formed from glycerol (propane-1,2,3-triol) and long-chain carboxylic acids (fatty acids) as shown by the general equation.

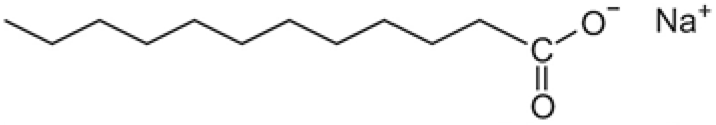


glycerol fatty acids triester

The major component of avocado oil is triolein, the triester formed from glycerol and three units of oleic acid (fatty acid).

(i) A student tried to flush his cup with water to wash away the avocado oil, but was not successful. The student then tried using soap to wash away the avocado oil in the cup, and was successful.

The following compound, sodium stearate is a typical soap for washing.



By reference to the type of intermolecular forces formed between the soap, avocado oil and water, explain why sodium stearate is able to wash away the avocado oil in the cup.

The alkyl group of the soap is non-polar and able to form instantaneous dipole – induced dipole attraction with the non-polar avocado oil, while the -COO^- part of the soap is able to form ion-dipole interaction with water molecules, these allow the avocado oil to be washed away by the water, in the presence of the soap.

(ii) Below shows the nutrition content of fats, carbohydrates and protein present in one serving of avocado milkshake.

	Mass present in 1 serving of milkshake	Fuel value/ kJ g^{-1}
Total Fat	30 g	
Saturated fat (tristearin)	6 g	42.4
Unsaturated fat (triolein)	24 g	x
Trans fat	0 g	-
Carbohydrates	18g	17
Protein	2g	17
Dietary Fiber	16g	8
Potassium	850 mg	-

Fats constitute the bulk of the milkshake, and are metabolised into carbon dioxide and water when subjected to combustion in a bomb calorimeter. There are two types of fats in the milkshake, saturated versus unsaturated fat.

You may assume that the unsaturated fat and saturated fat in the milkshake are triolein and tristearin respectively.

The combustion of triolein, $C_{57}H_{104}O_6$, the unsaturated fat is as follows:

$$C_{57}H_{104}O_6 + 80O_2 \rightarrow 57\ CO_2 + 52\ H_2O \quad \Delta H_c^\ominus = -35100\ \text{kJ mol}^{-1}$$

The **fuel value** of a substance is defined as the heat energy released, when **one gram** of the substance undergoes combustion.

Calculate *x*, the fuel value of triolein, the unsaturated fat, and hence deduce if triolein or tristearin is a better source of energy (M_r of triolein = 884).

No. of moles of triolein in 1 g = 1/884 = 1.131×10^{-3} mol

Fuel value of triolein = $1.131 \times 10^{-3} \times 35100 = 39.7$ kJ g^{-1}

- Since less energy is produced per gram, triolein is a poorer source of energy than tristearin (42.4 kJ g^{-1}).

[2]

[Total: 10]

6 Aluminium oxide is frequently used in organic reactions and is also a common component in cosmetics. It is primarily used in the production of aluminium.

(a) Aluminium oxide reacts with aqueous sodium hydroxide to give a homogeneous solution. Similarly, aluminium reacts with aqueous sodium hydroxide to give the same homogeneous solution and a gas that pops with a lighted splint.

(i) Write a balanced equation for the reaction of a piece of aluminium foil when it is placed into aqueous sodium hydroxide.

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$

(ii) In reaction **(a)(i)**, a white solid layer was first seen on the aluminium foil before the homogeneous solution was formed. Identify the solid and write an equation to explain how the homogeneous solution was formed from the solid. [2]

Solid: Aluminium hydroxide

$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$

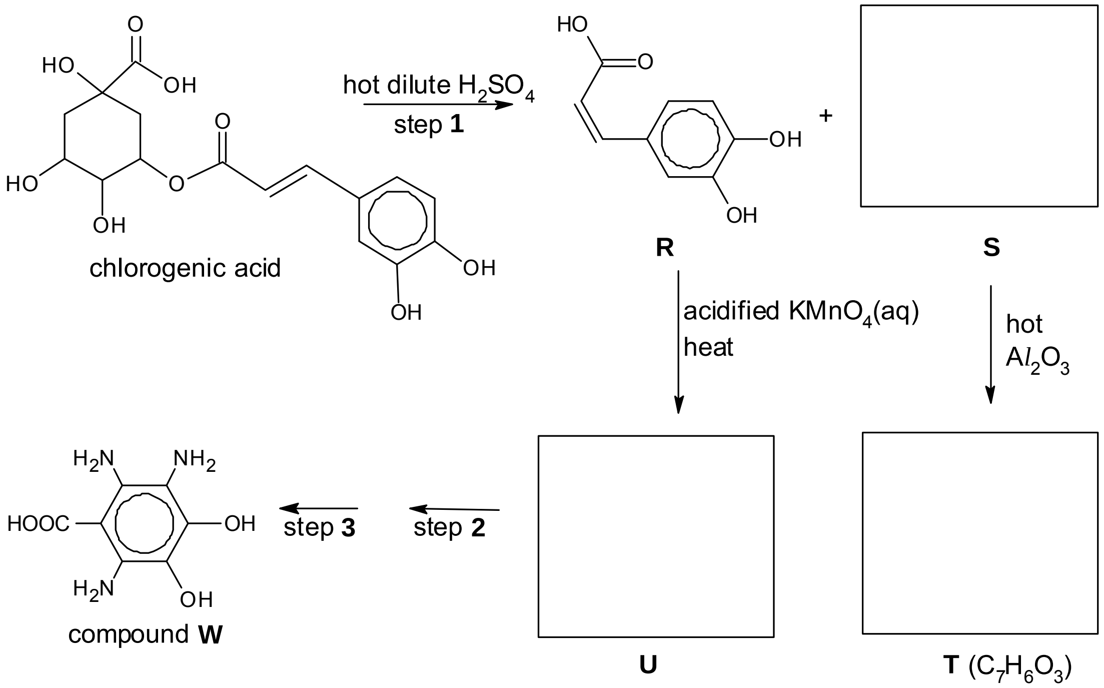
or

$Al(OH)_3(s) + NaOH(aq) \rightarrow Na[Al(OH)_4](aq)$

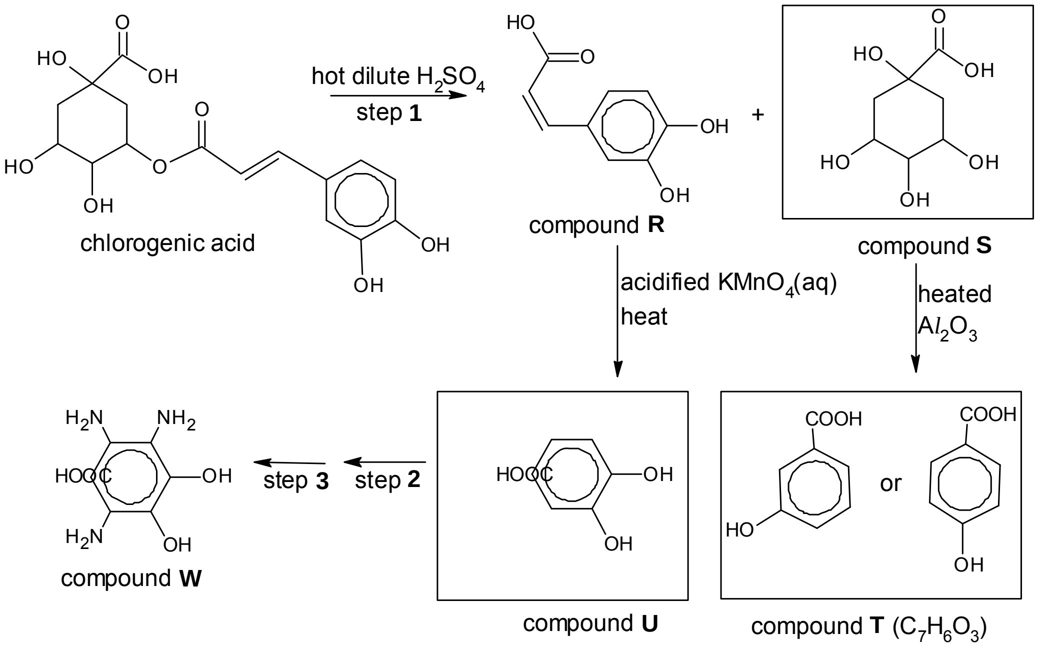
(b) Polyphenols are often reducing agents known as antioxidants.

An example of a polyphenol is chlorogenic acid.

The structure of chlorogenic acid and its reaction scheme is shown below. In the reaction scheme, compound **T**, $C_7H_6O_3$, is formed from compound **S** and heated Al_2O_3. Compound **T** reacts with neutral aqueous iron(III) chloride to form a violet solution.



(i) Draw the structures of organic compounds **S**, **T** and **U** in the boxes provided in the scheme above. [3]



(ii) Compound **U** can be converted to compound **W** in two steps.

Suggest reagents and conditions for steps **2** and **3**.

Step 2: .... [1]

Step 3: .... [1]

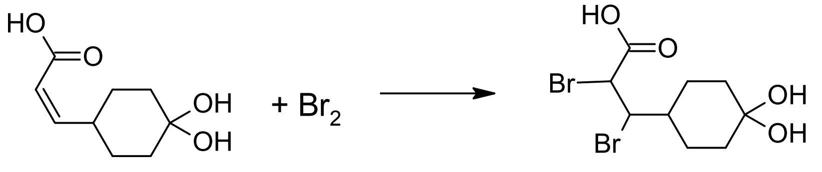
Step **2**:	dilute HNO_3 / $HNO_3(aq)$ / $HNO_3(l)$ / concentrated HNO_3
Step **3**:	Sn, concentrated HC*l*, heat, followed by <u>controlled</u> addition of NaOH(aq)

(iii) If hot dilute sodium hydroxide was used to react with chlorogenic acid, state the number of moles of NaOH that would be required to react with one mole of chlorogenic acid. [1]

Number of mol of NaOH: 4

(iv) Compound **X** shown below is an analog of compound **R** in the scheme. When compound **X** is added to bromine in CC*l*4 in the dark, there is a rapid reaction 2, that decolourises the bromine.

reaction 2:



X

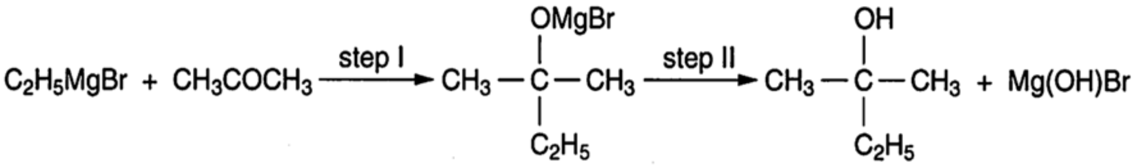
The product of this reaction 2, exists as a mixture of four stereoisomers. State the type of isomerism exhibited and draw all the stereoisomers.

Enantiomerism

[3]

(c) In a Grignard reaction, the Grignard reagent, RMgBr (alkyl or aryl magnesium halide), may be added to a carbonyl compound for the formation of an alcohol.

A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.

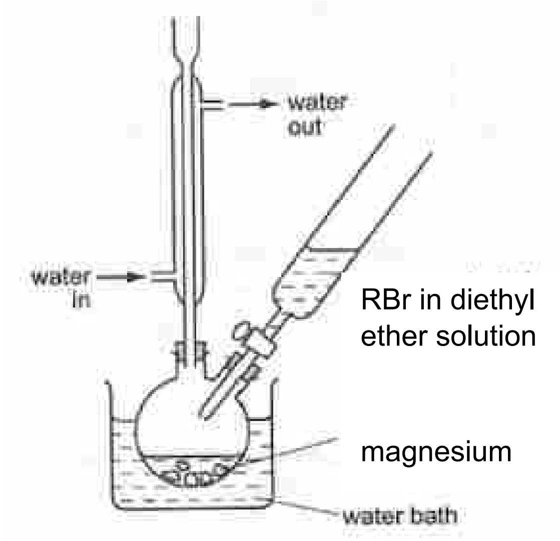


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} CH_3C(OMgBr)(C_2H_5)CH_3 \xrightarrow{\text{step II}} CH_3C(OH)(C_2H_5)CH_3 + Mg(OH)Br$$

(i) Draw the structural formula of the Grignard reagent that will react with propanone to form 2–methylhexan–2–ol in a similar two–step reaction. [1]

$CH_3CH_2CH_2CH_2MgBr$

(ii) To prepare 2–methylhexan–2–ol, the following set-up and procedure was used.



Preparation of the Grignard reagent:

1. Several small pieces of Mg was placed in a round-bottomed flask.
2. 9.6 g of an appropriate bromoalkane, RBr, was dissolved in anhydrous diethyl ether. It is important to exclude water as Grignard reagent undergoes acid-base reaction with water rapidly to form an alkane, destroying the Grignard reagent.
3. To initiate the reaction, add just enough RBr/ ether solution from the dropping funnel to cover the magnesium. Start stirring with a magnetic stir bar and use a water bath to heat the reaction flask as the RBr/ ether solution is slowly added dropwise into the metal.
4. The mixture was heated under reflux for about 15 minutes and cooled in an ice-bath.

Reaction of Grignard reagent with propanone:

5. Add 1.2 g of anhydrous propanone in the dropping funnel and add propanone dropwise to the Grignard reagent.
6. Allow the reaction mixture to stand at room temperature for 30 minutes.
7. The mixture was then slowly poured with vigorous stirring into an ice-cold substance **Z** in a beaker. Almost immediately, a solid precipitate is seen.
8. Filter the mixture and collect the ethereal solution in a clean and dry conical flask.
9. Add anhydrous magnesium sulfate to the ethereal solution, cork the flask tightly and leave the mixture to stand for a while.
10. Filter and collect the filtrate in a round-bottom flask which is then placed on a rotary dryer to evaporate all the solvent diethyl ether away.

I. Assuming that 1.9 g of 2–methylhexan–2–ol was prepared using the procedure, calculate the percentage yield for this synthesis. [2]

n(RBr) = 9.6 / 136.9 = 0.07012 mol (4 s.f)
n(propanone) = 1.2 / 58 = 0.02069 mol (4 s.f) (limiting reagent)
Recognising propanone is limiting reagent = no. of mol of 2–methylhexan–2–ol
n(2–methylhexan–2–ol = 0.02069 x 116 = 2.400g
% yield = 1.9/2.400 x 100 = 79.2%

II. During the preparation of the Grignard reagent, anhydrous diethyl ether was used as the solvent in step 2, as the Grignard reagent can be destroyed in the presence of water.

Write an equation to show the reaction of the Grignard reagent with water.
$RMgBr + HO \rightarrow RH + MgBr(OH)$

III. Identify substance **Z** in step 7, in the beaker.

Water

IV. Suggest what is removed when **anhydrous** magnesium sulfate added to the ethereal solution in step 9.

To remove water from the ethereal solution.

[Total: 18]

End of paper

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME	

CT GROUP	1	7				INDEX NUMBER					

CHEMISTRY 9729/03

Paper 3 Free Response **19 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **15** printed pages.

Section A

Answer all questions in this section.

1 **(a)** Steam reforming is an important industrial method for producing hydrogen and carbon monoxide, from hydrocarbon fuels. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fuel, such as methane gas.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +210 \text{ kJ mol}^{-1}$$

(i) Write an expression of K_p for the reaction, indicating its units. [2]

(ii) At temperature ***T***, a mixture of gaseous methane, steam and carbon monoxide were introduced into an evacuated reactor.

The table below shows the initial pressures of the gases before they were added to the reactor.

Gas	Initial pressure / atm
methane, CH_4	1.50
steam, H_2O	2.50
carbon monoxide, CO	0.70

Given that the percentage dissociation of methane is 20% at equilibrium, find the K_p for the reaction. [2]

(iii) A chemist decided to raise the temperature of the reactor. He suggested that this would result in a lower yield of the product.

Do you agree with the chemist? Explain your answer. [2]

In order to produce more hydrogen gas, the carbon monoxide gas that is produced from the steam reforming reaction can further react with steam. This is known as the "water-gas shift" reaction.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad \Delta H_1$$

(iv) Given that the reaction conditions were set at 500°C and 1.5 atm, determine the maximum volume of hydrogen gas that can be produced from 5kg of carbon monoxide gas.

State the assumption made in your calculation. [3]

(v) Given the following,

enthalpy change of formation of CO(g) / kJ mol^{-1}	-99
enthalpy change of formation of H_2O(g) / kJ mol^{-1}	-245
enthalpy change of formation of CO_2(g) / kJ mol^{-1}	-394

With reference to the above data, calculate the enthalpy change of reaction of the “water-gas shift” reaction, ΔH_1.

[1]

(b) The hydrogen gas obtained from the steam reforming process in part **(a)** can be reacted with nitrogen gas to produce ammonia gas.

This reaction is known as the Haber-Bosch Process, using iron as a catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Predict and explain the sign of ΔS for the Haber-Bosch reaction. [1]

(ii) Using your answer in **(b)(i)**, calculate the maximum temperature for the Haber-Bosch reaction to be spontaneous.

It is known that the numerical value of ΔS is 198 J K^{-1} mol^{-1}, and that ΔH = -92.0 kJ mol^{-1}. [2]

(c) The hydrogen gas obtained from steam reforming, and the ammonia gas obtained from the Haber-Bosch reaction, are the key reagents required for the reductive amination reaction. Many amines in the pharmaceutical drugs are synthesised through this reaction.

The diagram, **Fig. 1.1**, shows the 3 stages involved in reductive amination.

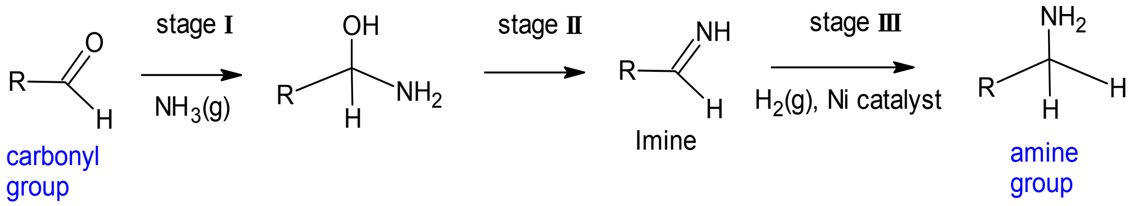


Fig. 1.1

During the reaction, a carbonyl group is converted into an amine group via an intermediate imine.

(i) State the types of reaction occurring in stage **I** and stage **II**. [2]

The reaction scheme below, **Fig.1.2**, shows the production of α-methylphenethylamine, which involves reductive amination in step **4**.

Step **4** in **Fig. 1.2** comprises of the 3 stages of reductive amination in Fig. 1.1.

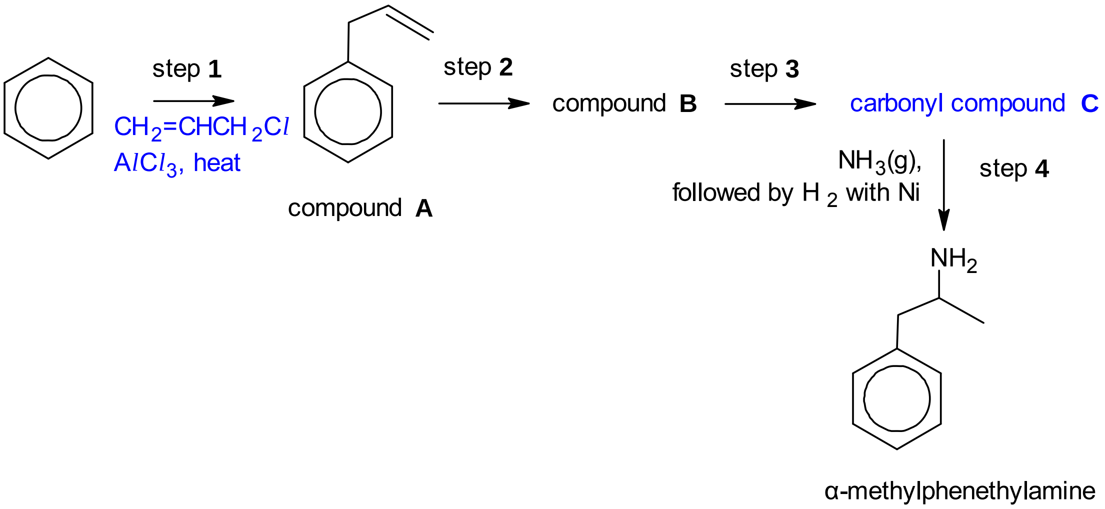


Fig.1.2

(ii) In step **1**, benzene undergoes a reaction with 3-chloroprop-1-ene with the aid of anhydrous aluminium chloride catalyst. Name and describe the mechanism for step **1**, showing clearly any relevant charges, dipoles or lone pairs of electrons that are important.

[4]

(iii) Deduce and draw the structure for carbonyl compound **C**, and suggest the structure of compound **B**. [2]

[Total: 21]

2 This question is on halogen-containing compounds.

(a) The following experiments are carried out starting from solid aluminium chloride.

$$AlCl_3(s) \xrightarrow{\text{water}} \text{acidic solution} \xrightarrow{Na_2CO_3(aq)} \text{white precipitate } \mathbf{D} + \text{effervescence}$$

(i) Explain with the aid of balanced equations, why $AlCl_3(s)$ dissolves to form an acidic solution. Suggest the pH of the acidic solution. [3]

(ii) Identify precipitate **D**. [1]

(b) When aqueous $AgNO_3$ is added to separate test-tubes containing aqueous KCl and KI, the various AgX ($X = Cl$, I) precipitates were observed.

With the aid of relevant equations, explain why a precipitate of $AgCl$ is soluble in excess aqueous NH_3 but a precipitate of AgI is insoluble in excess aqueous NH_3. [3]

(c) The standard redox potential of chlorate (V) ions is given below.

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\ominus = 1.45\ V$$

Predict what you expect to observe, when acidified potassium chlorate (V) is added separately to each of the following reagents.

State clearly if no reaction occurs. Write a balanced equation for any reaction that occurs. Explain your answer using $E^\ominus$ values from the *Data Booklet.*

(i) $FeSO_4$ (aq)

(ii) Acidified $KMnO_4$ (aq)

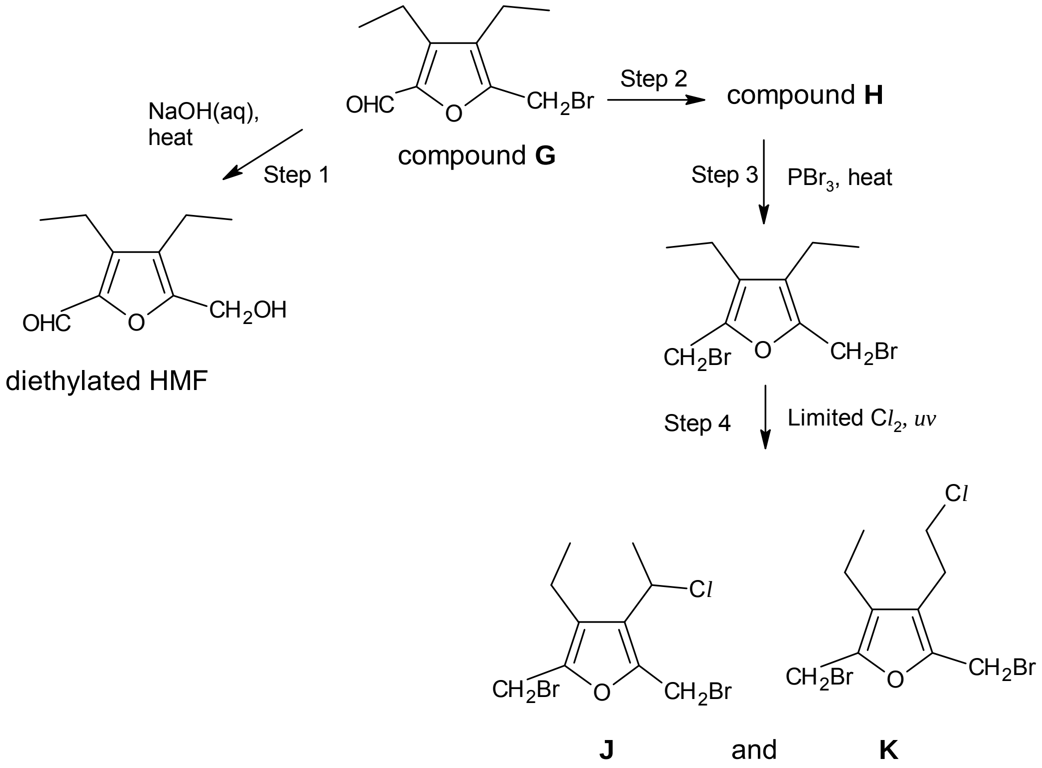
[3]

(d) PCl_5 reacts with hydrazine, N_2H_4, to give compound **E**, which has the following composition by mass: P, 20.5%; N, 9.2%; Cl, 70.3%. The molecule of **E** contains an N-N single bond.

Calculate the empirical formula of **E**, and suggest its molecular formula and the structure of its molecule, assuming its constituent atoms show their usual valencies.

[2]

(e) Diethylated HMF is used to synthesize a variety of pharmaceuticals. The flow-scheme below shows the reactions involving diethylated HMF and compound **G**, its precursor. Assume the C-O-C ether group is inert.



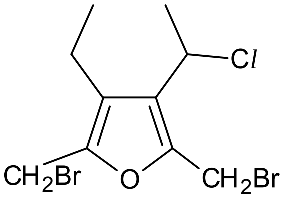
(i) When the reaction in step **1** was investigated kinetically, it was found that its rate was independent of [OH⁻], but was first order with respect to [compound **G**].

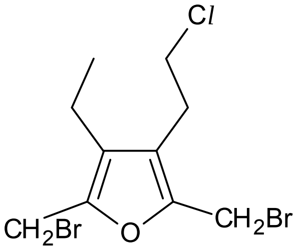
Name and describe a mechanism for this reaction, showing curly arrows in your answer. [3]

You may represent compound **G** as R-CH_2Br.

(ii) Draw the structure of compound **H**. [1]

(iii) When the mono-chlorination is carried out in step **4**, two possible monochloroalkanes **J** and **K** can be formed.





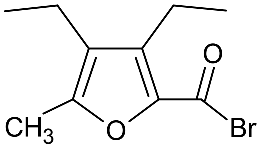
J and **K**

Predict the relative proportions of **J** and **K** formed. [1]

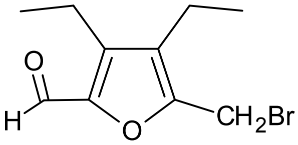
(iv) When the monochlorinated products of step **4** were analysed, it is found that the mole ratio of **J: K** formed was about 97: 3.

Suggest a reason for the difference between this ratio and the one you gave in (**iii**). [1]

(v) Compounds **M** and **G** are both bromine-containing compounds that are isomers of each other.



Compound **M**



Compound **G**

Compare the reactivities of **M** and **G** with water. Explain your answer. [2]

[Total:20]

3 **(a)** **(i)** Use the following data to construct an energy level diagram and hence calculate the enthalpy change for the hydrogenation of ethene gas to ethane gas.

	ΔH / kJ mol^{-1}
Enthalpy change of combustion of $CH_3CH_3(l)$	-1545
Enthalpy change of condensation of $CH_3CH_3(g)$	-15
Enthalpy change of combustion of $H_2(g)$	−286
Enthalpy change of combustion of $CH_2{=}CH_2(g)$	−1411

[4]

(ii) Define the term bond energy. [1]

(iii) Using appropriate bond energy values from the *Data Booklet* alone, calculate another value for the enthalpy change of the reaction in **(a)(i)**.

[2]

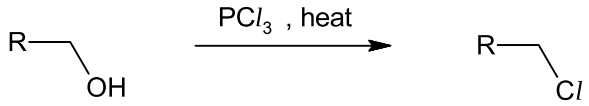
(iv) Suggest a reason for the discrepancy between the enthalpy change for the hydrogenation of ethene gas to ethane gas calculated in **(a)(i)** and **(a)(iii)**. [1]

(b) Hot sulfuric acid, H_2SO_4 is added to ethanol, an alcohol, to produce ethene.

Draw a 'dot-and-cross' diagram showing the electrons (outer shell only) in a H_2SO_4 molecule.

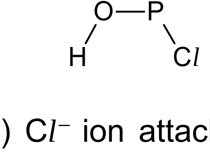
Use the VSEPR (valence shell electron pair repulsion) theory to predict the bond angle around sulfur in H_2SO_4. [3]

(c) Phosphorous halides such as PX_3 can act as both Lewis acids or Lewis bases. PCl_3 is used to convert an alcohol to an alkyl chloride.



The mechanism above involves 2 steps:

- Step **1**: The nucleophilic alcohol attacks PCl_3 to form the following intermediate, along with a Cl^- ion:



+ Cl^-

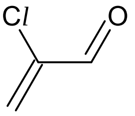
- Step **2**: (slow) Cl^- ion attacks the electrophilic carbon on the intermediate, simultaneously the C–O bond breaks heterolytically.

State and explain if PCl_3 acts as a Lewis acid or Lewis base in step **1** of the mechanism. [1]

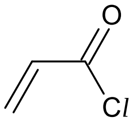
(d) For the following pair of compounds, describe **one** chemical test which would enable you to distinguish clearly between them.

State the observations for **each** compound.

State the type of reaction undergone for the compound that shows a positive test.



compound **N**

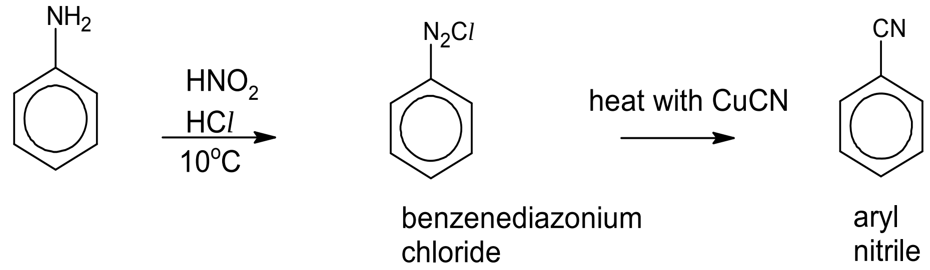


compound **O**

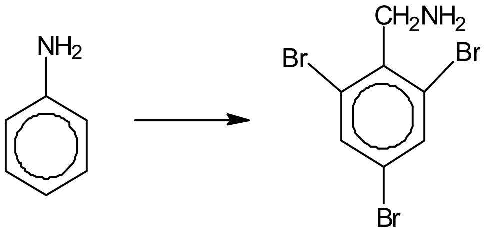
[3]

(e) Phenylamine reacts with nitrous acid, HNO_2, and hydrochloric acid at 10°C to form benzenediazonium chloride, $C_6H_5N_2Cl$.

This is an important intermediate in the synthesis of aromatic compounds. It undergoes the Sandmeyer reaction, shown below, in the presence of a copper(I) catalyst to form aryl nitriles.



Suggest a four-step reaction sequence for the following conversion. You are to make use of the Sandmeyer reaction in one of the steps.



[4]

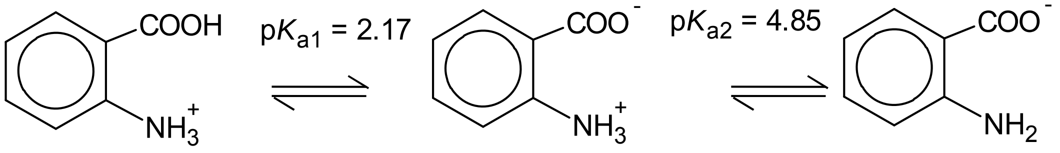
[Total:19]

Section **B**

Answer **one** question from this section.

4 **(a)** Vitamin L1, also known as 2-aminobenzoic acid, can be obtained from bovine liver, and its deficiency has been associated with lactation issues in females.

The diagram below shows how the protonated form of Vitamin L1 acts as a dibasic acid, which dissociates in two stages:



Protonated form
of Vitamin L1

(i) Calculate the pH of 10 cm^3 of 0.100 mol dm^{-3} of the protonated form of Vitamin L1. Ignore the effect of pK_{a2} on the pH of the sample. [1]

(ii) A sample containing 10 cm^3 of 0.100 mol dm^{-3} of the protonated form of Vitamin L1 was titrated with 30 cm^3 of 0.100 mol dm^{-3} of NaOH.

Sketch clearly the titration curve obtained, which should include the following key points:

- initial pH;
- points where pK_{a1} and pK_{a2} occur;
- isoelectric point of Vitamin L1 and its estimated value, given that: isoelectric point = (pK_{a1} + pK_{a2}) / 2

[4]

(iii) Define what is meant by a buffer. [1]

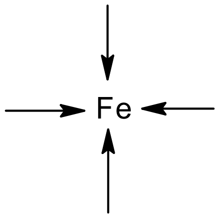
(iv) Draw the structures of the two chemical species present in a solution of Vitamin L1 at pH 5.00.

Hence, show by means of balanced equations, how this solution regulates the acidity on addition of H^+ ions and OH^- ions. [3]

(b) Iron ions can form transition metal complexes with the basic form of the amino acid, alanine. The formula of the complex formed is $Fe(CH_3CH(NH_2)COO)_2$.

(i) State the oxidation state of Fe in the transition complex. [1]

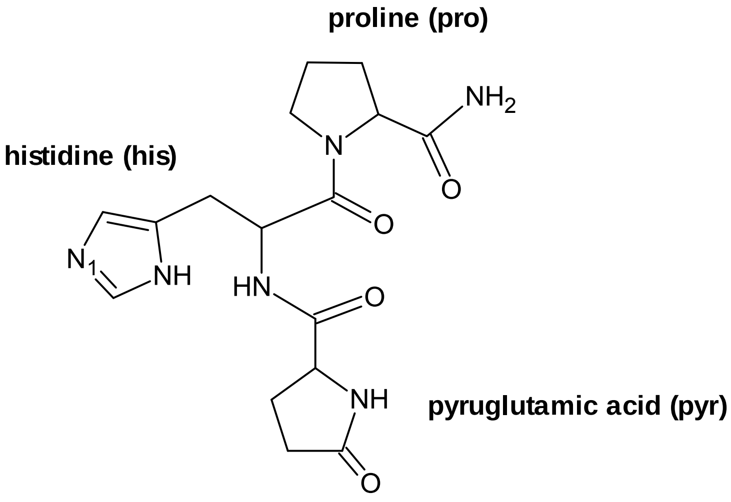
(ii) The diagram below shows the incomplete structure of the complex. Copy the diagram and draw the complete structure of this complex.



[1]

(c) Thyrotropin-releasing hormone (TRH) is a hormone that is produced by the hypothalamus in the brain. TRH has been used clinically for the treatment of the disturbance of consciousness in humans.

TRH is a tripeptide that is made of three amino acids proline, histidine and pyruglutamic acid, as shown in the diagram below.



TRH tripeptide

In the questions below, assume that the side chain for histidine (his) is inert.

(i) State the reagents and conditions for TRH to undergo hydrolysis. [1]

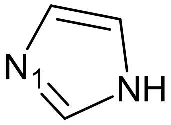
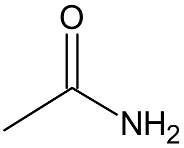
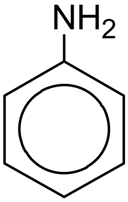
(ii) Draw the structures of the amino acids formed when TRH undergoes hydrolysis using the reagents and conditions stated in **(c)(i)**. [3]

(iii) Explain why amino acids exist as solids with high melting points. [1]

(iv) State the hybridisation state of nitrogen atom labeled N_1 in the histidine side chain of TRH. [1]

(v) The amino acid histidine has a cyclic imidazole side-chain.

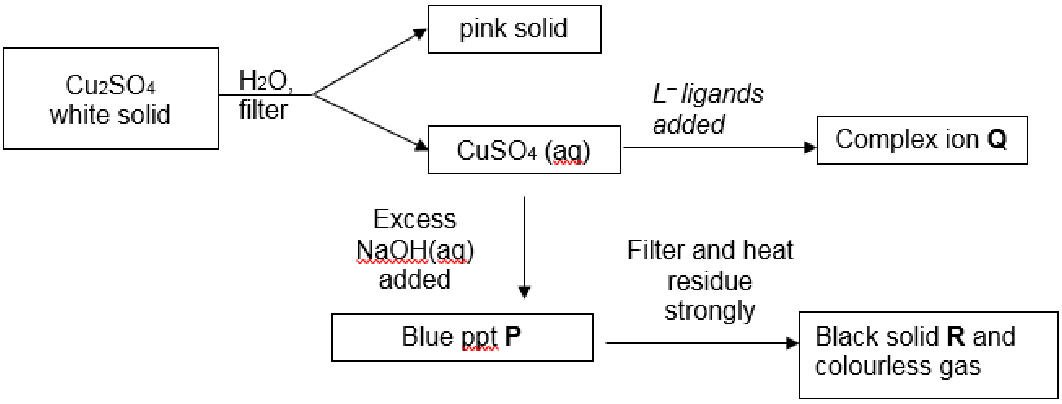
The table below compares the pK_b value of N_1 nitrogen atom of imidazole ring, with the pK_b values of ethanamide and phenylamine.

Compound name	**Structure**	**pK_b**
imidazole		8.8 (pK_b of N_1)
ethanamide		14.5
phenylamine		9.4

Using the data provided, list the 3 compounds in increasing basicity, and suggest explanations for their relative basicities. [3]

[Total: 20]

5 **(a)** The scheme below shows the reactions of different compounds of copper.



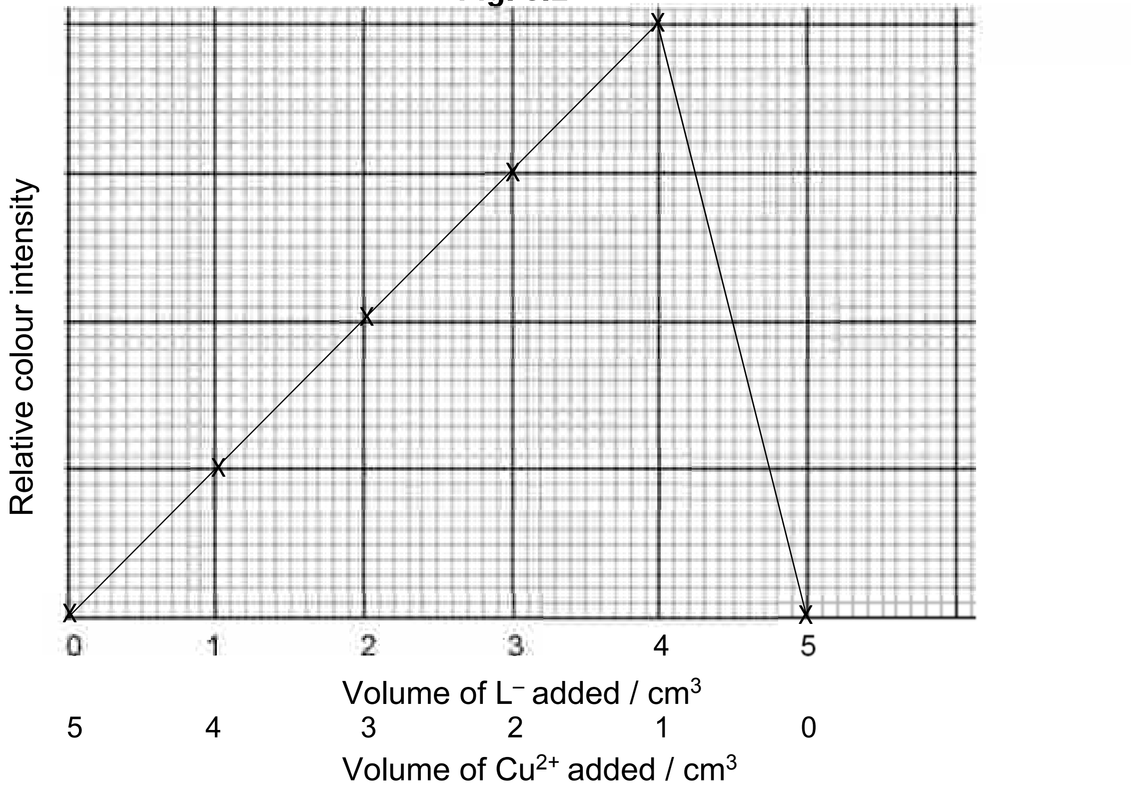
(a) **(i)** Suggest the formulae of blue ppt **P** and black solid **R**. [2]

(ii) Write an equation to show how the pink solid and $CuSO_4$ are obtained when Cu_2SO_4 is added to water. [1]

To determine the stoichiometry of the green complex ion **Q** formed between aqueous copper (II) sulfate and L^- ligands, the colour intensities of solutions containing different proportions of the ligand, L^-, and Cu^{2+} ion were measured.

The intensity of the green colour is directly proportional to the concentration of the complex ion. The higher the concentration of the complex, the higher is the colour intensity. In one such experiment, the results obtained for different volume mixtures of 1.0×10^{-3} mol dm^{-3} Cu^{2+}(aq) and 1.0×10^{-3} mol dm^{-3} L^-(aq) were plotted below.

Fig. 5.1



(iii) State the type of reaction that occurs when complex ion **Q** is formed from aqueous $CuSO_4$. [1]

(iv) Based on the plotted graph in **Fig. 5.1**, determine the mole ratio of Cu^{2+}(aq) to L^- (aq) in the complex **Q**.

Given that complex **Q** has an octahedral shape and it retains some water molecules as ligands, suggest a formula for the complex **Q**, including its overall charge. [2]

(b) Explain why complexes of Cu(II) are coloured whereas complexes of Cu(I) are colourless. [4]

(c) Chlorine can exist in different oxidation states.

Half-equation	***E*^⊖ / V**
$2\mathrm{C}lO_3^- + 12H^+ + 10e^- \rightleftharpoons \mathrm{C}l_2 + 6H_2O$	+1.47
$\mathrm{C}l_2 + 2e^- \rightleftharpoons 2\mathrm{C}l^-$	+1.36

A Latimer diagram shown below, summarises the standard electrode potential, $E^\ominus$ of different chlorine-containing species in acidic medium. The most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd} \mathrm{C}lO_3^- \arrow[r, "+1.47\ \mathrm{V}"] \arrow[rr, bend right, "E^\ominus(\mathrm{C}lO_3^-/\mathrm{C}l^-)"'] & \mathrm{C}l_2 \arrow[r, "+1.36\ \mathrm{V}"] & \mathrm{C}l^- \end{tikzcd}$$

The standard electrode potential of converting $\mathrm{C}lO_3^-$ to $\mathrm{C}l^-$, $E^\ominus(\mathrm{C}lO_3^-/\mathrm{C}l^-)$ is **NOT** the summation of +1.47 V and +1.36 V.

Determine the number of electrons involved in the conversion of 1 mole of $\mathrm{C}lO_3^-$ to 1 mole of $\mathrm{C}l^-$.

Hence, given that $\Delta G^\ominus$ for the conversion of $\mathrm{C}lO_3^-$ to $\mathrm{C}l^-$ is -150 kJ mol^{-1}, calculate $E^\ominus(\mathrm{C}lO_3^-/\mathrm{C}l^-)$. [2]

(d) *Use of the Data Booklet is relevant to this question.*

X, $C_5H_6O_3$, is soluble in dilute NaOH. **X** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and a yellow precipitate with warm alkaline aqueous iodine. **X** decolourises aqueous bromine.

When it is reacted with a methanolic solution of $NaBH_4$ it gives **Y**, $C_5H_8O_3$. Catalytic hydrogenation of **X** gives **Z**, $C_5H_{10}O_3$. When **Z** is reacted with alkaline aqueous iodine, it gives $^{-}O_2C(CH_2)_2CO_2^{-}$.

Oxidation of 1 mole of **X** with hot acidified potassium manganate(VII) gives 1 mole of CH_3COCO_2H and 2 moles of CO_2 gas.

*Additional optional information: **X**, **Y** and **Z** have a proton (^{1}H) chemical shift value of 13.0 ppm. (Refer to Data Booklet Section 6: Typical proton (^{1}H) chemical shift values (δ))*

Suggest structures for **X**, **Y** and **Z**. Explain your reasoning clearly. [8]

[Total: 20]

End of paper

H

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP	1	7			

INDEX NUMBER				

CHEMISTRY **9729/03**

Paper 3 Free Response **19 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Data Booklet Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name, index number and CT group on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **15** printed pages.

r

Section A

Answer all questions in this section.

1 **(a)** Steam reforming is an important industrial method for producing hydrogen and carbon monoxide, from hydrocarbon fuels. This is achieved in a processing device called a reformer which reacts steam at high temperature with the fuel, such as methane gas.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H = +210 \text{ kJ mol}^{-1}$$

(i) Write an expression of K_p for the reaction, indicating its units. [2]

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})} \quad \text{atm}^2$$

(ii) At temperature ***T***, a mixture of gaseous methane, steam and carbon monoxide were introduced into an evacuated reactor.

The table below shows the initial pressures of the gases before they were added to the reactor.

Gas	**Initial pressure / atm**
methane, CH_4	1.50
steam, H_2O	2.50
carbon monoxide, CO	0.70

Given that the percentage dissociation of methane is 20% at equilibrium, find the K_p for the reaction. [2]

	$CH_4(g)$	$+ H_2O(g) \rightleftharpoons$	$CO(g)$	$+ 3H_2(g)$
Initial P /atm	1.50	2.50	0.70	0
Change P /atm	-0.2(1.5) = -0.3	-0.3	+0.3	+0.9
Eqm P /atm	1.20	2.20	1.00	0.90

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$$

$$K_p = \frac{(1.00)(0.90)^3}{(1.20)(2.20)} = 0.276 \text{ atm}^2$$

(iii) A chemist decided to raise the temperature of the reactor. He suggested that this would result in a lower yield of the product.

Do you agree with the chemist? Explain your answer. [2]

No. When the temperature is raised, the endothermic reaction is favoured since it absorbs energy. The position of equilibrium shifts to the right in favour of the forward reaction, yield of H_2 should increase.

In order to produce more hydrogen gas, the carbon monoxide gas that is produced from the steam reforming reaction can further react with steam. This is known as the “water-gas shift” reaction.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

(iv) Given that the reaction conditions were set at 500°C and 1.5 atm, determine the maximum volume of hydrogen gas that can be produced from 5kg of carbon monoxide gas.

State the assumption made in your calculation. [3]

Amount of CO in 5kg = (5 x 1000)/28 = 178.6 mol = Amount of H_2 gas

Amount of H_2 produced = 178.6 mol

$pV=nRT$

$$V = \frac{nRT}{p}$$

$$V = \frac{178.6\times8.31\times(500+273)}{1.5\times1.01\times10^{-5}}$$

$= 7.55\ m^3$

Assumption: Hydrogen gas is behaving like an ideal gas

(v) Given the following,

enthalpy change of formation of $CO(g)$ / kJ mol^{-1}	-99
enthalpy change of formation of $H_2O(g)$ / kJ mol^{-1}	-245
enthalpy change of formation of $CO_2(g)$ / kJ mol^{-1}	-394

With reference to the above data, calculate the enthalpy change of reaction of the “water-gas shift” reaction, ΔH_1. [1]

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

$\Delta H_1 = \Delta H_f(CO_2(g)) – [\Delta H_f(CO(g)) + \Delta H_f H_2O(g))$
$= (-394) – (-99 + -245) = -50\ kJ\ mol^{-1}$

(b) The hydrogen gas obtained from the steam reforming process in part **(a)** can be reacted with nitrogen gas to produce ammonia gas.

This reaction is known as the Haber-Bosch Process, using iron as a catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) Predict and explain the sign of ΔS for the Haber-Bosch reaction. [1]

ΔS is negative as the there is a decrease in number of moles of gaseous particles (from 4 mol to 2 mol), hence less disorderliness.

(ii) Using your answer in **(b)(i)**, calculate the maximum temperature for the Haber-Bosch reaction to be spontaneous.

It is known that the numerical value of ΔS is 198 J K^{-1} mol^{-1}, and that ΔH = -92.0 kJ mol^{-1}. [2]

$\Delta G = \Delta H - T\Delta S$
$0 = (-92.0) - T(-198/1000)$
T = 465K

(c) The hydrogen gas obtained from steam reforming, and the ammonia gas obtained from the Haber-Bosch reaction, are the key reagents required for the reductive amination reaction.

Many amines in the pharmaceutical drugs are synthesised through this reaction.

The diagram, **Fig. 1.1**, shows the 3 stages involved in reductive amination.

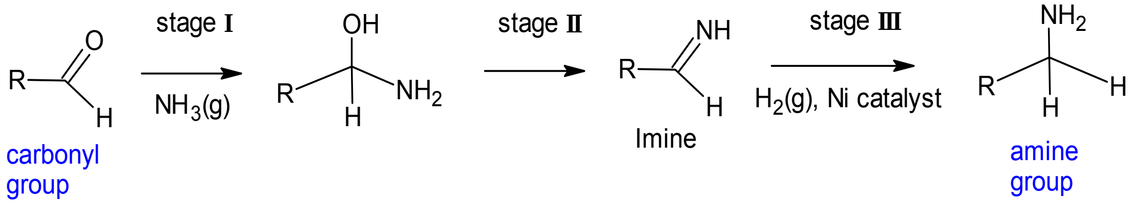


Fig. 1.1

During the reaction, a carbonyl group is converted into an amine group via an intermediate imine.

(i) State the types of reaction occurring in stage **I** and stage **II**. [2]

stage **I:** Nucleophilic addition.
stage **II:** elimination

The reaction scheme below, **Fig.1.2**, shows the production of α-methylphenethylamine, which involves reductive amination in step **4**.

Step **4** in **Fig. 1.2** comprises of the 3 stages of reductive amination in Fig. **1.1**.

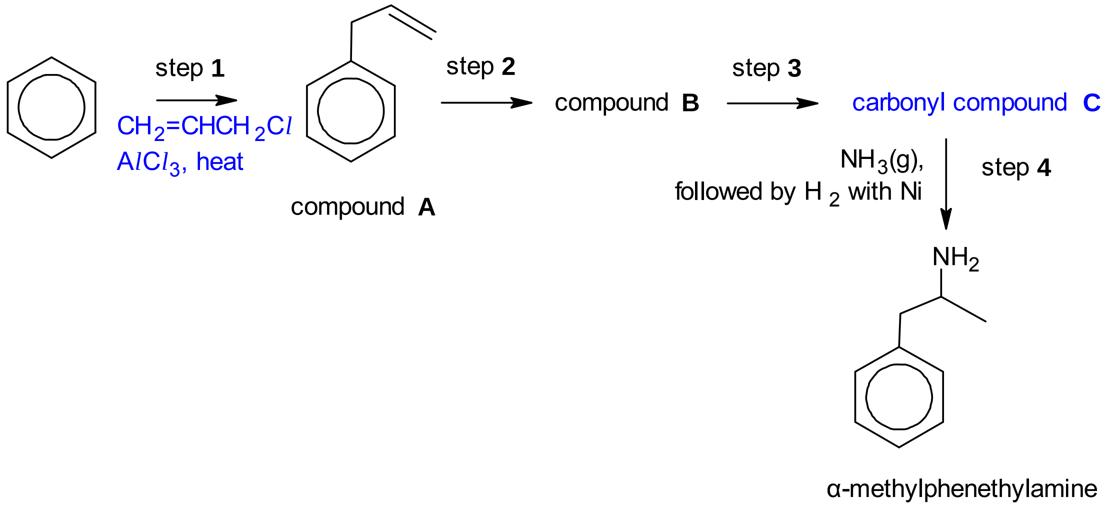


Fig.1.2

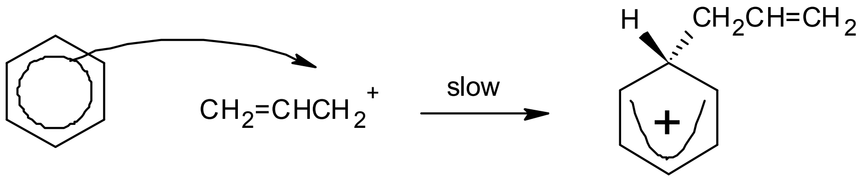
(ii) In step **1**, benzene undergoes a reaction with 3-chloroprop-1-ene with the aid of anhydrous aluminium chloride catalyst.

Name and describe the mechanism for step **1**, showing clearly any relevant charges, dipoles or lone pairs of electrons that are important. [4]

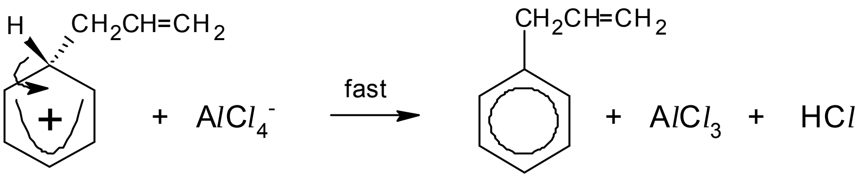
Electrophilic Substitution

Step 1: $CH_2{=}CHCH_2Cl + AlCl_3 \rightleftharpoons AlCl_4^- + CH_2{=}CHCH_2^+$

Step 2:

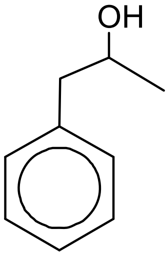


Step 3:

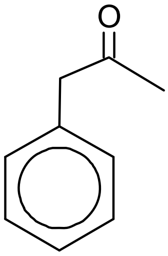


(iii) Deduce and draw the structure for carbonyl compound **C**, and suggest the structure of compound **B**. [2]

compounds **B**:



compounds **C**:



[Total: 21]

2 This question is on halogen-containing compounds.

(a) The following experiments are carried out starting from solid aluminium chloride.

$$AlCl_3(s) \xrightarrow{\text{water}} \text{acidic solution} \xrightarrow{Na_2CO_3(aq)} \text{white precipitate } \mathbf{D} + \text{effervescence}$$

(i) Explain with the aid of balanced equations, why $AlCl_3(s)$ dissolves to form an acidic solution. Suggest the pH of the acidic solution. [3]

$AlCl_3(s)$ dissolves in water to form $[Al(H_2O)_6]^{3+}(aq)$

- $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

A hydrolysis reaction occurs, making the solution acidic.

- $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
- Since Al^{3+} has high charge density, it polarises and weakens the O-H bond of the water attached to it, causing the O-H bond to break to release H^+ (hydrolysis)
- pH=3

(ii) Identify precipitate **D**.
[1]
$Al(OH)_3$

(b) When aqueous $AgNO_3$ is added to separate test-tubes containing aqueous KCl and KI, the various AgX (X = Cl, I) precipitates were observed.

With the aid of relevant equations, explain why a precipitate of AgCl is soluble in excess aqueous NH_3 but a precipitate of AgI is insoluble in excess aqueous NH_3. [3]

$Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$ ....(1)
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ....(2)

When excess NH_3 is added (high $[NH_3]$), the position of equilibrium for (2) shifts to the right **to form complex $[Ag(NH_3)_2]^+$** and **$[Ag^+]$ decreases**, resulting in **eqm (1) to shift left** & a **decrease** in ionic product of AgX .
For AgCl, IP decreases, **ionic product becomes smaller than $K_{sp}(AgCl)$** and the position of equilibrium (1) to shift to the left and AgCl dissolves completely.
For AgI, although IP decreases, ionic product is **still higher** than $K_{sp}(AgI)$ (as $K_{sp}(AgI)$ is very small) and thus there is no dissolution of AgI in excess aqueous ammonia.

(c) The standard redox potential of chlorate (V) ions is given below.

$$ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O \qquad E^\ominus = 1.45\text{ V}$$

Predict what you expect to observe, when acidified potassium chlorate (V) is added separately to each of the following reagents.

State clearly if no reaction occurs. Write a balanced equation for any reaction that occurs. Explain your answer using $E^\ominus$ values from the *Data Booklet.*

(i) $FeSO_4$ (aq)

From the eqn given and highly positive $E^{\ominus}$ = 1.45 V, $ClO_3^-$is easily reduced.
For redox to occur, Fe^{2+} must be oxidised.
$Fe^{2+} \rightleftharpoons Fe^{3+} + e$ $E^{\ominus}_{ox}$ = -0.77 V
$E^{\ominus}_{cell}$ =+1.45 +-0.77 =+0.68V>0 (3 s.f) reaction is energetically feasible
Solution turns yellow (from green).

(ii) Acidified $KMnO_4$ (aq)
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^{\ominus}_{red}$ = + 1.52V
MnO_4^- and ClO_3^- both can only be reduced – thus no redox possible and solution remains purple

[3]

(d) PCl_5 reacts with hydrazine, N_2H_4, to give compound **E**, which has the following composition by mass: P, 20.5%; N, 9.2%; Cl, 70.3%. The molecule of **E** contains an N-N single bond.

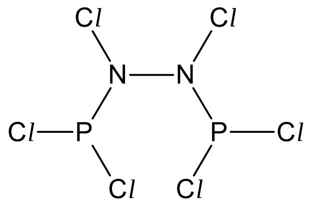
Calculate the empirical formula of **E**, and suggest its molecular formula and the structure of its molecule, assuming its constituent atoms show their usual valencies.

[2]

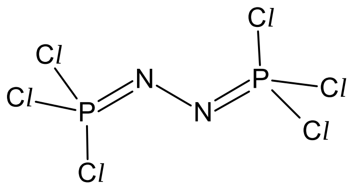
	P	N	Cl
Mass / g	20.5	9.2	70.3
Amt / mol	0.661	0.657	1.98
Mole ratio	1	1	3

Empirical formula = $PNCl_3$

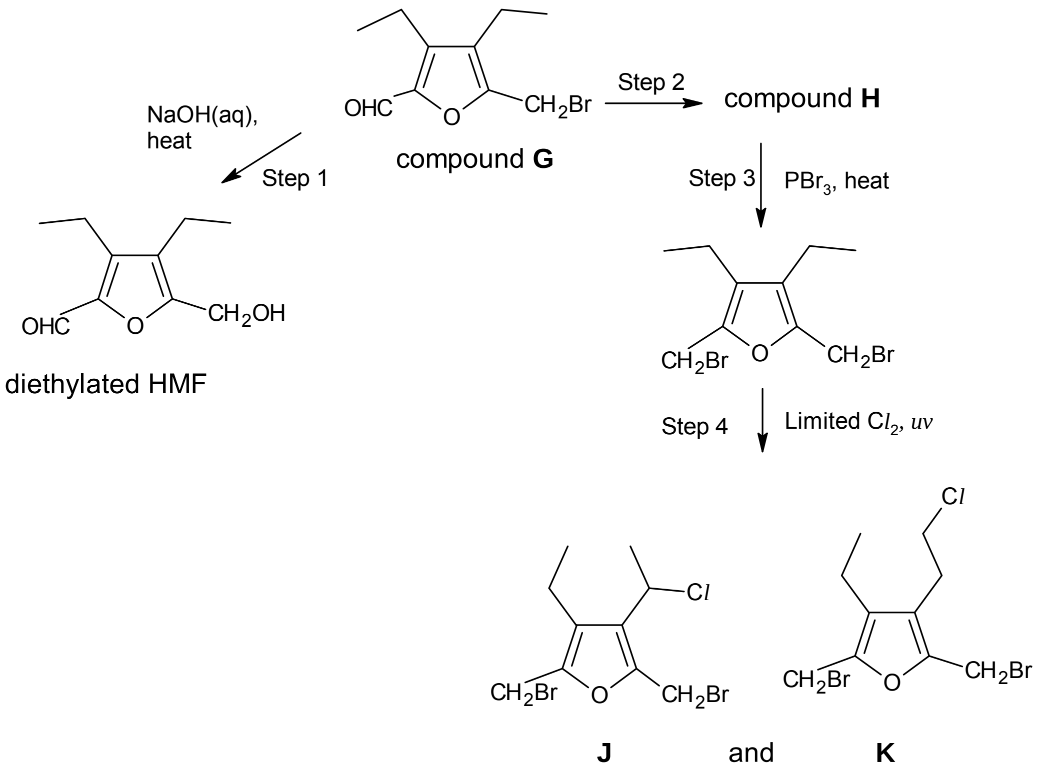
Since S contains one N-N single bond, E will contain 2 N atoms.
Molecular formula of E = $P_2N_2Cl_6$ and correct structures of E:



or



(e) Diethylated HMF is used to synthesize a variety of pharmaceuticals. The flow-scheme below shows the reactions involving diethylated HMF and compound **G**, its precursor. Assume the C-O-C ether group is inert.



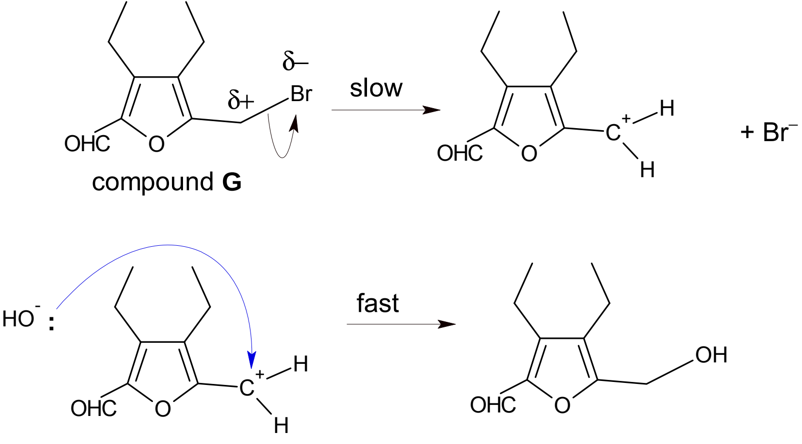
(i) When the reaction in step **1** was investigated kinetically, it was found that its rate was independent of [OH⁻], but was first order with respect to [compound **G**].

Name and describe a mechanism for this reaction, showing curly arrows in your answer. [3]

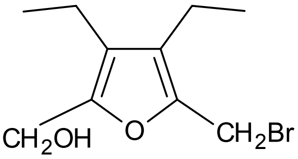
You may represent compound **G** as R-CH_2Br.

Nucleophilic substitution (S_N1)

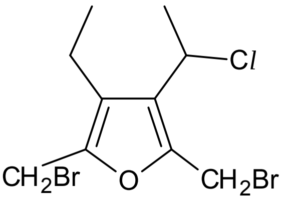
Students can represent G as R-CH_2Br in answer



(ii) Draw the structure of compound **H**. [1]

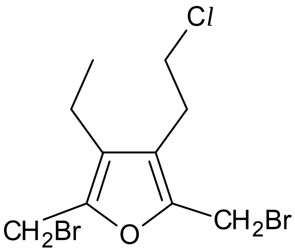


(iii) When the mono-chlorination is carried out in step **4**, two possible monochloroalkanes **J** and **K** can be formed.



J

and



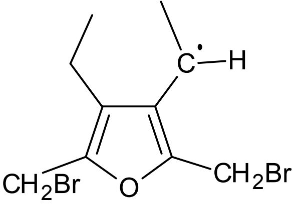
K

Predict the relative proportions of **J** and **K** formed. [1]

J : K
4: :6
OR 2: 3

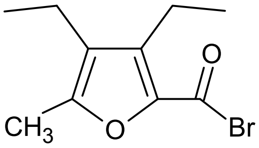
(iv) When the monochlorinated products of step **4** were analysed, it is found that the mole ratio of **J: K** formed was about 97: 3.

Suggest a reason for the difference between this ratio and the one you gave in (**iv**). [1]

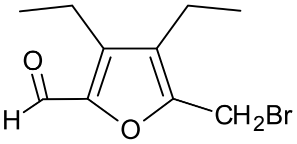


is exceptionally stable due to the overlap of p-orbital between the Carbon with unpaired electron (or resonance stabilised), and the p-orbitals of the adjacent alkene carbon atoms. This is an allylic radical. Being highly stable, it is formed in greater amount / faster and leads to major product.

(v) Compounds **M** and **G** are both bromine-containing compounds that are isomers of each other.



Compound **M**



Compound **G**

Compare the reactivities of **M** and **G** with water. Explain your answer. [2]

- Rate/ ease of hydrolysis: M > G

M, an acyl bromide is most reactive; it undergoes hydrolysis most readily
Reason

- The additional strongly electronegative oxygen atom in acyl bromide M further increases the partial positive charge on carbon atom (of COBr) or make it more delta $\delta+$ positive compared to carbon atom (of C-Br) in G.

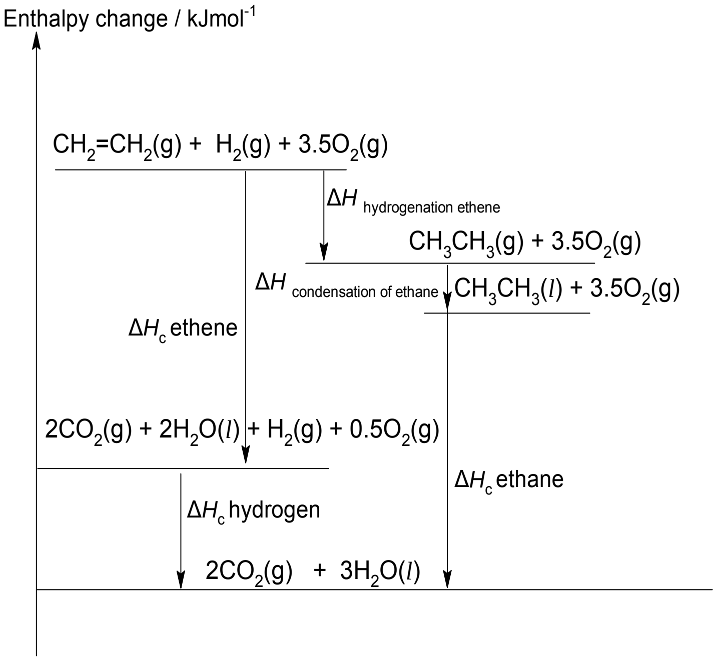
Thus the carbon atom in X is *more* readily attacked by nucleophile or X undergoes hydrolysis by water readily to give bromide ions.

[Total:20]

3 **(a)** **(i)** Use the following data to construct an energy level diagram and hence calculate the enthalpy change for the hydrogenation of ethene gas ($CH_2=CH_2$) to ethane gas (CH_3CH_3).

	ΔH / kJ mol^{-1}
Enthalpy change of combustion of $CH_3CH_3(l)$	-1545
Enthalpy change of condensation of $CH_3CH_3(g)$	-15
Enthalpy change of combustion of $H_2(g)$	−286
Enthalpy change of combustion of $CH_2=CH_2(g)$	−1411

[4]



By Hess' Law,
$\Delta H_{hydrogenation} + (-15) + (-1545) = (-1411) + (-286)$
$\Delta H_{hydrogenation} = -137$ kJ mol^{-1}

(ii) Define the term bond energy. [1]

Bond energy is the energy absorbed to break one mole of a covalent bond between two atoms in the gaseous state.

(iii) Using appropriate bond energy values from the *Data Booklet* alone, calculate another value for the enthalpy change of the reaction in **(a)(i)**.

$\Delta H = \sum$B.E.(reactants) – $\sum$B.E.(products)

= B.E.(C=C) + 4B.E.(C-H) + B.E.(H-H) – [6B.E.(C-H) + B.E.(C-C)]

= (+610) + 4(+410) – [(+350) + 6(+410)]= – 124 kJ mol^{-1}

[2]

(iv) Suggest a reason for the discrepancy between the enthalpy change for the hydrogenation of ethene gas to ethane gas you calculated in **(a)(i)** and **(a)(iii)**.

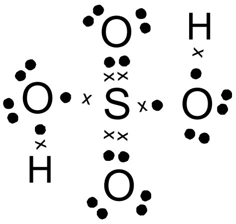
[1]

The bond energy values given in the Data Booklet are average values.

(b) Hot sulfuric acid, H_2SO_4 is added to ethanol, to produce ethene.

Draw a ‘dot-and-cross’ diagram showing the electrons (outer shell only) in a H_2SO_4 molecule.

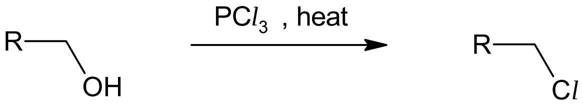
Use the VSEPR (valence shell electron pair repulsion) theory to predict the bond angle around sulfur in H_2SO_4. [3]



According to VSEPR, order of repulsion is given by: Lone pair – lone pair electrons > Lone pair – bond pair electrons > Bond pair – bond pair electrons

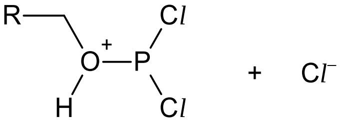
- The S atom has 4 bond pairs of electrons, no lone pair of electrons
- The bond angle is 109.5^{o}

(c) Phosphorous halides such as PX_3 can function as both Lewis acids or Lewis bases. PCl_3 is used to convert an alcohol to an alkyl chloride.



The mechanism of the above reaction involves two steps:

- Step **1**: The nucleophilic alcohol attacks PCl_3 to form the following intermediate, along with a chloride ion:



- Step **2**: (slow step) the chloride ion attacks the electrophilic carbon on the intermediate, at the same time the C–O bond breaks heterolytically.

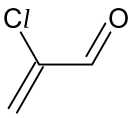
(i) State and explain if PCl_3 acts as a Lewis acid or Lewis base in step **1** of the mechanism. [1]

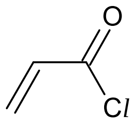
PCl_3 is a Lewis acid because it accepted lone pair of electrons.

(d) For the following pairs of compounds, describe one chemical test which would enable you to distinguish clearly between them.

State the observations for each compound.

State the type of reaction undergone for the compound that shows a positive test.


compound **N**


compound **O**

Distinguishing test: Add Tollens' reagent, warm

Observations: Silver mirror for N, no silver mirror for O

Type of reaction: Oxidation

OR

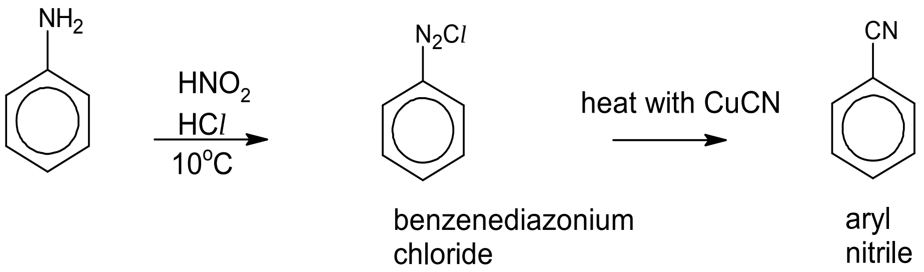
Distinguishing test: Add $AgNO_3(aq)$, r.t.p

Observations: White ppt for O, no white ppt for N

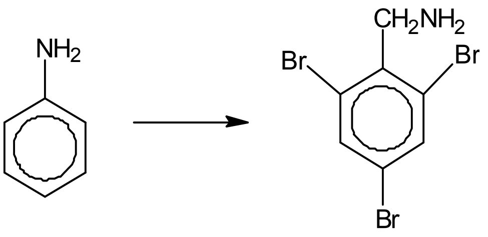
Type of reaction: Nucleophilic acyl substitution [3]

(e) Phenylamine reacts with nitrous acid, HNO_2, and hydrochloric acid at 10°C to form benzenediazonium chloride, $C_6H_5N_2Cl$.

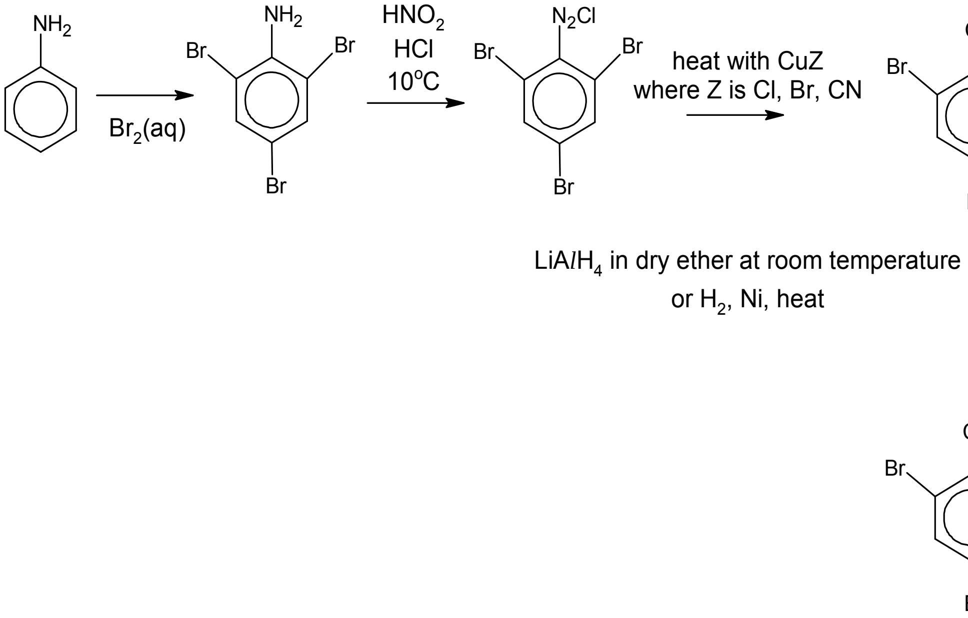
This is an important intermediate in the synthesis of aromatic compounds. It undergoes the Sandmeyer reaction, shown below, in the presence of a copper(I) catalyst to form aryl nitriles.



Suggest a four-step reaction sequence for the following conversion. You are to make use of the Sandmeyer reaction in one of the steps.



[4]

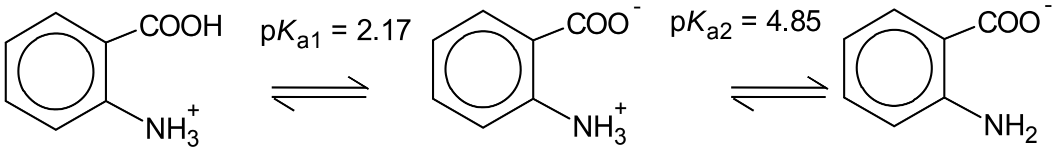

NH$_2$
Br$_2$(aq)
HNO$_2$
HCl
10^{o}C
N$_2$Cl
heat with CuZ
where Z is Cl, Br, CN
CN
LiA*l*H$_4$ in dry ether at room temperature
or H$_2$, Ni, heat
CH$_2$NH$_2$
Br

[Total:19]

Section **B**
Answer **one** question from this section.

4 **(a)** Vitamin L1, also known as 2-aminobenzoic acid, can be obtained from bovine liver, and its deficiency has been associated with lactation issues in females.

The diagram below shows how the protonated form of Vitamin L1 acts as a dibasic acid, which dissociates in two stages:



Protonated form
of Vitamin L1

(i) Calculate the pH of 10 cm^3 of 0.100 mol dm^{-3} of the protonated form of Vitamin L1. Ignore the effect of $\mathrm{p}K_{a2}$ on the pH of the sample. [1]

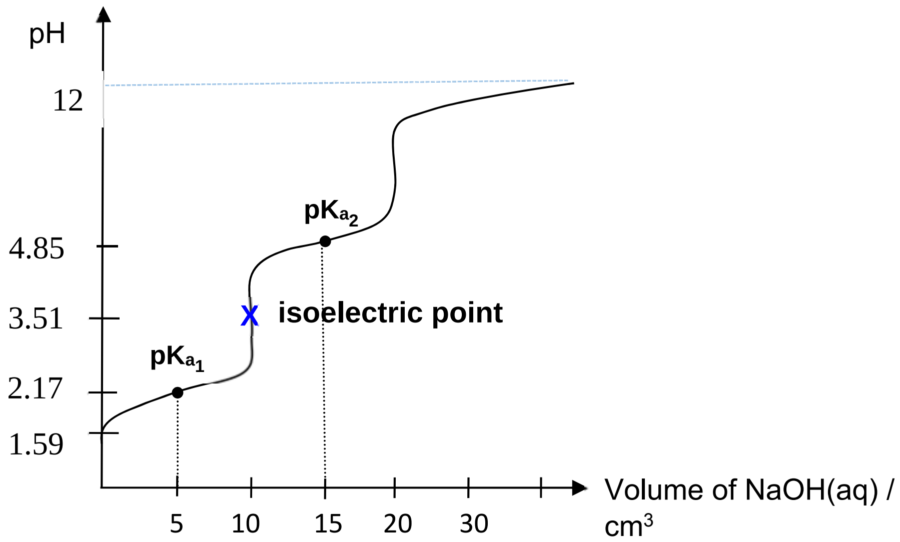
Given $\mathrm{p}K_{a1} = 2.17$
$K_{a1} = 10^{-2.17}$
$K_{a1} \approx [H^+]^2 / (0.100)$
$[H^+] = 0.02600\ \mathrm{moldm^{-3}}$
pH = 1.59

(ii) A sample containing 10 cm^3 of 0.100 mol dm^{-3} of the protonated form of Vitamin L1 was titrated with 30 cm^3 of 0.100 mol dm^{-3} of NaOH.

Sketch clearly the titration curve obtained, which should include the following key points:

- initial pH;
- points where $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ occur;
- isoelectric point of Vitamin L1 and its estimated value, given that: isoelectric point = $(\mathrm{p}K_{a1} + \mathrm{p}K_{a2}) / 2$

[4]



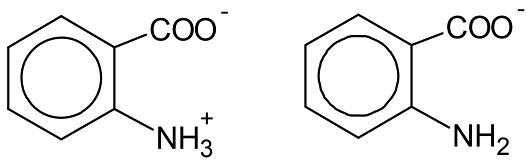
Correct shape of graph with correct axes
Correct locations of pK_{a1} and pK_{a2}
Correct initial pH AND correct equivalence volumes
Credit for show pH tapering off at about 12-13 at about 30 cm^3
value of pH at isoelectric point
isoelectric point = (pK_{a1} + pK_{a2}) / 2 = (2.17+4.85)/2 = 3.51

(iii) Define what is meant by a buffer. [1]

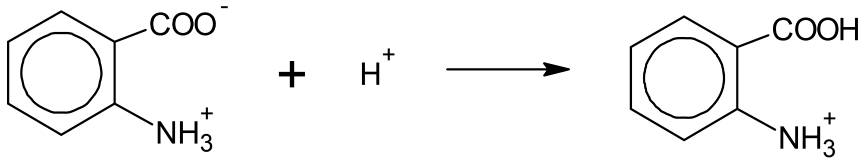
A buffer resists change to pH when small amount of acid or base is added to it and upon dilution.

(iv) Draw the structures of the two chemical species present in a solution of Vitamin L1 at pH 5.00.

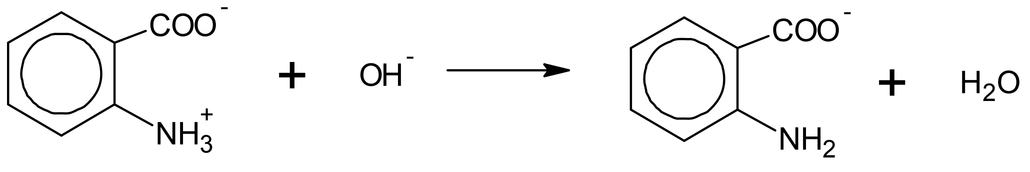
Hence, show by means of balanced equations, how this solution regulates the acidity on addition of H^+ ions and OH^- ions. [3]



When a small amount of acid is added,



When a small amount of base is added,



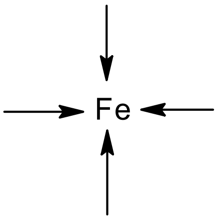
(b) Iron ions can form transition metal complexes with the basic form of the amino acid, alanine. The formula of the complex formed is $Fe(CH_3CH(NH_2)COO)_2$.

(i) State the oxidation state of Fe in the transition complex. [1]

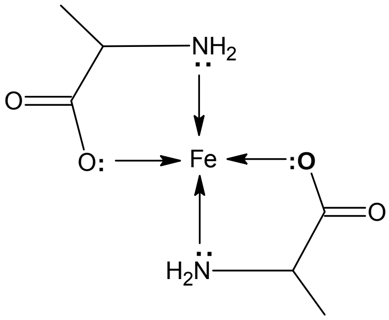
+2

Since the charge of each $CH_3CH_2(NH_2)COO^-$ is -1, iron has to be +2 for the complex to be electrically neutral as given.

(ii) The diagram below shows the incomplete structure of the complex. Copy the diagram and draw the complete structure of this complex.

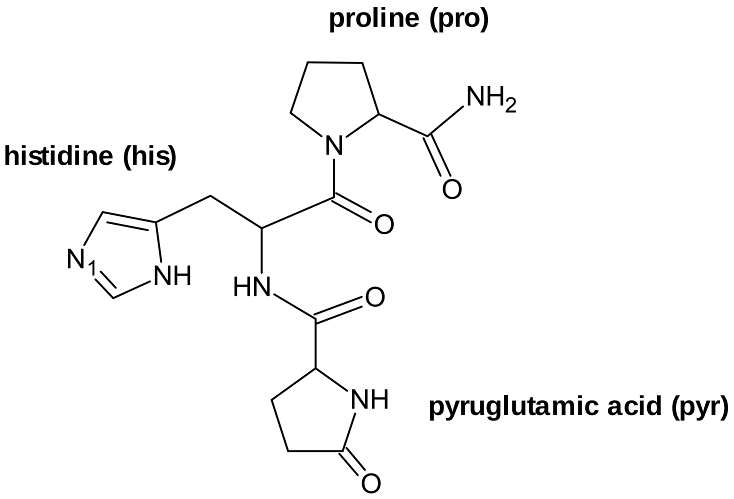


[1]



(c) Thyrotropin-releasing hormone (TRH) is a hormone that is produced by the hypothalamus in the brain. TRH has been used clinically for the treatment of the disturbance of consciousness in humans.

TRH is a tripeptide that is made of three amino acids proline, histidine and pyruglutamic acid, as shown in the diagram below.



TRH tripeptide

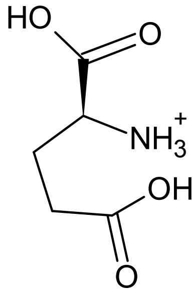
In the questions below, assume that the side chain for histidine (his) is inert.

(i) State the reagents and conditions for TRH to undergo hydrolysis. [1]

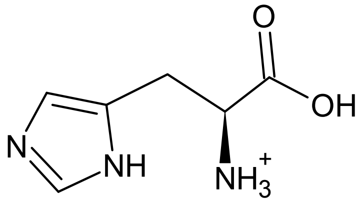
H_2SO_4(aq), heat
OR
NaOH(aq), heat

(ii) Draw the structures of the amino acids formed when TRH undergoes hydrolysis using the reagents and conditions stated in **(c)(i)**. [3]

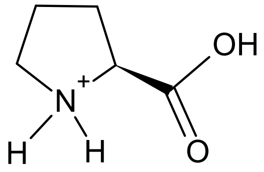
Products of acidic hydrolysis:



pyroglutamic acid (pyr)



histidine (his)



proline (pro)

**accept products of alkaline hydrolysis, if the candidate indicated that in (c)(i).*

(iii) Explain why amino acids exist as solids with high melting points. [1]

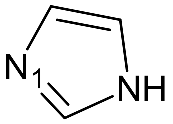
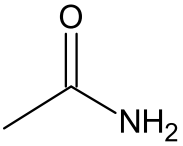
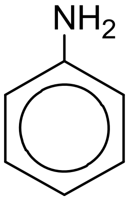
Amino acids can exist as zwitterions, with strong ionic bonds/electrostatic forces of attractions between oppositely charged ions.

(iv) State the hybridisation state of nitrogen atom labeled N_1 in TRH. [1]

nitrogen atom 1: sp^2

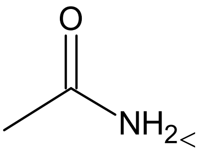
(v) The amino acid histidine has a cyclic imidazole side-chain.

The table below compares the pK_b value of N_1 nitrogen atom of imidazole ring, with the pK_b values of ethanamide and phenylamine.

Compound name	**Structure**	**pK_b**
imidazole		8.8 (pK_b of N_1)
ethanamide		14.5
phenylamine		9.4

Using the data provided, list the 3 compounds in increasing basicity, and suggest explanations for their relative basicities. [3]

Basicity increases from: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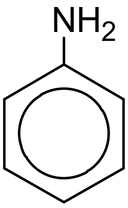
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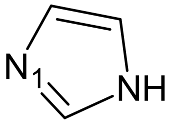
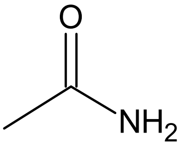
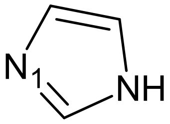
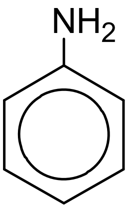
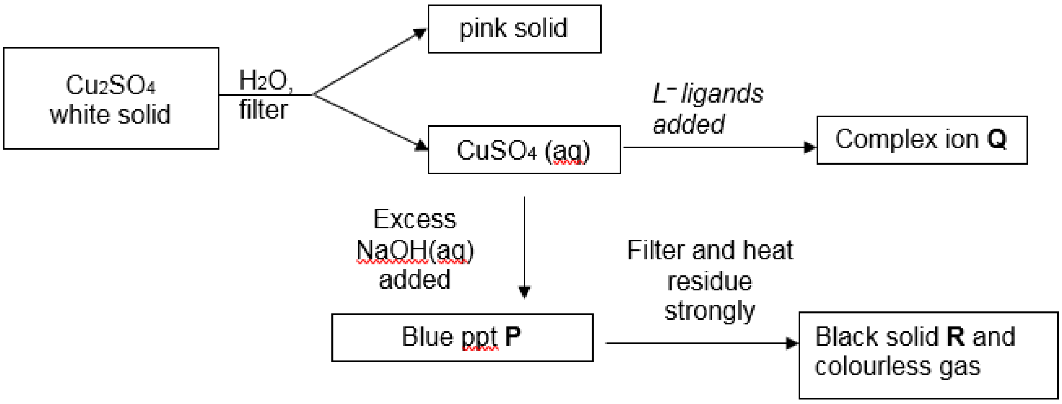



is neutral as the lone pair of electrons on N is delocalised into C=O. Hence, the lone pair of electrons on the N atom is not available for protonation.


is more basic than

as the p orbital of nitrogen lies perpendicular to the plane of the C=N bond, hence, the lone pair of electrons are not delocalized and are readily available for protonation, compared to the lone pair of electrons on N atom in phenylamine which is delocalized into the benzene ring and not so readily available.

[Total: 20]

5 **(a)** The scheme below shows the reactions of different compounds of copper.



(a) **(i)** Suggest the formulae of blue ppt **P** and black solid **R**. [2]

P: $Cu(OH)_2$

R: CuO

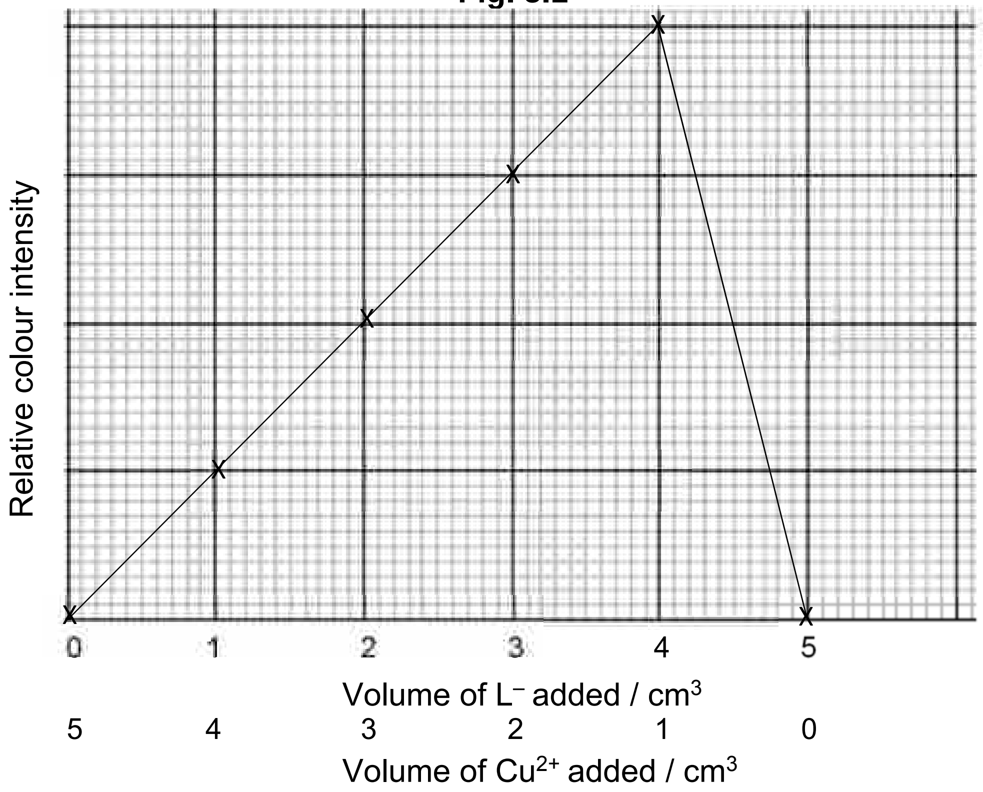
(ii) Write an equation to show how the pink solid and $CuSO_4$ are obtained when Cu_2SO_4 is added to water. [1]

$Cu_2SO_4 (s) \rightarrow CuSO_4(aq) + Cu(s)$

To determine the stoichiometry of the green complex ion **Q** formed between aqueous copper (II) sulfate and L⁻ ligands, the colour intensities of solutions containing different proportions of the ligand, L⁻, and Cu^{2+} ion were measured.

The intensity of the green colour is directly proportional to the concentration of the complex ion. The higher the concentration of the complex, the higher is the colour intensity. In one such experiment, the results obtained for different volume mixtures of 1.0×10^{-3} mol dm^{-3} $Cu^{2+}(aq)$ and 1.0×10^{-3} mol dm^{-3} $L^{-}(aq)$ were plotted below.

Fig. 5.1



(iii) State the type of reaction that occurs when complex ion **Q** is formed from aqueous $CuSO_4$. [1]

Ligand exchange

(iv) Based on the plotted graph in **Fig. 5.1**, determine the mole ratio of $Cu^{2+}(aq)$ to L^{-} (aq) in the complex **Q**.

Given that complex **Q** has an octahedral shape and it retains some water molecules as ligands, suggest a formula for the complex **Q**, including its overall charge. [2]

Mole ratio of $Cu^{2+}(aq)$ to L^{-} (aq) in the complex Q: 1:4

$[Cu(H_2O)_2(L)_4]^{2-}$

(b) Explain why complexes of Cu(II) are coloured whereas complexes of Cu(I) are colourless. [4]

Cu(I) has fully filled 3 d-orbitals ($3d^{10}$). Hence, d-to-d electron transition cannot occur, and no visible light is absorbed, which accounts for it being colourless and Cu(II) has partially filled 3d-orbitals

- In presence of ligands,
- the originally degenerate 3d orbitals split into 2 sets of different energy levels, separated
- by a small energy gap (ΔE).
- ΔE corresponds to the energy of visible light.
- An electron from the lower energy d orbital absorbs a specific wavelength of visible light and
- is promoted to a half-filled, higher energy 3d orbital. d-to-d transition can take place and
- colour observed is complementary to the colour absorbed.

(c) Chlorine can exist in different oxidation states.

Half-equation	***E*⊖ / V**
$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

A Latimer diagram shown below, summarises the standard electrode potential, $E^\ominus$ of different chlorine-containing species in acidic medium. The most highly oxidised form of the element is on the left, with successively lower oxidation states to the right. The electrode potentials are shown on the arrows.

$$\begin{tikzcd} ClO_3^- \arrow[r, "+1.47\ V"] \arrow[rr, bend right, "E^\ominus(ClO_3^-/Cl^-)"'] & Cl_2 \arrow[r, "+1.36\ V"] & Cl^- \end{tikzcd}$$

The standard electrode potential of converting ClO_3^- to Cl^-, $E^\ominus(ClO_3^-/Cl^-)$ is **NOT** the summation of +1.47 V and +1.36 V.

Determine the number of electrons involved in the conversion of 1 mole of ClO_3^- to 1 mole of Cl^-.

Hence, given that $\Delta G^\ominus$ for the conversion of ClO_3^- to Cl^- is -150 kJ mol^{-1}, calculate $E^\ominus(ClO_3^- / Cl^-)$. [2]

No of electrons involved = 6 (+5 to -1)

$\Delta G^\ominus = -nFE^\ominus$

$-150\,000 = -(6)(96500)\,E^\ominus$

$E^\ominus = +0.259$ V

(d) *Use of the Data Booklet is relevant to this question.*

X, $C_5H_6O_3$, is soluble in dilute NaOH. **X** gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and a yellow precipitate with warm alkaline aqueous iodine. **X** decolourises aqueous bromine.

When it is reacted with a methanolic solution of $NaBH_4$ it gives **Y**, $C_5H_8O_3$. Catalytic hydrogenation of **X** gives **Z**, $C_5H_{10}O_3$. When **Z** is reacted with alkaline aqueous iodine, it gives $^-O_2C(CH_2)_2CO_2^-$.

Oxidation of 1 mole of **X** with hot acidified potassium manganate(VII) gives 1 mole of CH_3COCO_2H and 2 moles of CO_2 gas.

Additional optional information: ***X**, **Y** and **Z** have a proton (^1H) chemical shift value of 13.0 ppm. (Refer to Data Booklet Section 6: Typical proton (^1H) chemical shift values (δ))*

Suggest structures for **X**, **Y** and **Z**. Explain your reasoning clearly. [8]

- **X** is a carboxylic acid which undergoes acid base with NaOH.
- **X** is a ketone or aldehyde compound as it undergoes condensation reaction with 2,4-dinitrophenylhydrazine to form an orange ppt.
- **X** undergoes oxidation with warm alkaline aqueous iodine to form a yellow ppt, CHI_3. **X** has $CH_3CO–$ structure.
- **X** is an alkene as it undergoes electrophilic addition with Br_2.
- Ketone or aldehyde group in **X** is reduced by $NaBH_4$ to give **Y** as no. of H atoms increases by 2.
- Both alkene and ketone group in **X** are reduced by hydrogen to give **Z** as no. of H atoms increases by 4.
- **Z** contains $CH_3CH(OH)–$ structure (not $CH_3CO–$) as it undergoes oxidation by alkaline aqueous iodine to give $^-O_2C(CH_2)_2CO_2^-$.

X is $CH_3COCH=CHCO_2H$
Y is $CH_3CH(OH)CH=CHCO_2H$
Z is $CH_3CH(OH)CH_2CH_2CO_2H$

[Total: 20]

End of paper

PIONEER JUNIOR COLLEGE

JC2 Prelim Practical Exam
HIGHER 2

CANDIDATE NAME

CT GROUP	1	7			

INDEX NUMBER				

CHEMISTRY **9729/04**

Paper 4 Practical **14 August 2018**

2 hours 30 min

Candidates answer on the Question Paper
Additional Materials: As listed in your apparatus list

READ THESE INSTRUCTIONS FIRST

Write your CT group, index number and name on all work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift: _______________

Lab: _______________

For Examiner's Use	
Q1	/26
Q2	/13
Q3	/16
Total	/55

This document consists of **11** printed pages.

[Turn over

1 **FA 1** is an aqueous solution prepared by mixing equal volumes of **y** mol dm^{-3} hydrochloric acid, HC*l*, and **y** mol dm^{-3} of sulfuric acid, H_2SO_4.

FA 2 is 2.00 mol dm^{-3} sodium hydroxide, NaOH.

Take care as aqueous solutions of sodium hydroxide are corrosive.

When an alkali is run into an acid, an exothermic reaction takes place and the temperature of the mixture increases until the end-point is reached. If alkali is added beyond the end-point, the temperature will decrease as no further reaction takes place and the alkali is at a lower temperature than the mixture.

You are to follow the neutralisation of the acids in **FA 1** by measuring the temperature as known volumes of **FA 2** are added.

(a) Fill the burette to 0.00 cm^3 with **FA 2**. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup.

Use the measuring cylinder to place 50.0 cm^3 of **FA 1** into the cup and record the steady temperature of the acid in Table 1.1 on page 3.

Read through the following instructions before starting the experiment.

Record all temperatures in Table 1.1 on page 3.

Run 3.00 cm^3 of **FA 2** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature.

Immediately run a further 3.00 cm^3 of **FA 2** from the burette into the cup, stir and record the maximum temperature as before.

Continue the addition of **FA 2**, in 3.00 cm^3 portions, until 48.00 cm^3 of solution have been run from the burette.

Table 1.1

Volume of **FA 2** added / cm^3	Total volume of solution in cup / cm^3	Temperature / °C		Δt (t_x – t_0) / °C	Total volume x Δt / …….
0.00	50.0	t_0	30.4	0.0	0.0
3.00	53.0	t_3	31.9		
6.00	56.0	t_6	33.3		
9.00	59.0	t_9	34.5		
12.00	62.0	t_{12}	35.6		
15.00	65.0	t_{15}	36.6		
18.00	68.0	t_{18}	37.7		
21.00	71.0	t_{21}	38.4		
24.00	74.0	t_{24}	37.8		
27.00	77.0	t_{27}	37.2		
30.00	80.0	t_{30}	36.8		
33.00	83.0	t_{33}	36.4		
36.00	86.0	t_{36}	36.0		
39.00	89.0	t_{39}	35.6		
42.00	92.0	t_{42}	35.2		
45.00	95.0	t_{45}	34.9		
48.00	98.0	t_{48}	34.6		

[3]

Complete the table by calculating Δt and (total volume x Δt) for each measurement. Determine the units for the final column.
Units for (total volume x Δt): ……………………….[1]

	(b)	Plot (total volume x Δt) against the volume of **FA 2** added. Draw two straight lines of best-fit through the plotted points to find the end-point for the titration. [4]	
	(c)	Read from the graph the end-point of the titration: ……20.80………. cm^3 [3]	
	(d)	**(i)**	Calculate the amount of **FA 2** used to reach the end-point of the titration.
			nNaOH = 20.80 / 1000 x 2.00 = 0.0416 mol

amount of **FA 2** for end-point = ……………………… [1]

(ii) Calculate the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**. [1]

$[H^+] = 0.0416 / 0.050 = 0.832$ mol dm^{-3}

concentration of H^+ in **FA 1** = ……………………… [1]

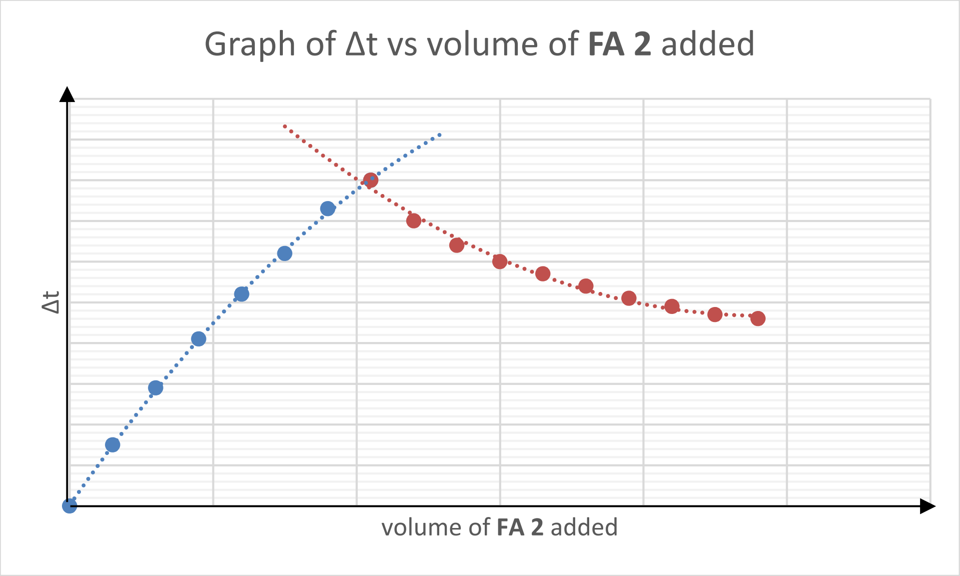
(iii) Equal volumes of y mol dm^{-3} H_2SO_4 and y mol dm^{-3} $\mathrm{HC}l$ were mixed to produce **FA 1**. Use your answer to **(d)(ii)** to calculate the value of y.

$3y/2 = 0.832$

y = 0.555 mol dm^{-3}

y = ……………………… [1]

(e) When Δt was plotted against the volume of **FA 2** added, the following graph is obtained. Explain why the shape of this graph differs from that in **(b)**.



The heat evolved from the neutralization is spread over an increasing volume of solution, leading to a smaller Δt, hence curved lines are obtained instead.

[1]

(f) In the experiment you have performed, determine whether using a measuring cylinder or a burette to measure each 3.00 cm^3 portion will be more accurate.

Show calculations to justify your answer.

% error of measuring cylinder = 0.5 / 3 x 100 = +/- 16.7%

% error of burette = 2 x 0.05 / 3 x 100 = +/- 3.34%

The burette would be a better apparatus as it has a smaller percentage error.

[5]

(g) **Plan**

The reaction between an acid and a metal hydroxide is exothermic.
The experimental procedure used in **1(a)** is known as a thermometric titration where the equivalence-point of a neutralisation reaction can be determined without the use of an indicator. This process can also be used to calculate the basicity of an acid.

A modification of the thermometric titration can be done by performing several experiments in which varied volumes of acid and base are mixed together, keeping the total volume constant. The highest temperature for each experiment is then recorded.

The data obtained can then be used to plot a graph of Δt against volume of NaOH used to determine the basicity of an acid.

Using the informaton above, plan an investigation to determine the basicity of an unknown acid H_nA of concentration 2.00 mol dm^{-3} (where n = 1 or 2).

You may assume that you are provided with

- 2.00 mol dm^{-3} sodium hydroxide, NaOH
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the volumes of reactants that you would use,
- the apparatus that you would use
- the procedure that you would follow and the measurements that you would take,
- how you would determine the basicity of the unknown acid, H_nA via sketches of the graphs you would expect to obtain.

1. Fill up one 50 cm^3 burette with the unknown acid, and another burette with 2.00 mol dm^{-3} NaOH.

2. Using a burette, measure 10.00 cm^3 of acid into a Styrofoam cup labelled acid. Place the cup inside a second styrofoam cup which is placed in a 250 cm^3 beaker to support it.

3. Using another burette, measure out 50.00 cm^3 of NaOH into another styrofoam cup labelled FA 2.

4. Record the initial temperature of acid solution, and record the initial temperature of NaOH solution separately with a thermometer of 0.2 ºC interval.

5. Add the NaOH(aq) from the cup containing NaOH, into the Styrofoam cup containing the acid and cover with a plastic lid.

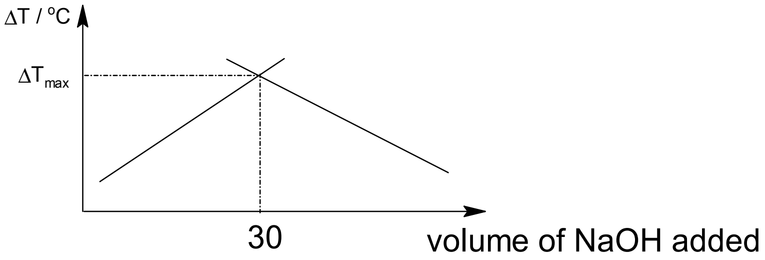
6. Stir gently the mixture with the thermometer and record the highest temperature reached

7. Wash the cups and dry them carefully with paper.

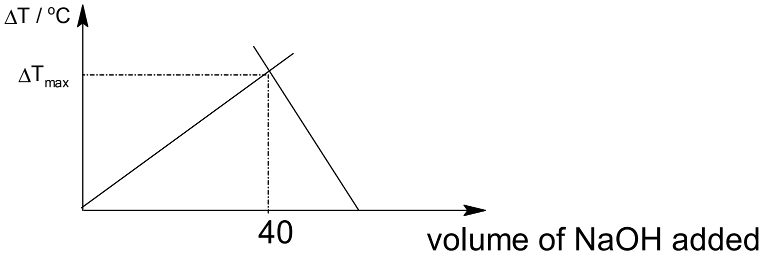
8. Repeat steps 1 to 6 for 15, 30, 40 and 50 cm^3 of acid and varying volumes of NaOH(aq) to make the total volume of mixture constant at 60 cm^3.

9. Sketch a graph of Δt vs volume of NaOH used.

If HA,



If H_2A,



[6]

[Total: 26]

2 **Determination of the rate equation for the reaction between peroxodisulfate ions and iodide ions.**

FA 3 is 0.200 mol dm^{-3} aqueous ammonium peroxodisulfate, $(NH_4)_2S_2O_8$.
FA 4 is an aqueous solution of 1:1 mixture of 0.300 mol dm^{-3} aqueous potassium iodide, KI and 0.00800 mol dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$.

If potassium iodide and ammonium peroxodisulfate are mixed in the presence of starch and sodium thiosulfate, the iodine liberated reacts with the thiosulfate ions until they are all used up.

$$S_2O_8^{2-} + 2I^- \rightarrow I_2 + 2SO_4^{2-}$$
$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

When no thiosulfate ions are left, any iodine formed reacts with starch and the dark blue colour of the starch-iodine complex appears. The time taken for the dark blue colour to appear with a constant quantity of sodium thiosulfate present depends on the rate of formation of iodine

You are required to carry out a total of **four** experiments at different concentration of peroxodisulfate ions and note the time taken, ***t***, for the solutions to turn dark blue.

The end-point of the reaction is the first appearance of a dark blue colour.
You need to swirl the reaction mixture well as insufficient swirling will lead to a dark blue colour appearing before the true end-point is reached. Keep to the same number of swirls in each experiment.

Prepare a table in the space provided on page 10 in which to record, for each experiment:

- volume of **FA 3**
- volume of deionised water
- values of ***t***
- calculated values of **1/t**

Note: As the volume of ***FA 4*** *is constant for each experiment, you do not need to record its volume in your table.*

You are advised to read the procedure and to prepare a table for your results before starting the practical work.

(a)	**Procedure**	
	Experiment 1	
	1.	Fill the burette labelled **FA 3** with **FA 3**.
	2.	Run 20.00 cm^3 of **FA 3** into a 100 cm^3 beaker.
	3.	Using a 25 cm^3 measuring cylinder, measure out 20 cm^3 of **FA 4** and add 10 drops of starch solution.

4. Add the contents of the measuring cylinder to the beaker and start the stopwatch when half of the contents has been added.

5. Swirl the mixture and place the beaker on a white tile.

6. Stop the stopwatch as soon as the dark blue colour appears. Record the time, ***t***, to the nearest second.

7. Wash both the measuring cylinder and the beaker with water and wipe dry.

Experiment 2

1. Run 10.00 cm^3 of **FA 3** into a 100 cm^3 beaker.

2. Using a 25 cm^3 measuring cylinder, measure out 10 cm^3 of deionised water into the beaker containing **FA 3**.

3. Using another 25 cm^3 measuring cylinder, measure out 20 cm^3 of **FA 4** and add 10 drops of starch solution.

4. Add the contents of the measuring cylinder to the beaker and start the stopwatch when half of the contents has been added.

5. Swirl the mixture and place the beaker on a white tile.

6. Stop the stopwatch as soon as the dark blue colour appears. Record the time, ***t***, to the nearest second.

7. Wash both the measuring cylinder and the beaker with water and wipe dry.

Experiment 3 – 4

Perform **two** additional experiments using different volume of the peroxodisulfate solution and the deionised water. Note that the combined volume of **FA 3** and deionised water must always be 20 cm^3. Do not use a volume of **FA 3** that is less than 6 cm^3.

(b) In the series of experiments where the total volume of the mixture is kept constant and the same end-point (appearance of dark blue colour) is timed at different concentrations of peroxodisulfate solution,

- $[S_2O_8^{2-}] \propto V_{\mathbf{FA3}}$ used
- rate $\alpha \ \frac{1}{t}$

Record the results of your four experiments below.

Table of results

Experiment	Volume of FA3/ cm^3	Volume of deionised water/ cm^3	*t* / *s*	1/t s^{-1}
1	20.00	0.0	23	
2	10.00	10.0	49	
3	17.00	3.0	27	
4	13.00	7.0	31	
5	7.00	13.0	71	

[5]

(c) Using the results in your table, deduce the order of the reaction with respect to the peroxodisulfate ions. Explain clearly how you arrived at your answer.

Order is 1 .

Comparing expt 1 and 2,
Halve [$S_2O_8^{2-}$], time is doubled

[1]

(d) **(i)** Based on experiments 1 – 4, indicate, with reasoning, which experiment is most likely to have the largest error in the time measured.

The time measured for experiment 1 is the shortest and hence have the greatest percentage error.

[1]

(ii) Instead of washing the beaker as required before performing the next experiment, a student simply just poured away the reaction mixture. There were some left over reaction mixture in the beaker when he performed the subsequent experiment. State and explain what will happen to the time, ***t***.

The excess I_2 left in the flask will react with the $S_2O_3^{2-}$ in the new experiment. As there is lesser $S_2O_3^{2-}$ for the new experiment, less I_2 is reacted. Given that the rate of reaction is the same, the time taken to produce the I_2 will be shorter and hence observe the blue colour faster.

[2]

(e) **(i)** Explain why a fixed amount of sodium thiosulfate is required.

To ensure an equal amount of iodine is reacted before the solution turns dark blue in each experiment.

[1]

(ii) If the concentration of sodium thiosulfate used in **FA 4** is changed to 0.0160 mol dm^{-3}, state and explain the effect on the time taken to reach the end-point?

Longer time required to reach end-point.

There is a larger amount of sodium thiosulfate, so it will take more time to produce enough iodine to reach the end point.

[1]

(f) Two other experiments were carried out to determine the order of reaction with respect to iodide ions and the following results were obtained.

Experiment	volume of $(NH_4)_2S_2O_8$ / cm^3	volume of KI / cm^3	volume of H_2O / cm^3	volume of $Na_2S_2O_3$ / cm^3	time / s
5	50	40	0	10	40
6	50	20	20	10	82

From the data given above, state the order of reaction with respect to KI. Explain clearly how you arrived at your answer.

Order of reaction = 1

Since total volume of reaction mixture is kept constant,

- **[KI]$\propto$ V_{KI} used**

Also since rate α $\frac{1}{t}$

AND

- **when the volume of KI is doubled, the time taken for the iodine to appear is halved. Rate of reaction is directly proportional to [KI].**

OR

- **V_{KI} x t = constant**

[1]

(g) Write the rate equation for the reaction between peroxodisulfate ions and iodide ions.

Rate = k[$S_2O_8^{2-}$][I^-]

[1]

[Total: 13]

3 **FA 5** contains Ni^{2+} and one other cation and one anion.

In all tests, the reagents should be added gradually until no further change is observed after shaking with each addition.
Record your observations and the deductions you make from them in the spaces provided
Your answers should include

- Details of colour changes and precipitates formed
- The names of gases evolved and details of the test used to identify each one.

You should indicate clearly at what stage in a test, an observation occurs
No additional or confirmatory tests for ions present should be attempted

Test	Observations
(i) Test the **FA 5** solution with Universal Indicator paper**.**	pH is 3
(ii) To 2 cm depth of **FA 5** in a test tube, add aqueous sodium carbonate until no further change is observed.	green ppt Effervescence seen , gas forms white ppt when passes through limewater
(iii) To 3 cm depth of **FA 5** in a boiling tube, add aqueous sodium hydroxide until no further change is observed. Filter the mixture and collect the filtrate, label it **FA 6**. State the colour of the residue and filtrate. Divide **FA 6** into two portions in two separate test tubes for use in **(iv)** and **(v)**.	Green ppt insoluble in excess aqueous sodium hydroxide (light) Green residue and Colourless filtrate
(iv) To 2 cm depth of **FA 6** in a test-tube, add dilute nitric acid, drop by drop, until no further change is observed.	No effervescence / no gas evolved (Thin cloudy) White ppt appears which is soluble in excess nitric acid
(v) To 2 cm depth of **FA 6** add aqueous silver nitrate.	White ppt forms
Add an excess of dilute aqueous ammonia.	soluble in excess aqueous ammonia

[5]

Conclusion

(a) Consider your observations in **(ii)**. Suggest an explanation for the evolution of gas observed. Write an equation, including state symbols in your answer.

FA 5 contains an **acidic salt** which undergoes hydrolysis to produce H^+.
The H^+ would react with carbonate to produce CO_2
$2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$

[2]

(b) Consider your observations in **(v)**. Suggest an explanation for the observations in terms of the chemistry involved.

Cl^- reacts with $AgNO_3$ to form white ppt of $AgCl$ or show equation
With $NH_3(aq)$, complex $[Ag(NH_3)_2]^+$ is formed or show equation .
This reduces $[Ag^+]$
and shifts the equilibrium: $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
to the right OR ionic product becomes lower than K_{sp},

so $AgCl$ solid dissolves.

[2]

(c) **(i)** **FA 5** contains the cations: Ni^{2+} and **Al^{3+}**

[1]

(ii) **FA 5** contains the anion: **Cl^-**

[1]

(d) **Plan**

FA 7 is a solution that contains Fe^{2+} and Al^{3+} ions

Plan a sequence of steps by which the two ions could be separated so that each ion is present in a separate precipitate. For each of the steps, you are to specify the location of the ions and their formulae.

You are also required to specify the amount (dropwise or excess) of reagents that you add.

You may assume that the usual bench reagents and apparatus are available for use.

1. **Add <u>excess</u> NaOH (aq) to the mixture.**
   Carry out filtration to separate the insoluble ppt / $Fe(OH)_2$ from the solution
   Residue: $Fe(OH)_2$ (s)
   Filtrate: $Al(OH)_4^-$ (aq)

2. **To the filtrate[1], Add HCl dropwise**

3. **Carry out filtration to separate the insoluble ppt/$Al(OH)_3(s)$ from the solution**
   Residue: <u>$Al(OH)_3$</u>

		[5]	
			[Total: 16]