2019

H2 Chemistry

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2.	Anglo Chinese Junior College	
3.	Catholic Junior College	
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ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/01**

Higher 2 **19 September 2019**

Paper 1 Multiple Choice **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 and class 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 **18** printed pages and **2** blank pages.

1 *Use of the Data Booklet is relevant to this question.*

The ^{68}Ge isotope is medically useful because it undergoes a natural radioactive process to give an isotope of a different element, ^{68}Q, which can be used to detect tumours. This transformation of ^{68}Ge occurs when an electron enters the nucleus and changes a proton into a neutron.

Which statement about the composition of an atom of ^{68}Q is correct?

A It has 4 electrons in its outer p orbitals.

B It has 13 electrons in its outer shell.

C It has 37 neutrons.

D Its proton number is 32.

2 The successive ionisation energies (IE) of two elements **X** and **Y** are given in the table.

IE / kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th	7th	8th
X	786	1580	3230	4360	16000	20000	23600	29100
Y	1300	3380	5310	7460	8670	9330	22060	27070

What compound is most likely to be formed when **X** and **Y** are combined?

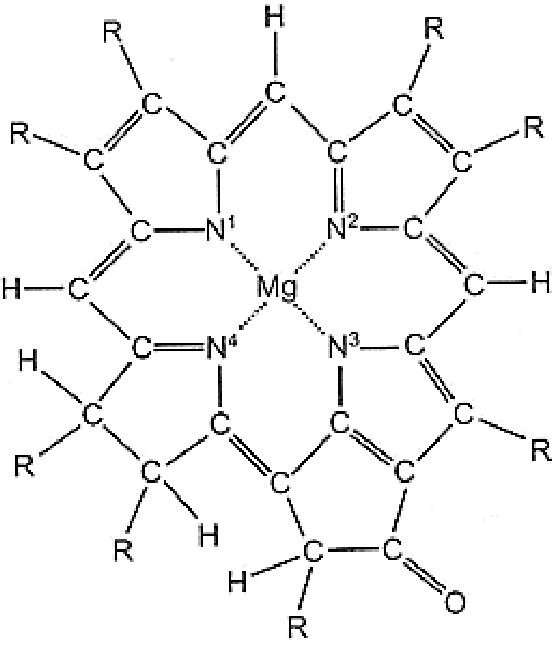
A ionic, with formula $\mathbf{X_2Y}$

B ionic, with formula $\mathbf{XY_2}$

C covalent, with formula $\mathbf{XY_2}$

D covalent, with formula $\mathbf{X_2Y}$

3 Plants appear green due to the presence of chlorophyll. There are several closely related chlorophylls and the diagram shows a simplified version of one. The various different side–groups are all shown as R.



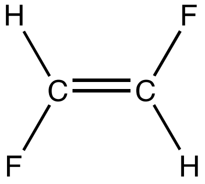
Note that the four N atoms and the Mg ion are planar.

Which of the descriptions of the bonds between Mg and the numbered N atoms is most likely to be correct?

	N atoms numbered	
	1 and 3	2 and 4
A	co–ordinate	ionic
B	co–ordinate	π
C	ionic	co–ordinate
D	π	co–ordinate

4 Which molecule has the largest dipole?

A



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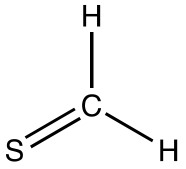

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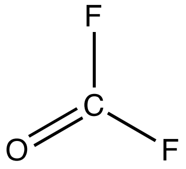
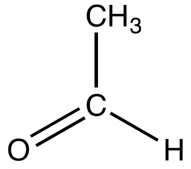


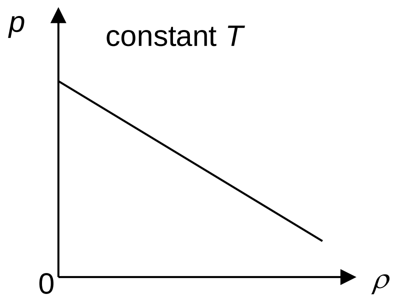
D



5 Which graph best represents the behaviour of a fixed mass of an ideal gas under the given conditions?

(ρ is the density of the gas)

A



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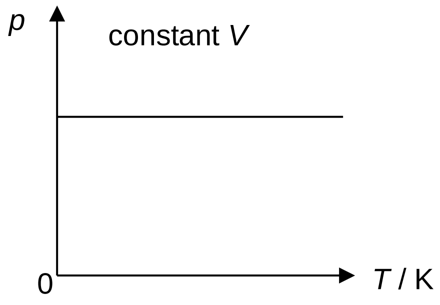

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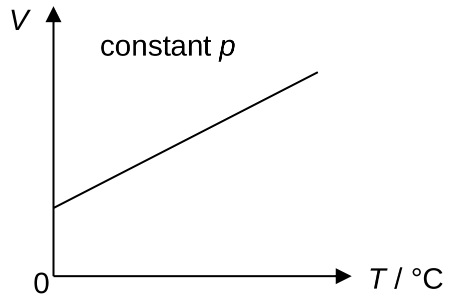

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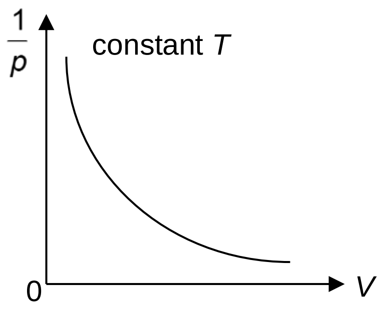


6 Which of the following, in aqueous solution, could be used to maintain the pH at about 5?

A ammonia and ammonium chloride

B ethanoic acid and sodium ethanoate

C sodium hydroxide and sodium ethanoate

D ethanoic acid only

7 Values of the ionic product of water, K_w, at different temperatures are given in the table.

temperature / °C	K_w / mol^2 dm^{-6}
15	4.50×10^{-15}
30	1.47×10^{-14}

What can be deduced from this information?

A The association of water molecules by hydrogen bonding increases as temperature increases.

B Water is not a neutral liquid at 15 °C.

C The concentrations of both H^+ and OH^- increase as temperature increases.

D The ionic dissociation of water is an exothermic reaction.

8 Which property of the halogens increases on descending Group 17?

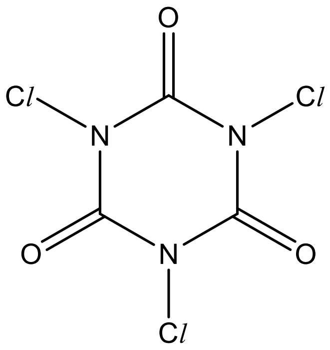
A volatility of the halogens

B bond energy of the halogen–halogen bond

C ease of oxidation of the halide ion

D thermal stability of the hydrogen halide

9 Trichloroisocyanuric acid is commonly used in swimming pools as a disinfectant. The recommended concentration level of the acid is 1.50 mg per litre of water.



trichloroisocyanuric acid

$M_r = 232.5$

How many chlorine atoms are present in a 2.50×10^6 litre Olympic–sized swimming pool filled with the recommended concentration level of trichloroisocyanuric acid?

A 2.91×10^{25}

B 2.91×10^{28}

C 9.71×10^{24}

D 9.71×10^{27}

10 When 720 cm^3 of hydrogen sulfide gas, H_2S, is passed through 40 cm^3 of 0.500 mol dm^{-3} nitric acid, HNO_3, a yellow solid of sulfur and a nitrogen–containing compound are formed.

The half–equation for oxidation of H_2S is shown below.

$$H_2S \rightarrow S + 2H^+ + 2e^-$$

What could be the nitrogen–containing compound formed from the complete reaction?

[All volumes are measured at room temperature and pressure conditions under which H_2S is a gas.]

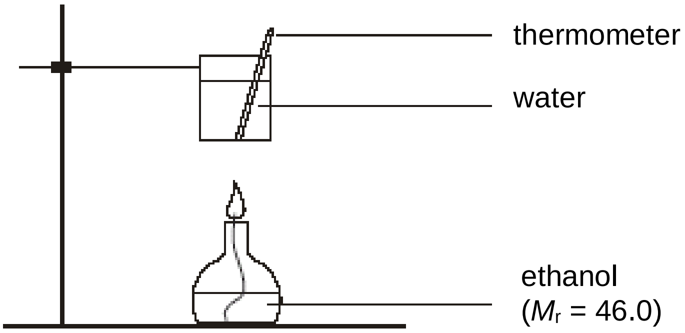
A N_2

B NO

C NO_2

D NH_3

11 When *m* g of ethanol was burned under a container of water, it was found that the temperature of 300 g of water rose by *T* °C.



The enthalpy change of combustion of ethanol is –1371 kJ mol^{-1} and the specific heat capacity of water is 4.2 J g^{-1} K^{-1}.

Which expression below gives the percentage efficiency of this process?

A $\dfrac{m \times 4.2 \times T \times 46.0}{300 \times 1371 \times 1000} \times 100\%$

B $\dfrac{m \times 1371 \times 1000}{300 \times 4.2 \times T \times 46.0} \times 100\%$

C $\dfrac{300 \times 4.2 \times (T + 273) \times 46.0}{m \times 1371 \times 1000} \times 100\%$

D $\dfrac{300 \times 4.2 \times T \times 46.0}{m \times 1371 \times 1000} \times 100\%$

12 The enthalpy change of the thermal decomposition of magnesium carbonate is given as +117 kJ mol^{-1}.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

What information, other than that given above, is required to calculate a value for the enthalpy change of formation of $MgCO_3(s)$?

A enthalpy change of formation of magnesium oxide and enthalpy change of combustion of carbon

B lattice energy of magnesium carbonate and of magnesium oxide

C first and second ionisation energies of magnesium

D bond energy of the C=O bonds in carbon dioxide

13 What will be the signs of the enthalpy and entropy changes when a liquid boils?

	ΔH	ΔS
A	+	+
B	–	+
C	–	–
D	+	–

14 The alkaline hydrolysis of 2–chloro–2–methylpropane, $(CH_3)_3CCl$, with 0.2 mol dm^{-3} NaOH produces 2–methylpropan–2–ol, $(CH_3)_3COH$.

$$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$$

20% of $(CH_3)_3CCl$ in a solution of concentration 0.02 mol dm^{-3} hydrolyses in 5 minutes at a certain temperature.

With reference to the overall order of this reaction, what percentage of $(CH_3)_3CCl$ in a solution of concentration 0.04 mol dm^{-3} would hydrolyse in 5 minutes at the same temperature?

A 10% **B** 20% **C** 30% **D** 40%

15 The equation for the oxidation of nitrogen monoxide is shown below.

$$O_2 + 2NO \rightarrow 2NO_2$$

The following rate equation was derived from initial rates experiments.

$$\text{rate} = k\,[O_2]\,[NO]^2$$

The results of the initial rates experiments are shown.

initial $[O_2]$ / mol dm^{-3}	initial [NO] / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
2.0	1.0	8.0
1.0	1.0	*s*
1.0	*t*	16.0
0.5	0.5	*u*

What are the missing values, *s*, *t* and *u*?

	s	*t*	*u*
A	4.0	1.0	0.5
B	4.0	2.0	0.5
C	2.0	1.0	1.0
D	2.0	2.0	1.0

16 Which suggested mechanisms are consistent with the experimentally obtained rate equation?

	chemical equation	rate equation	suggested mechanism
1	$H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$	rate = $k_1\,[H_2O_2]\,[I^-]$	$H_2O_2 + H^+ \rightarrow H_2O + OH^+$ (fast) $OH^+ + 2I^- + H^+ \rightarrow H_2O + I_2$ (slow)
2	$CO + NO_2 \rightarrow CO_2 + NO$	rate = $k_2\,[NO_2]^2$	$NO_2 + NO_2 \rightarrow N_2O_3 + O$ (slow) $N_2O_3 + CO \rightarrow CO_2 + 2NO$ (fast)
3	$H_2 + I_2 \rightarrow 2HI$	rate = $k_3\,[H_2]\,[I_2]$	$H_2 \rightarrow 2H$ (slow) $2H + I_2 \rightarrow 2HI$ (fast)

A 1, 2 and 3

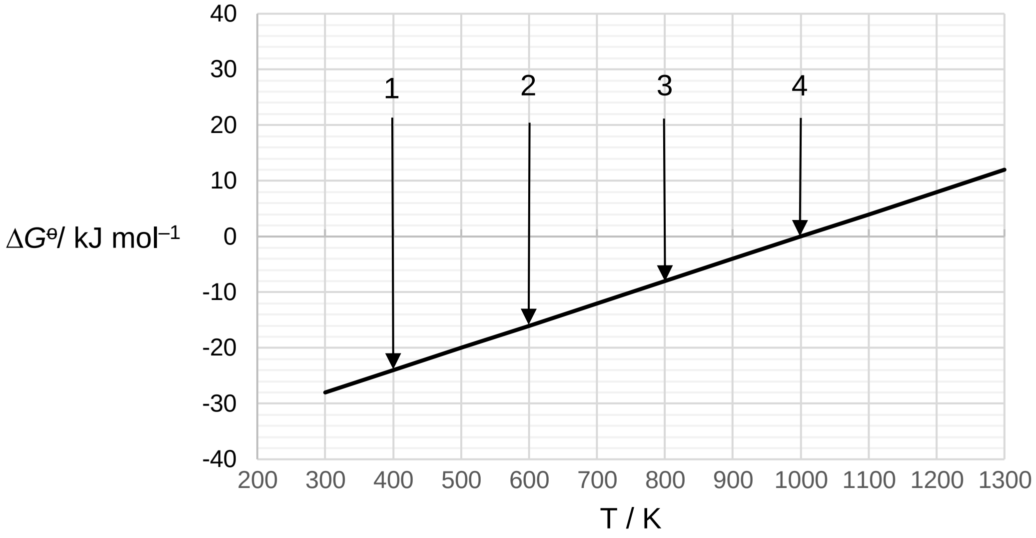
B 1 and 2 only

C 2 and 3 only

D none

17 The graph shows how $\Delta G^\ominus$ changes with temperature for the reaction shown.

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$



Equimolar amounts of H_2O and CO were introduced into a sealed container and allowed to reach equilibrium.

At which points on the graph above will the value of K_c be more than 1?

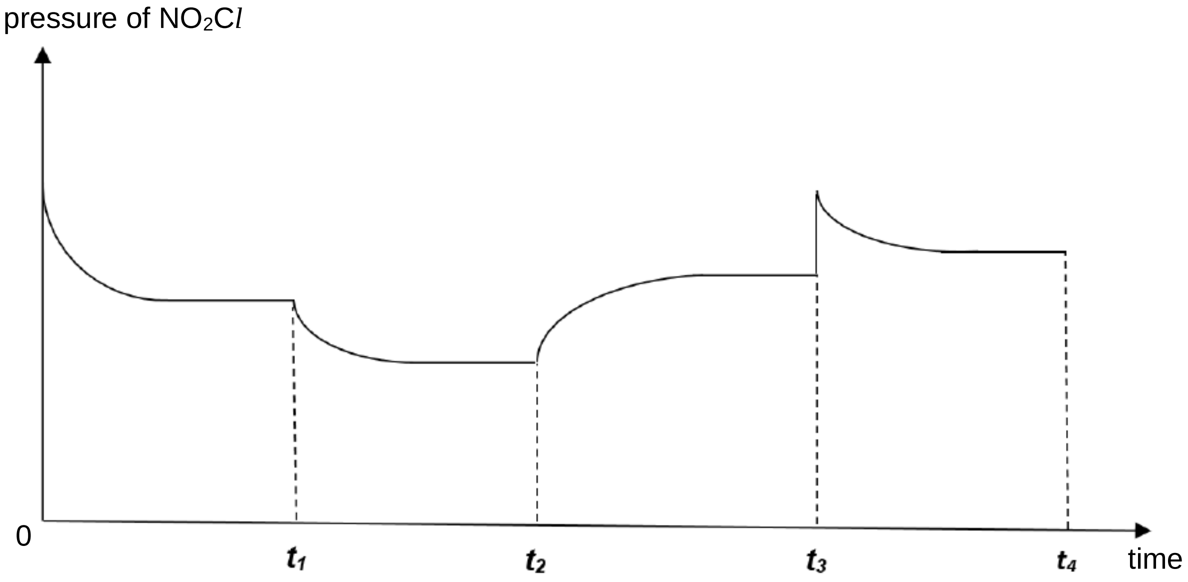
A 1 and 2 **B** 2 and 3 **C** 1, 2 and 3 **D** 1, 2, 3 and 4

18 Nitrosyl chloride, NOC*l*, is a yellow gas that can be formed between nitryl chloride, NO_2Cl, and nitric oxide, NO, in the following reaction.

$$NO_2Cl(g) + NO(g) \rightleftharpoons NOCl(g) + NO_2(g) \qquad \Delta H < 0$$

NO_2Cl and NO were initially allowed to react in a closed vessel at 800 K and equilibrium was established.

The graph below shows how the pressure of NO_2Cl varied with time.

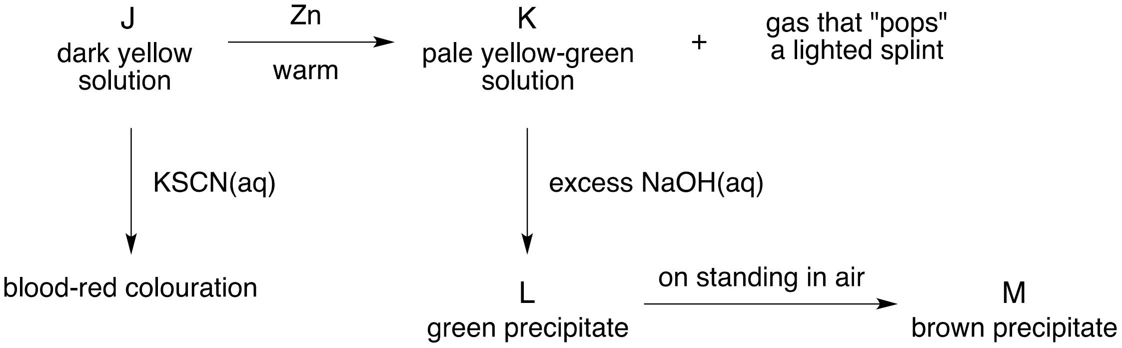


What could be the changes made to the system at t_1, t_2 and t_3?

	t_1	t_2	t_3
A	NO_2Cl was removed	temperature was increased	NO_2Cl was added
B	temperature was decreased	NO_2Cl was added	NO_2 was added
C	NO_2 was removed	temperature was increased	NO_2Cl was added
D	NO_2Cl was removed	NO_2Cl was added	temperature was decreased

19 *Use of the Data Booklet is relevant to this question*.

Consider the following reaction scheme starting from solution J.



Which of the following statements are correct?

1 The gas produced is able to reduce Fe^{2+} to Fe.

2 The conversion from K to L involves a ligand exchange reaction.

3 The cation present in solution K reacts with Na_2CO_3 to produce a gas that gives a white precipitate with $Ca(OH)_2$(aq).

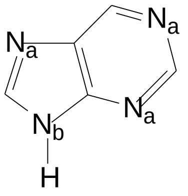
A 3 only

B 1 and 3

C 2 and 3

D none

20 Purine is a heterocyclic aromatic compound. The nitrogen atoms, labelled as N_a and N_b, in purine have different basicity. N_a is basic whereas N_b is non–basic.



Purine

Based on the above information, which bond is **not** present in purine?

A A σ bond formed by $2sp^2$–$2sp^3$ overlap

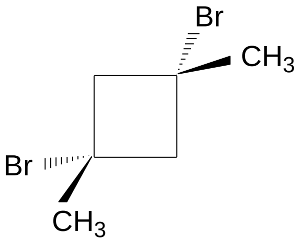
B A σ bond formed by $1s$–$2sp^2$ overlap

C A π bond formed by $2p$–$2p$ overlap

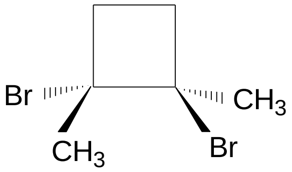
D A σ bond formed by $2sp^2$–$2sp^2$ overlap

21 Which molecules are optically active?

1



2



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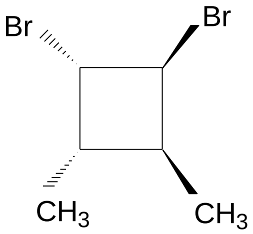


A 1 and 2 only

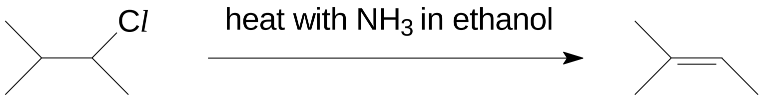
B 1 and 3 only

C 2 and 3 only

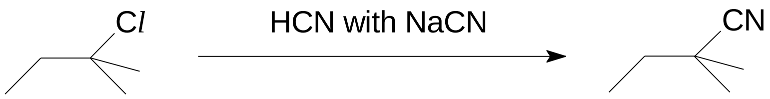
D none

22 Which reactions would give the products stated?

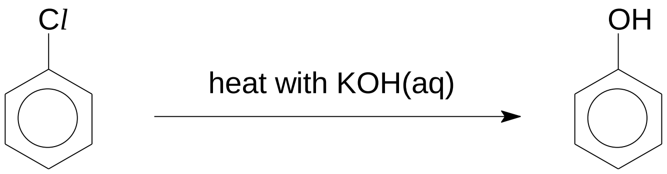
1



2



3



A 1 and 2 only

B 2 only

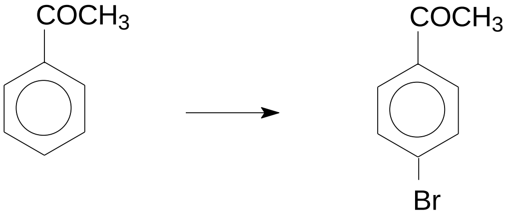
C 2 and 3 only

D none

23 *Use of the Data Booklet is relevant to this question.*

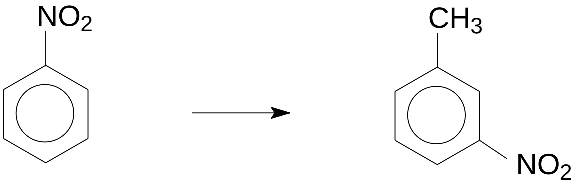
Which transformation can be readily achieved by only one substitution reaction?

A



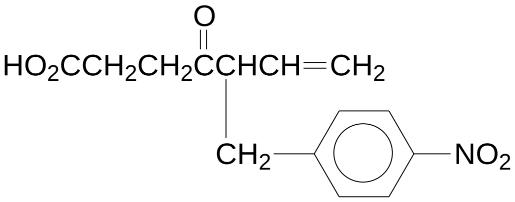
B $(CH_3)_3CCH_2F \longrightarrow (CH_3)_3CCH_2NH_2$

C



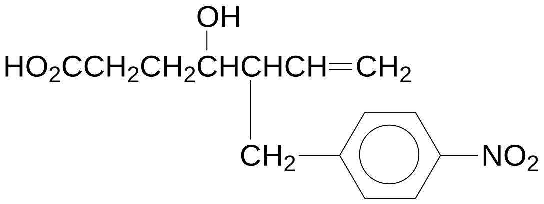
D $CH_3CH{=}CH_2 \longrightarrow CH_3CH{=}CHCl$

24 Compound **Y** has the following structure.

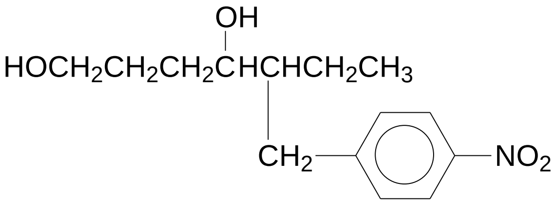


When **Y** is treated with sodium borohydride, what is the final product obtained?

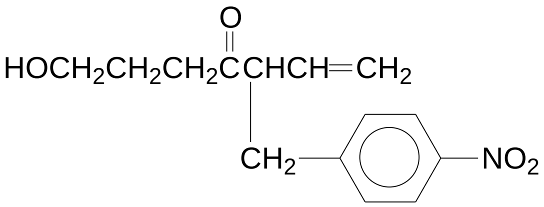
A



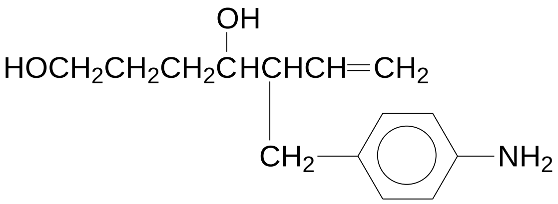
B



C



D



25 Compound **Z** shows the following chemical properties.

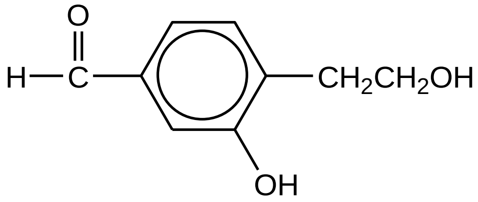
- It does not give any observation with Fehling's solution.
- 1 mole of **Z** reacts with 2 moles of sodium metal.
- When PCl_5(s) is added to **Z**, a sweet smelling product is obtained.

What could **Z** be?

A $HO_2CCH_2CH_2CH_2CO_2H$

B $HO_2CCH_2CH_2CH_2CHO$

C



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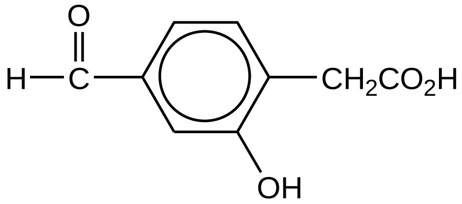


26 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water.

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 sequence shows the correct order of **decreasing** pH of the solutions formed?

A **P**, **R**, **S**, **Q**

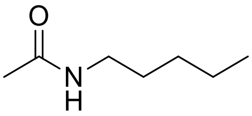
B **P**, **S**, **R**, **Q**

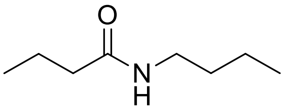
C **Q**, **P**, **S**, **R**

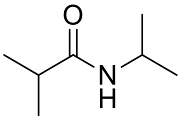
D **Q**, **S**, **R**, **P**

27 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 

2 

3 

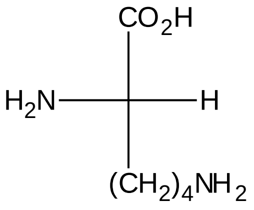
A 1, 2 and 3

B 2 and 3 only

C 1 only

D 3 only

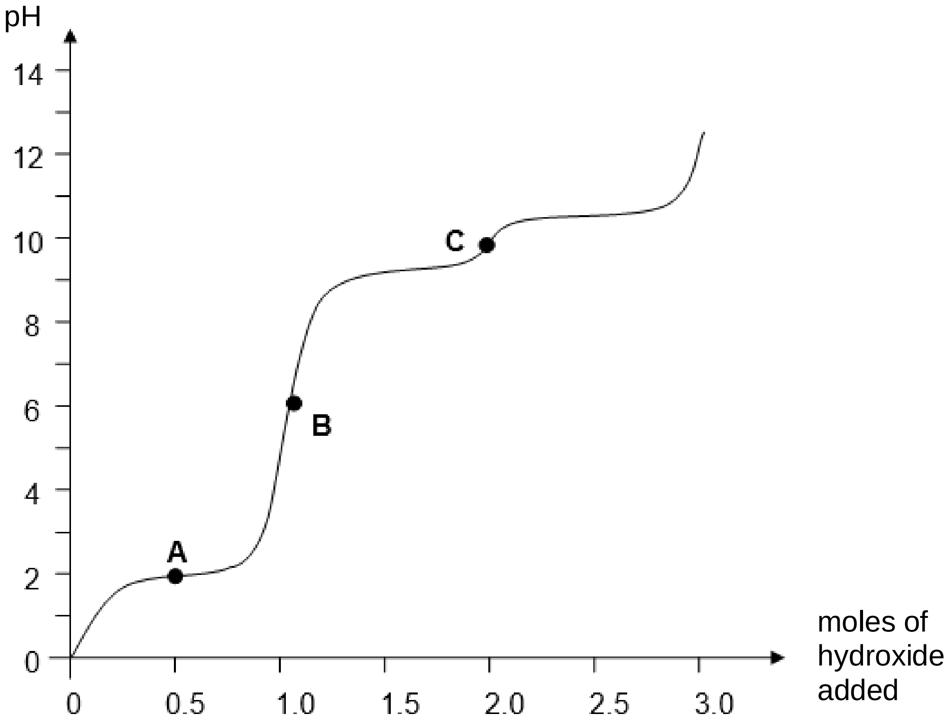
28 Lysine is an essential amino acid found in the body.



lysine

Lysine has pK_a values of 2.2, 9.0 and 10.5.

When one mole of protonated lysine was titrated against hydroxide ions, the following titration curve is obtained.



Which statements are correct 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

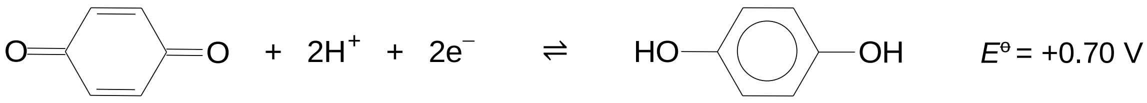
B 2 and 4 only

C 3 and 4 only

D 1, 2 and 4 only

29 *Use of the Data Booklet is relevant to this question.*

Quinone can be formed by oxidising quinol.



quinone quinol

Which statements about this reaction are correct?

1 C bonded to O in quinone has an oxidation state of +2 while C bonded to O in quinol has an oxidation state of +1.

2 $E^\ominus_{cell}$ for the reaction between quinol and acidified $KMnO_4$ is positive.

3 SO_2 gas can be used to reduce quinone to quinol.

A 1, 2 and 3

B 1 and 3 only

C 2 and 3 only

D 1 only

30 Two separate electrolysis were performed as follows.

1. When aqueous sulfuric acid was electrolysed for 5 minutes, 0.01 mol of oxygen was collected at the anode.
2. When molten aluminium oxide was electrolysed for 5 minutes, 0.01 mol of aluminium was collected at the cathode.

If the current used in electrolysis 1 was I, what was the current used in electrolysis 2?

A $\frac{3}{4}I$ **B** I **C** $\frac{4}{3}I$ **D** $2I$

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ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

NAME:___________________________________ (   ) **CLASS:** 19 /____

CHEMISTRY **9729/02**
Higher 2 **4 September 2019**
Paper 2 Structured Questions **2 hours**
Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number and class 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	/ 11
	3	/ 18
	4	/ 13
	5	/ 12
	6	/ 9
	Total	/ 75

This document consists of **26** printed pages and **2** blank pages.

1 **(a)** Use the data from Table 1.1 to state and explain the relative reactivity of Group 2 elements as reducing agents.

Table 1.1

Element	$E^\ominus$ [M^{2+}(aq)/M(s)] / V
Mg	–2.38
Ca	–2.87
Sr	–2.89
Ba	–2.90

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……

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………………………………………………………………………………………………….… [2]

(b) Table 1.2 gives data about some physical properties of calcium and copper.

Table 1.2

	calcium	copper
relative atomic mass	40.1	63.5
atomic radius (metallic) / nm	0.197	0.128
ionic radius (2+) / nm	0.099	0.069
electrical conductivity / 10^6 S cm^{-1}	0.298	0.596
density / g cm^{-3}	1.54	8.92

(i) Explain why the electrical conductivity of copper is higher than that of calcium.

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………...…………………………………………………………………………………..… [2]

(ii) Using relevant data from Table 1.2, explain why the density of copper is significantly greater than that of calcium (no calculations are required).

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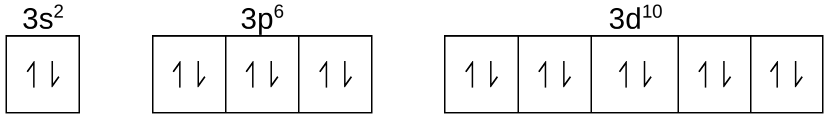
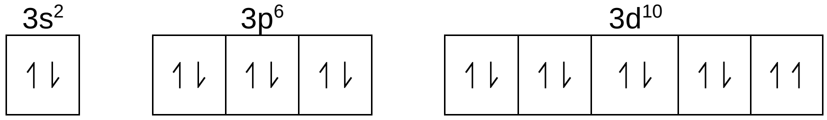
(c) **(i)** Copper is a typical transition element and is used in alloys for aircraft engine parts.

Which of the following "electrons–in–boxes" diagrams best describes the valence ground–state electronic configuration of a Cu$^+$ ion? Explain your answer.

A



B



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…………………………………………………………………………………………………… [1]

(ii) Using the Cartesian axes shown in Fig. 1.1, draw fully–labelled diagrams of any **two** d–orbitals of **different shapes** found in a Cu$^+$ ion.

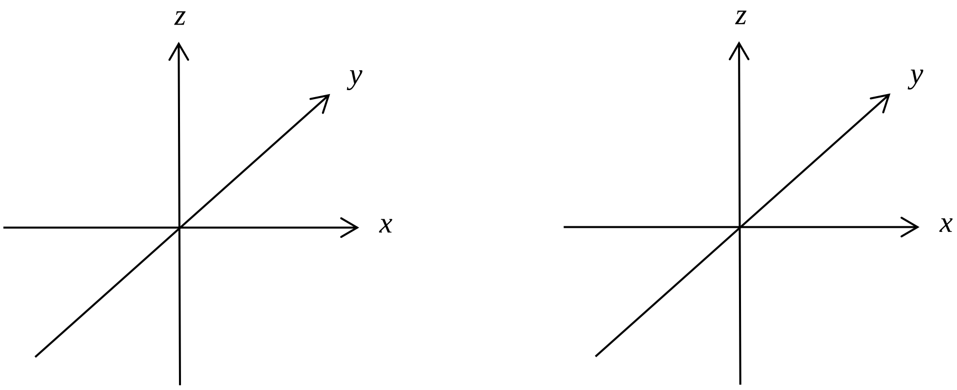

Fig. 1.1

[2]

(d) Silicon is the eighth most common element in the universe by mass. It very rarely occurs as the pure element in the Earth's crust.

Table 1.3 shows the melting points of silica (SiO_2) and silicon.

Table 1.3

	melting point / °C
silica	1710
silicon	1414

Silica and silicon each form a solid with the same type of structure.

(i) State the type of structure present in solid silica and silicon.

…………………………………………………………………………………………….. [1]

(ii) Using relevant data from the *Data Booklet*, suggest why the melting point of silica is higher than that of silicon.

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……………………………………………………………………………………………. [2]

[Total: 12]

Question 2 starts on the next page.

2 **(a)** Alkene **C**, C_7H_{10}, on treatment with hot, concentrated potassium manganate(VII) forms an optically inactive compound **D**, $C_5H_8O_3$, and carbon dioxide gas.

D reacts with both Na_2CO_3 and alkaline aqueous iodine.

(i) Suggest **two** structural features that are present in **D**.

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…………………………………………………………………………………………………… [2]

(ii) Hence, deduce the structures of **C** and **D**.

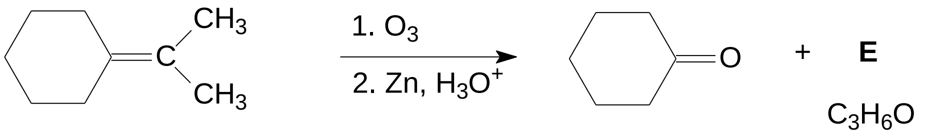
C	**D**

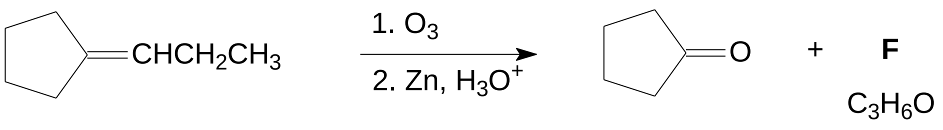
[2]

Ozone, O_3, is an oxidising agent that causes carbon–to–carbon double bond cleavage.

When an alkene is treated with ozone, followed by zinc metal in acetic acid, two carbonyl–containing products are obtained.

The following reactions illustrate two oxidations using ozone as the oxidising agent.





Both **E** and **F** react with 2,4–dinitrophenylhydrazine but only **F** reacts with Fehling's solution. **E** reacts with alkaline aqueous iodine but not **F**.

(iii) Suggest the identities of **E** and **F**.

E	**F**

[2]

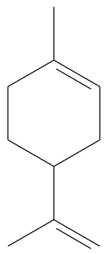
(iv) Use the above information and your answers to **(a)(iii)** to suggest the structure for compound **G** in the following reaction.

$$\mathbf{G} \xrightarrow[\text{2. Zn, } H_3O^+]{\text{1. } O_3} CH_3CHO + (CH_3)_2CHCHO$$

G

[1]

(b) **(i)** Limonene occurs in oil of lemons and is used to flavour some citrus drinks.



limonene

Draw the structural formula of the product, and describe what you might observe, when limonene reacts with bromine in an inert solvent, until in excess.

observation ……………………………………………………………………………………

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Fig. 2.1 shows a reaction scheme involving an isomer of limonene, **H**.

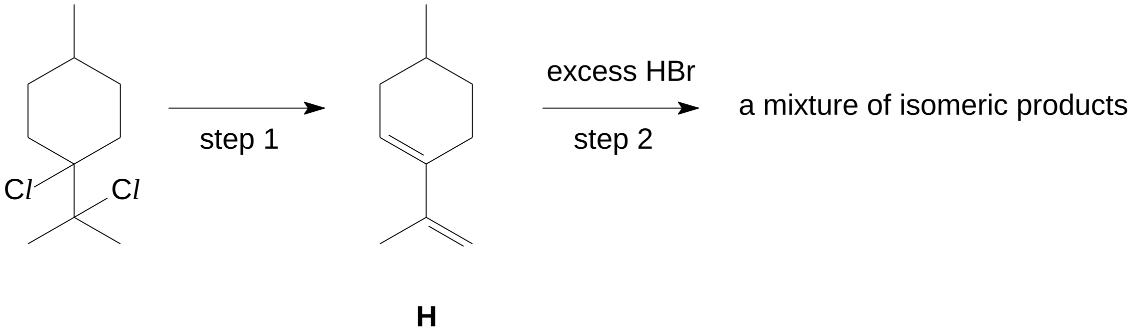

Fig. 2.1

(ii) Suggest reagents and conditions for step 1.

………………………………………………………………………………………………. [1]

(iii) Draw the structure of the major product for step 2.

[1]

[Total: 11]

3 Transition metals are building blocks for life and they make up the middle block of the Periodic Table.

(a) Catalase is an important enzyme that reduces the damaging effects of hydrogen peroxide in the biological system. It contains four iron–containing heme groups that allow the enzyme to react with the hydrogen peroxide.

It catalyses the decomposition of hydrogen peroxide into water and molecular oxygen.

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2$$

(i) With the aid of a sketch of the Boltzmann distribution, explain why the addition of catalase speeds up the decomposition of hydrogen peroxide.

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…………………………………………………………………………………………………… [3]

An investigation to study the rate of the catalysed decomposition of H_2O_2 can be conducted as follows:

1 cm^3 of catalase, extracted from a liver sample, was added to a 50 cm^3 of 2 mol dm^{-3} H_2O_2 solution connected to a sealed glass pressure tube which measures the volume of O_2 collected. The time taken for 20 cm^3 of O_2 to produce was then measured.

(ii) Outline how you would determine the effect of changing the concentration of H_2O_2 on the rate of the catalysed decomposition of H_2O_2.

You are provided with the same solution used in the experiment described above.

State clearly the measurements you would take.

No details regarding use of specific glassware are required.

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…………………………………………………………………………………………………… [3]

(iii) Sketch a graph to show how, for a fixed concentration of catalase, the rate of decomposition varies with the concentration of H_2O_2 and explain the shape of the graph.

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…………………………………………………………………………………………………… [2]

(b) Transition metal sulfides are generally insoluble in water.

Metal ions can be precipitated as metal sulfides by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \rightarrow MS(s)$$

Solution **J** containing 0.100 mol dm^{-3} of Fe^{2+} and 0.100 mol dm^{-3} of Mn^{2+} can be separated easily by selective precipitation of the metal sulfides.

The K_{sp} values of two metal sulfides are shown in Table 3.1.

Table 3.1

	K_{sp} / $mol^2\ dm^{-6}$
FeS	3.7×10^{-19}
MnS	3.7×10^{-13}

(i) State which metal ion, Fe^{2+} or Mn^{2+}, precipitates first when solid sodium sulfide is slowly added to 100 cm^3 of solution **J**.

.... [1]

(ii) Hence, calculate the concentration, in mol dm^{-3}, of sulfide ions when first trace of the precipitate appears.

[1]

(iii) Determine the concentration, in mol dm^{-3}, of the metal ion you have stated in **(b)(i)** remaining in the solution when the other metal ion just starts to precipitate.

[1]

(iv) An effective separation means that less than 1% of the metal ion should remain in the solution when the other metal ion just starts to precipitate. Using your answer to **(b)(iii)**, deduce if the separation is effective.

…………………………………………………………………………………………………..

……………………………………………………………………………………………...... [1]

One advantage of using sulfide ion as a precipitating reagent is that its concentration can be controlled by regulating the pH of the solution.

Hydrogen sulfide behaves as a weak dibasic acid that dissociates in two steps:

Equilibrium (1) $H_2S \rightleftharpoons H^+ + HS^-$ $K_a = 9.1 \times 10^{-8}$

Equilibrium (2) $HS^- \rightleftharpoons H^+ + S^{2-}$ $K_a = 1.0 \times 10^{-15}$

(v) Using the above equilibria, explain how varying the pH of a mixture containing solution **J** and sulfide ions can allow selective precipitation to take place.

You are **not** expected to perform any calculations.

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…………………………………………………………………………………………………..

……………………………………………………………………………………………… [2]

(c) The most important ore of chromium is the mineral ferrous chromite, $FeO.Cr_2O_3$.

Fig. 3.1 shows a reaction scheme illustrating many of the characteristic properties of transition metal compounds.

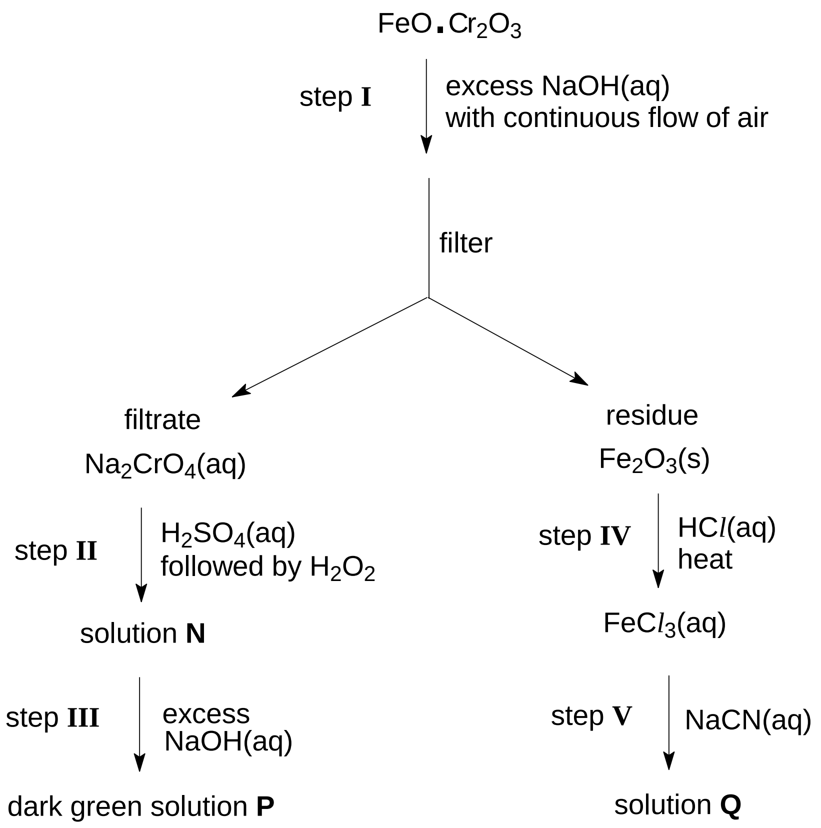

Fig. 3.1

(i) Construct a balanced equation for the reaction involving Cr_2O_3 in step **I**, by using changes in oxidation numbers, or otherwise. In this reaction, H_2O is a by–product.

……………………………………………………………………………………………..... [1]

(ii) State the series of colour changes that occurs in step **II**.

…………………………………………………………………………………………… [1]

(iii) State the type of reaction that occurs in step **III** and give the formula of the complex ion in solution **P**.

type of reaction ……………………………………………………………………………….....

formula of complex ion ………………………………………………………………….. [1]

The oxidation number of iron in the iron–containing complex ion in solution **Q** and in $FeCl_3$(aq) is the same.

(iv) Suggest the formula of the compound in solution **Q**.

………………………………………………………………………………………………..… [1]

[Total: 18]

4 Ethylamine, $CH_3CH_2NH_2$, and phenylamine, $C_6H_5NH_2$, are both weak bases, with pK_b values of 3.35 and 4.63 respectively.

(a) Explain why the pK_b value of ethylamine is lower than that of phenylamine.

……

……

……

…… [2]

(b) 20.0 cm^3 of an aqueous solution of ethylamine was titrated against 0.20 mol dm^{-3} hydrochloric acid, HC*l*. It was found that the pH at the equivalence point was 5.91.

(i) Suggest an appropriate indicator for the titration, giving a reason for your choice.

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…………………………………………………………………………………………………… [1]

(ii) Calculate the concentration of $CH_3CH_2NH_3^+$, in mol dm^{-3}, at the equivalence point.

[1]

(iii) Hence, calculate the volume of hydrochloric acid needed to neutralise the ethylamine.

[1]

(iv) Prove that the initial concentration of ethylamine is 0.102 mol dm^{-3}.

[1]

(v) Hence, calculate the initial pH of ethylamine.

[1]

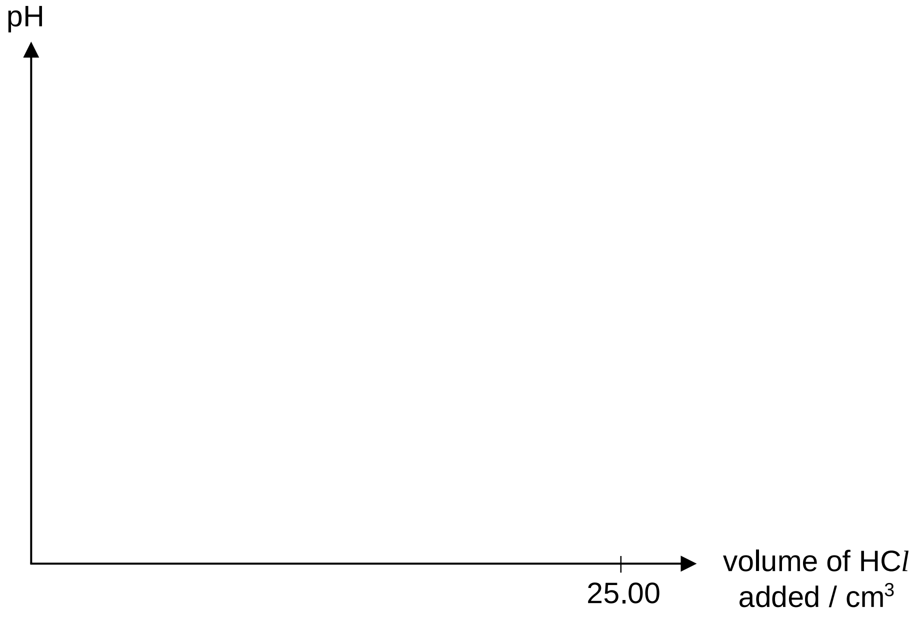
(vi) A total of 25.00 cm^3 HC*l* was added in this titration. Calculate the final pH of the resulting solution.

[1]

(vii) Using the information given in the question and your answers to **(b)(iii)**, **(b)(v)** and **(b)(vi)**, sketch the pH changes that occur during the titration when a total of 25.00 cm^3 of HCl was added to 20.0 cm^3 of an aqueous solution of ethylamine.

Label the following points on your sketch:

- pH and volume at maximum buffer capacity
- pH and volume at equivalence point
- final pH



[2]

(c) A buffer solution was prepared by mixing 200 cm^3 of 0.15 mol dm^{-3} of phenylamine and 100 cm^3 of 0.20 mol dm^{-3} of HCl.

(i) Calculate the pH of this buffer solution.

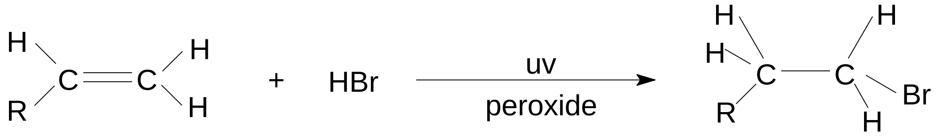
[2]

(ii) Write an equation to show how this solution can act as a buffer on the addition of an alkali.

…………………………………………………………………………………………………..... [1]

[Total: 13]

5 Radical initiators are substances that can produce radicals under mild conditions and promote radical reactions. These substances generally possess weak bonds. An example of a radical reaction involving peroxide as the initiator is shown below:



(a) Explain what is meant by the term *radical* and explain, with the aid of a diagram, how the bond in the peroxide initiator, R–O–O–R, would break to produce radicals.

....

....

.... [2]

(b) The mechanism continues with the following steps.

Step 1: The radical produced from the peroxide initiator reacts with a HBr molecule to generate a •Br radical and an alcohol molecule.

Step 2: The •Br radical formed approaches an alkene molecule, $RCH=CH_2$, to form a stable alkyl radical.

Step 3: The alkyl radical reacts with another HBr molecule to form the organic product and regenerates the •Br radical.

Draw the displayed formula of the stable alkyl radical formed in Step 2 and the final organic product formed when 2–methylbut–2–ene undergoes this radical reaction with HBr.

stable alkyl radical	final organic product

[2]

(c) Benzoic acid is often added to soft drinks as a preservative in the form of its salt, e.g. sodium benzoate. However, it is reported that in the presence of ascorbic acid, benzoic acid can undergo decarboxylation to form benzene, which is a known carcinogen.

The mechanism of this reaction is thought to involve four steps:

Step I: The hydroxyl radical, •OH, is produced from the catalysed reduction of oxygen by ascorbic acid.

Step II: The hydroxyl radical abstracts a proton from benzoic acid to form an intermediate.

Step III: This intermediate then forms a phenyl radical and carbon dioxide gas.

Step IV: The phenyl radical abstracts a proton from water to produce benzene and regenerates the hydroxyl radical.

Complete Fig. 5.1 to suggest the mechanism for Step III and Step IV. Show the structural formulae of the intermediates, the movement of unpaired electron by using curly arrow (⌒) and indicate any unpaired electron with a dot (●).

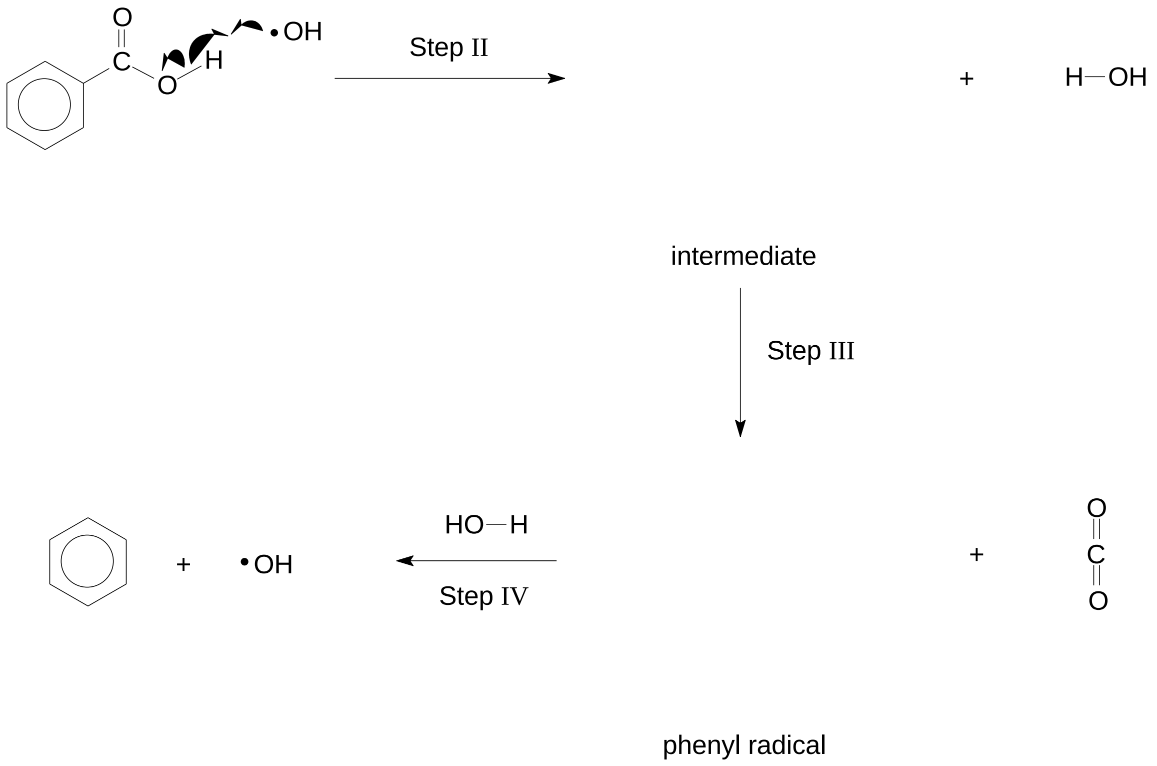
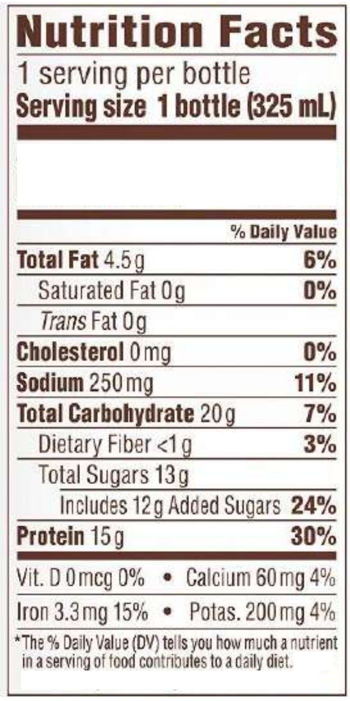


Fig. 5.1

[3]

(d) Fig. 5.2 shows the food label of a bottle of coffee.



Nutrition Facts

1 serving per bottle

Serving size 1 bottle (325 mL)

	% Daily Value
Total Fat 4.5 g	**6%**
Saturated Fat 0 g	**0%**
Trans Fat 0 g	
Cholesterol 0 mg	**0%**
Sodium 250 mg	**11%**
Total Carbohydrate 20 g	**7%**
Dietary Fiber <1 g	**3%**
Total Sugars 13 g	
Includes 12 g Added Sugars	**24%**
Protein 15 g	**30%**

Vit. D 0 mcg 0% • Calcium 60 mg 4%

Iron 3.3 mg 15% • Potas. 200 mg 4%

*The % Daily Value (DV) tells you how much a nutrient in a serving of food contributes to a daily diet.

Fig. 5.2

Table 5.1 shows the fuel values of some substances found in the bottle of coffee. The fuel value is the amount of energy generated when one gram of a substance undergoes complete combustion.

Table 5.1

substance	**fuel value / kJ g^{-1}**
carbohydrate	17
protein	17
fat	38

(i) Energy is provided by the carbohydrates, proteins and fats in the food and drinks consumed.

If a student uses on average 7 kJ of energy per minute while studying, how many minutes of this activity can be sustained by the energy obtained from one serving of bottled coffee?

[2]

Fats are metabolised into carbon dioxide and water when subjected to combustion in a bomb calorimeter. The reaction of a typical unsaturated fat (triglyceride), $C_{55}H_{98}O_6$, found in the bottle of coffee is as follows:

$$C_{55}H_{98}O_6 + \frac{153}{2}O_2 \rightarrow 55CO_2 + 49H_2O \qquad \Delta H = -x \text{ kJ mol}^{-1}$$

(ii) Using relevant data from Table 5.1, determine the value of x.

[1]

(e) Compounds **R** and **S** are structural isomers with the molecular formula of $C_6H_{12}O$.

Table 5.2 shows results of the chemical tests carried out on **R** and **S**.

Table 5.2

test	reagent	observation	
		R	**S**
1	Tollens' reagent	grey solid formed	grey solid not formed
2	aqueous bromine	orange solution remained	orange solution remained

When **R** and **S** were separately subjected to chlorine in the presence of sunlight, both gave only two monochlorinated products (not including stereoisomers).

Suggest a possible structure for **R** and **S**.

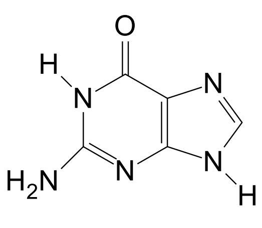
R	**S**

[2]

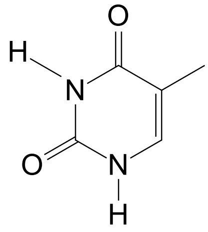
[Total: 12]

6 Nitrogenous bases such as guanine and thymine contribute to the structure of deoxyribonucleic acid (DNA). If the compositions of these bases are altered significantly, it may lead to a change in the DNA structure, which could cause cancer.

The structures of guanine and thymine are given below:



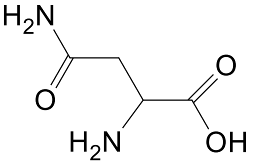
guanine



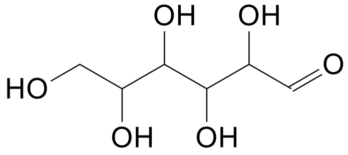
thymine

Studies have suggested that consumption of overcooked carbohydrates such as french fries may lead to cancer. This is partly contributed by the Maillard reaction that takes place during cooking, which typically occurs on the surface of the cooked food. This reaction occurs at temperatures above 140 °C.

This question focuses on the Maillard reaction between asparagine and glucose, both of which are found in potatoes. Fig 6.1 shows the structures of asparagine and glucose.



asparagine

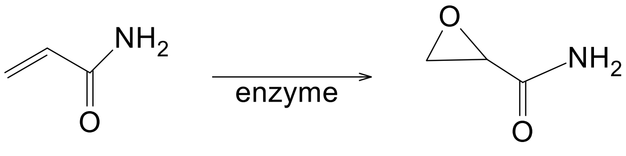


glucose

Fig 6.1

Nucleophilic attack by the amine group in asparagine on the electrophilic carbon of the aldehyde group in glucose results in an imine, characterised by a carbon–nitrogen double bond. Water is produced as a by–product.

If food containing this imine is consumed, gastric acid breaks down the imine to produce acrylamide, a carcinogen. Acrylamide is then metabolised by an enzyme in the body, producing glycidamide.



acrylamide glycidamide

Glycidamide has a highly reactive epoxide group (a three–membered ring of two carbon atoms and an oxygen atom). The lone pair of electrons on a nitrogen atom in guanine (one of the nitrogenous bases) attacks one of the electrophilic carbon atoms of the epoxide group in glycidamide. This eventually changes the DNA structure and causes cancer.

(a) Table 6.1 shows the acrylamide content in some potato products.

Table 6.1

potato product	preparation method	amount of acrylamide (ug / kg)
boiled potato	cut into half, lengthwise	69
baked potato	cut into half, lengthwise	1270
deep fried potato (french fries)	cut into strips, lengthwise	4080

(i) Explain why boiled potato has the lowest amount of acrylamide.

…………………………………………………………………………………………………....

…………………………………………………………………………………………… [1]

(ii) By considering the preparation method, suggest why deep fried potato has a higher amount of acrylamide compared to baked potato.

…………………………………………………………………………………………………....

…………………………………………………………………………………………… [1]

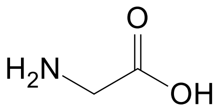
(b) Some recommendations have been proposed to reduce the production of acrylamide. Explain why the following methods are effective.

(i) Soak the sliced potatoes in a weak acid, such as vinegar.

……………………………………………………………………………………………………

…………………………………………………………………………………………… [1]

(ii) Soak the sliced potatoes in a solution of amino acid, such as glycine.



glycine

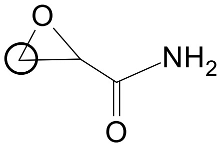
……………………………………………………………………………………………………

…………………………………………………………………………………………… [1]

(c) Using the structures of asparagine and glucose given in Fig 6.1, draw the structure of the specific imine produced.

[1]

(d) **(i)** With reference to the structure of glycidamide below, explain why the circled carbon atom in the epoxide group is more susceptible to nucleophilic attack by guanine.



glycidamide

....

.... [1]

(ii) State why the reaction between guanine and glycidamide affects the DNA structure.

....

.... [1]

(iii) Guanine reacts with glycidamide as described on page 24. Suggest why glycidamide does **not** undergo the same nucleophilic attack by thymine.

....

.... [1]

(iv) Phenylethene is a suspected carcinogen like acrylamide. Suggest an explanation for this.

....

.... [1]

[Total: 9]

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ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/03**

Higher 2 **18 September 2019**

Paper 3 Free Response **2 hours**

Candidates answer on separate Answer Booklet.

Additional Materials: Answer Booklet
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 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.

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.

This document consists of **15** printed pages and **1** blank page.

Section A

Answer **all** the questions from this section.

1 **(a)** Iron(III) cation complexes with a thiocyanate anion (SCN^-) to form the iron(III) thiocyanate complex, $[Fe(SCN)]^{2+}$ at 298 K, according to the following equation.

$$\underset{\text{yellow}}{Fe^{3+}(aq)} + \underset{\text{colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{blood red}}{[Fe(SCN)]^{2+}(aq)} \qquad \Delta H < 0$$

(i) Write an expression for K_c for this reaction, stating its units. [2]

(ii) The K_c value of this reaction is 4.99 x 10^2. Calculate the percentage of $[Fe(SCN)]^{2+}$ in a Fe^{3+}–$[Fe(SCN)]^{2+}$ mixture when $[SCN^-] = 5.00 \times 10^{-3}$ mol dm^{-3}. [2]

(iii) State and explain the difference in observations when the reaction is carried out at 500 K. [2]

(b) Describe the variations in melting points of the elements sodium to chlorine and explain these variations in terms of their structures and bonding. [5]

(c) Compounds **B**, **C**, **D** and **E** are oxides or chlorides of Period 3 elements.

B and **C** have high melting points while **D** and **E** have low melting points.

B is insoluble in water but soluble in hot concentrated sodium hydroxide.

When water was added separately to 0.100 mol each of **C**, **D** and **E**, a neutral solution was obtained for **C** while an acidic solution was obtained for **D** and **E**. The resulting solution of **D** required 0.500 mol of silver nitrate for complete precipitation.

1 mol of **E** requires 2 mol of aqueous sodium hydroxide for complete neutralisation.

Identify compounds **B** to **E**, and write equations for the reactions described above. [6]

[Total: 17]

Question 2 starts on the next page.

2 **(a)** Helium is used to fill party balloons.

A 60.0 dm^3 industrial tank of helium gas at 27 °C and 125 atm was used to fill up some balloons. After some balloons were filled, the pressure in the tank was reduced to 50 atm.

(i) How many moles of helium was used to fill the balloons? [2]

(ii) Assuming each filled balloon is a sphere with a radius, r, of 0.15 m and has an internal pressure of 1.2 atm, what is the maximum number of balloons that can be filled with the **remaining** gas in the tank at the same temperature?

(volume of sphere $= \frac{4\pi r^3}{3}$)

[2]

(iii) State and explain if helium gas behaves more ideally in the tank, or when present in balloons. [2]

(b) **(i)** Using the thermochemical data shown in Table 2.1, draw a fully labelled energy cycle to calculate the standard enthalpy change of combustion of liquid propan–2–ol.

Table 2.1

Standard enthalpy change of formation of liquid propan–2–ol	-318 kJ mol^{-1}
Standard enthalpy change of combustion of carbon	-394 kJ mol^{-1}
Standard enthalpy change of formation of water	-286 kJ mol^{-1}
Standard enthalpy change of vapourisation of water	$+41$ kJ mol^{-1}

[2]

(ii) By using your answer to **(b)(i)**, and relevant data from the *Data Booklet* and Table 2.1, calculate the standard enthalpy change of vapourisation of propan–2–ol. [2]

(iii) Hence, explain why combustion of liquid propan–2–ol takes place at all temperatures. [2]

(c) **(i)** State and explain how the acidities of 2–methylpropan–2–ol, 2–chloro–2–methylpropanoic acid and 2,2–dimethylpropanoic acid might compare with each other.

$(CH_3)_3COH$
2–methylpropan–2–ol

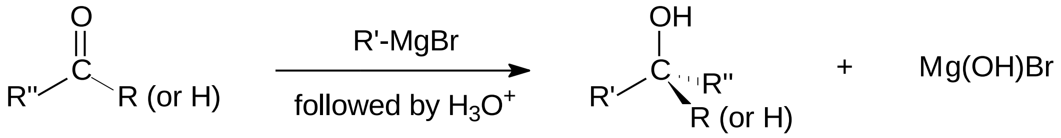
$(CH_3)_3CCO_2H$
2,2–dimethylpropanoic acid

$(CH_3)_2CClCO_2H$
2–chloro–2–methylpropanoic acid

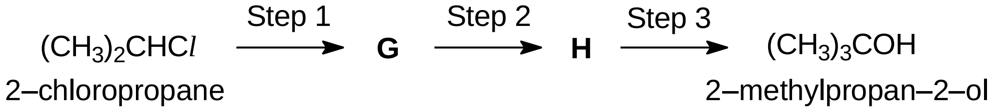
[3]

(ii) Outline how 2,2–dimethylpropanoic acid may be produced from 2–chloro–2–methylpropane, $(CH_3)_3CCl$. Include the structure of the intermediate compound in your answer. [3]

(iii) Grignard reagents, with different alkyl or aryl groups (R'–MgBr), react with carbonyl compounds to yield alcohols.



Use the above information to suggest a synthesis of 2–methylpropan–2–ol from 2–chloropropane according to the scheme in Fig. 2.1. Include reagents and conditions for all steps, and the structures of the intermediate organic compounds, **G** and **H**, in your answer.



$$\underset{\text{2–chloropropane}}{(CH_3)_2CHCl} \xrightarrow{\text{Step 1}} \mathbf{G} \xrightarrow{\text{Step 2}} \mathbf{H} \xrightarrow{\text{Step 3}} \underset{\text{2–methylpropan–2–ol}}{(CH_3)_3COH}$$

Fig. 2.1

[5]

[Total: 23]

3 **(a)** Nitrate, NO_3^-, and phosphate, PO_4^{3-}, are oxoanions of nitrogen and phosphorous respectively.

(i) Draw dot–and–cross diagrams to show the bonding in NO_3^- and PO_4^{3-}. Hence, suggest the shape of **each** of these ions. [3]

(ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

Suggest the hybridisation state of nitrogen in NO_3^-. [1]

(iii) Table 3.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table 3.1

Bond	N–O	N=O
Bond length (pm)	136	115

The experimental bond length of each nitrogen–oxygen bond in the nitrate ion, NO_3^-, is 128 pm.

By reference to your answers to **(a)(i)** and **(a)(ii)**, explain this observed bond length in NO_3^-. [1]

(b) Fig. 3.1 shows the synthesis of compound **K** from phenylamine.

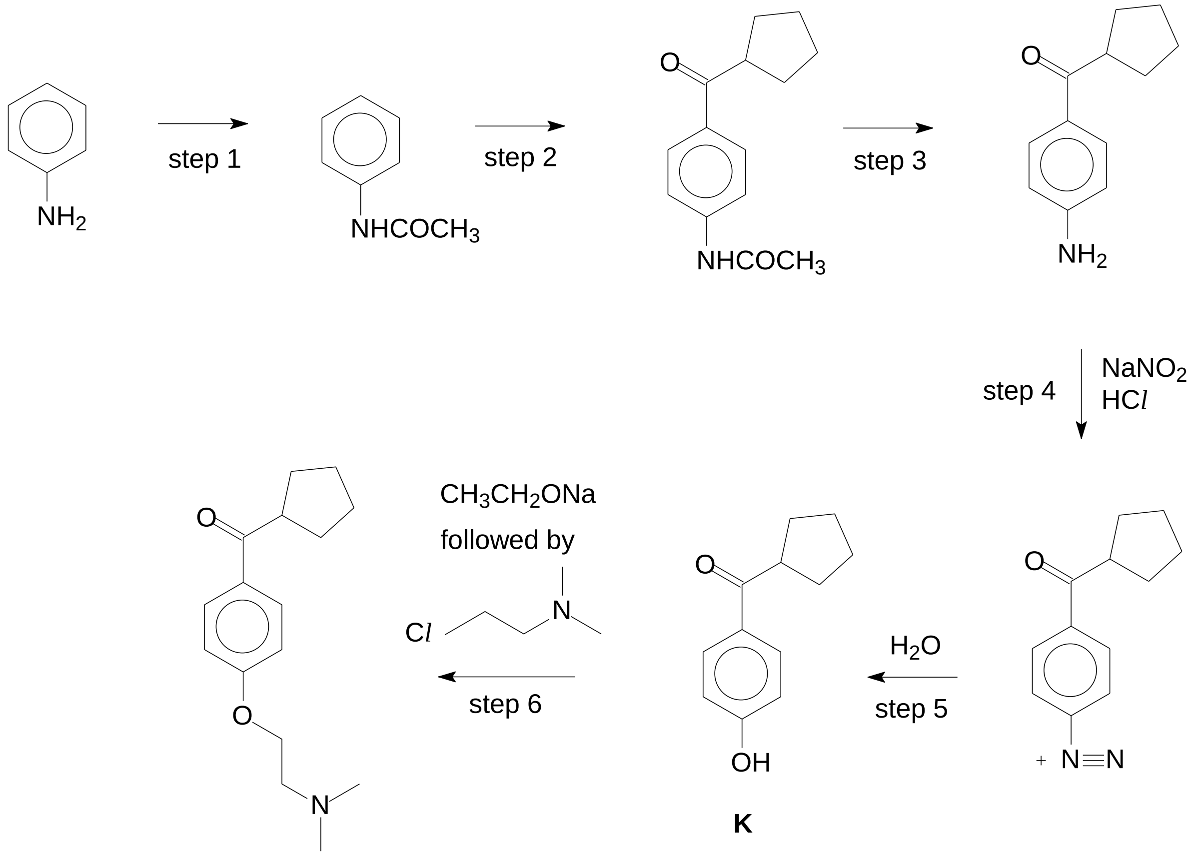


Fig. 3.1

(i) Suggest the reagents and conditions in steps 1 and 2. [2]

(ii) Explain why step 1 needs to be carried out **before** step 2. [1]

(iii) Explain why step 6 would **not** occur in the **absence** of sodium ethoxide, CH_3CH_2ONa. [1]

The reaction in step 6 is carried out in a suitable solvent and is found to be bimolecular.

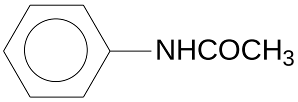
(iv) Describe the mechanism for this reaction. In your answer, you should show all charges, lone pairs and the movement of electrons using curly arrows.

You may use R to represent any part of the molecule that does not take part in the reaction. [3]

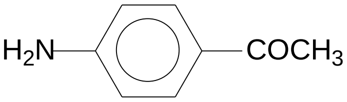
(v) Predict the effect on the rate of the reaction in step 6 if the volume of solvent used is doubled. [1]

(vi) Explain whether compound **K** or phenol undergoes electrophilic substitution more readily. [2]

(c) Both acetanilide and 4–aminoacetophenone are solids at room temperature and pressure.



acetanilide



4-aminoacetophenone

(i) Suggest and explain, with the aid of equations, the solubility of **each** of the compounds in HC*l*(aq). [3]

(ii) Using your answer to **(c)(i)**, outline how these two compounds could be separated from each other in a mixture and recovered in their original solid forms using chemicals normally found in the laboratory. [2]

[Total: 20]

Question 4 starts on the next page.

Section B

Answer **one** question from this section.

4 **(a)** Alkenes have many diverse industrial applications. They are used as starting materials for many chemicals.

One of the reactions of alkenes involves the addition of hydrogen to form alkanes. This process of hydrogenation of alkenes at room temperature requires the use of a catalyst. The Wilkinson's catalyst precursor, $RhCl(PPh)_3$ (where Ph represents a phenyl group), is one of them.

When the Wilkinson's catalyst precursor was added to propene dissolved in benzene with hydrogen gas being passed through the solution, the following dissociation took place:

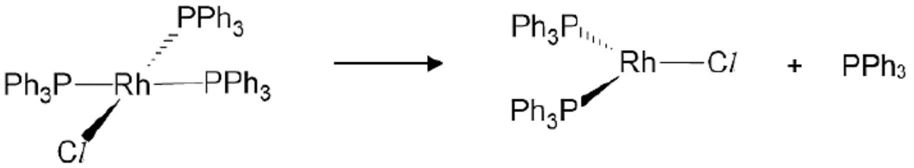


Fig. 4.1 shows the proposed mechanism for the hydrogenation of propene.

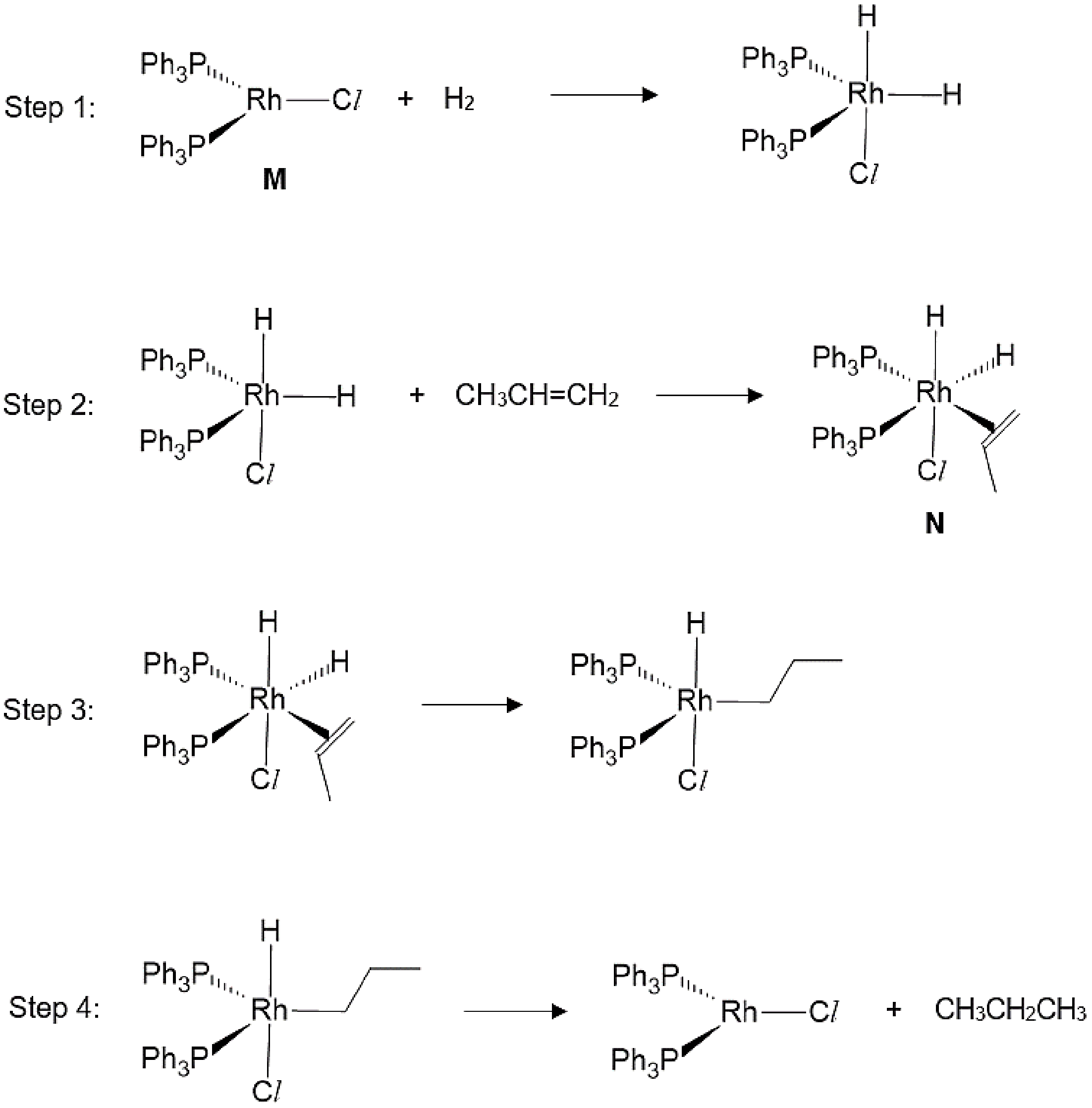


Fig. 4.1

(i) Triphenylphosphine, PPh_3, is a ligand in the Wilkinson's catalyst precursor, $RhCl(PPh_3)_3$.

Explain what is meant by the term *ligand*. [1]

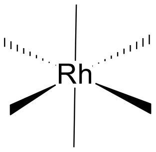
(ii) Determine the oxidation state of rhodium in $RhCl(PPh_3)_3$. [1]

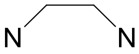
(iii) The species in the equations shown in Fig. 4.1 have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason in each case, the roles of the species **M** and **N**. [2]

(iv) Rhodium can also form octahedral complexes with bidentate ligands like ethane–1,2–diamine, *en*.

Copy and complete the diagram below to suggest the structure for this complex.



(You may use  to represent *en.*) [1]

(b) Scientists have recently made vanadium into a useful catalyst for hydrogenation.

Vanadium was named after Vanadis, the Scandinavian goddess of beauty, because of the wide range of colours it exhibits in its complexes.

(i) Explain why a solution of $[V(H_2O)_6]^{2+}$ is violet whereas a solution of $[V(H_2O)_6]^{3+}$ is green. [1]

(ii) Nitric acid is an oxidising agent.

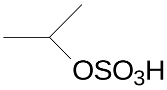
$$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO + 2H_2O \qquad E^\ominus = +0.96\text{ V}$$

Predict the products of, and write an equation for the reaction that occurs when nitric acid is added to a solution containing V^{2+}(aq) ions. [2]

(c) Alkenes can be hydrated to form alcohols using various reagents. One such reagent is concentrated sulfuric acid.

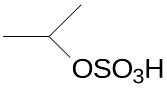
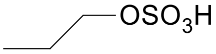
Alkenes react with concentrated sulfuric acid in the cold to produce alkyl hydrogensulfates. Addition of water with heating then produces the alcohol product.

(i) Suggest a mechanism for the reaction of propene with concentrated sulfuric acid to produce the alkyl hydrogensulfate as shown.



isopropyl hydrogensulfate

Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows. [3]

(ii) Explain why  is preferentially produced instead of . [1]

(d) Chromium(VI) is an important high oxidation state chromium and it occurs in two well–known anions, chromate(VI), CrO_4^{2-}, and dichromate(VI), $Cr_2O_7^{2-}$.

Acidified potassium dichromate(VI) is a common oxidising agent that can be used to oxidise sulfur dioxide.

(i) Construct a balanced equation for the reaction between acidified potassium dichromate(VI) and sulfur dioxide. [1]

(ii) Calculate the $E^{\ominus}_{cell}$ and hence, the standard Gibbs free energy change for this reaction. [2]

(iii) Both potassium dichromate(VI) and potassium manganate(VII) are useful oxidising agents in organic chemistry.

The scheme shown in Fig. 4.2 shows the different products formed when compound **P** is oxidised by potassium dichromate(VI) and potassium manganate(VII).

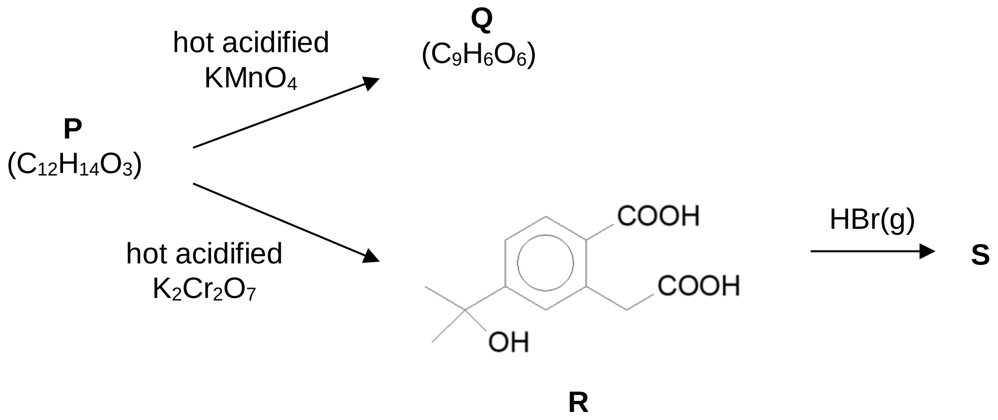
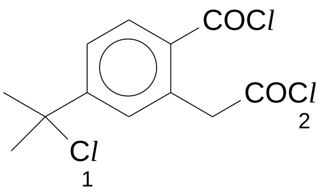


Fig. 4.2

Compound **P** does **not** react with an acid or a base at room temperature.

Suggest the structures of compounds **P**, **Q** and **S**. [3]

(iv) Compound **R** can also be converted to compound **T** which contains an acyl chloride and an alkyl chloride functional groups.



T

Explain the different reactivities of the two chlorine atoms, C*l* 1 and C*l* 2, in **T**. [2]

[Total: 20]

5 Metals like cobalt and nickel have been widely used since ancient times.

(a) In the presence of ligands, the d–orbitals in a transition metal ion are split into two levels.

Fig. 5.1 shows how the d–orbitals are split in an octahedral environment.

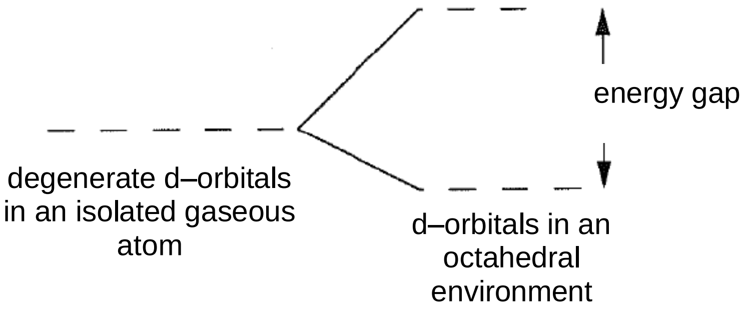


Fig. 5.1

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 in first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Use diagrams like the one above to show the electronic distribution of the cobalt(II) ion in a high spin state, and in a low spin state. Label your diagrams. [2]

(ii) Transition elements with unpaired 3d electrons are paramagnetic. In the presence of a magnetic field, these unpaired electrons align themselves in such a way that they are attracted to the field. The strength of paramagnetism shown in transition metal complexes depends on the total number of unpaired 3d electrons.

Using your answer from **(a)(i)**, explain which spin state of the cobalt(II) ion is relatively more paramagnetic. [1]

When air is bubbled through an aqueous solution containing $CoCl_2$, NH_4Cl and NH_3, and the resulting solution evaporated, crystals of a salt **Ω** can be isolated. **Ω**, which contains an octahedral cation, has the following composition by mass:

Co, 25.2%; N, 24.1%; H, 5.1%; C*l*, 45.6%

(iii) Calculate the empirical formula of **Ω**. [1]

(iv) On adding an excess of $AgNO_3$(aq) to an aqueous solution containing 0.01 mol of **Ω**, 1.43 g of AgC*l*(s) is precipitated.

The cation in **Ω** can exist as two isomers. One of the isomers of the cation in **Ω** has **no** net dipole moment. Draw the structure of this cation. Show clearly the arrangement of the ligands and the oxidation number of the central metal ion in your diagram. [2]

(b) The nickel–cadmium (Ni–Cd) battery is a common rechargeable battery used in portable power tools and emergency lightings. It is made up of a cadmium electrode, Cd, and nickel oxyhydroxide electrode, NiO(OH), immersed in sodium hydroxide.

During discharge, cadmium hydroxide, $Cd(OH)_2$, is deposited at the cadmium electrode.

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

Nickel(II) hydroxide, $Ni(OH)_2$, is formed at the nickel oxyhydroxide electrode.

(i) Construct a half–equation for the reaction that occurs at the cathode during discharge and hence, write the equation for the overall reaction during discharge. [2]

(ii) When a Ni–Cd battery is recharged, $Cd(OH)_2$ is converted back to Cd. Given that the charging process is 86% efficient, how many hours does it take to restore 5.5 g of Cd metal using a current of 2.0 A? [3]

(c) Reduction reactions involving organic compounds are commonly carried out using reducing agents like hydrogen gas with nickel metal catalyst and lithium aluminium hydride, $LiAlH_4$.

Compound **F** is reacted with both as shown in Fig. 5.2.

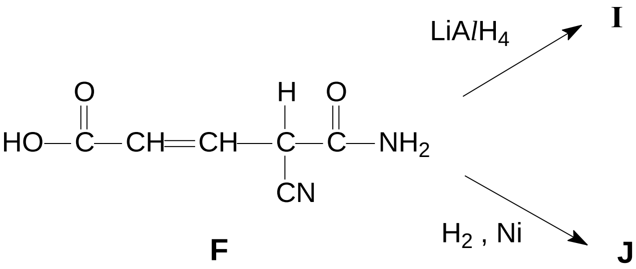


Fig. 5.2

Draw the structures of products **I** and **J**. [2]

(d) Compound **W**, $C_9H_9NO_4$, rotates plane–polarised light. **W** reacts with tin and concentrated hydrochloric acid, followed by careful neutralisation to give compound **X**, $C_9H_{11}NO_2$.

X liberates carbon dioxide with sodium hydrogencarbonate and decolourises aqueous bromine to give **Y**, $C_9H_9NO_2Br_2$. When **X** reacts with PCl_5, compound **Z**, C_9H_9NO, is formed.

Deduce the structures of **W**, **X**, **Y** and **Z**, stating clearly your reasoning. [7]

[Total: 20]

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ANDERSON SERANGOON JUNIOR COLLEGE

2019 JC 2 PRELIMINARY EXAMINATIONS

NAME:_________________________ (   ) **CLASS:** 19 /____

CHEMISTRY **9729/04**

Paper 4 Practical **27 August 2019**

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 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 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 **To determine the order of reaction with respect to the concentration of iodine in the iodination of propanone reaction**

FA 1 is 1.00 mol dm^{-3} propanone, CH_3COCH_3
FA 2 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4
FA 3 is an aqueous solution of iodine, I_2
FA 4 is 0.0100 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$
FA 5 is 0.50 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$

You are also provided with a starch indicator.

The iodination of propanone, to form iodopropanone, proceeds as shown in the equation below.

Reaction 1: $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$

This reaction is first order with respect to both CH_3COCH_3 and H^+ ions.

You are to investigate the order of reaction with respect to I_2.

A reaction mixture containing **FA 1**, **FA 2**, and **FA 3** is first prepared. At different chosen times, aliquots (fixed volumes) of this reaction mixture is removed and quenched using excess **FA 5.**

The remaining amount of I_2 at different times can then be determined by titration against **FA 4**. Each titration can only be performed once.

Reaction 2: $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

The required order of reaction can be obtained by the graphical analysis of your results.

The first aliquot should be removed approximately 4 minutes after the reagents were mixed. You will then remove four further aliquots, at time intervals of your choice, up to a maximum time of 20 minutes.

Prepare a table in the space provided on **page 4** in which to record, to an appropriate level of precision, your chosen time, the actual time and your titration results for each of your aliquots. All values of actual time should be converted to decimal value, ***t***, in minutes and recorded to one decimal place.

For example if actual time = 4 min 33 s then ***t*** = 4 min + 33/60 min = 4.6 min

Experiment

Safety: Propanone is flammable. Transfer your titrated solutions into the waste bottle for later disposal. Keep this bottle stoppered when not in use.

Keep the conical flask (**reaction mixture**) stoppered except when removing aliquots.

Preparing the boiling tubes

1. Label each of the boiling tubes with one of your chosen times.
2. Add approximately 10 cm^3 of **FA 5** to each of these boiling tubes.

Preparing the reaction mixture

3. Using a pipette, transfer 25.0 cm^3 of **FA 1** into the 100 cm^3 beaker.
4. Using a different pipette, transfer 25.0 cm^3 of **FA 2** into the same 100 cm^3 beaker.
5. Using a burette, transfer 50.00 cm^3 of **FA 3** into the 250 cm^3 conical flask, labelled **reaction mixture.**
6. Pour the contents of the 100 cm^3 beaker into this 250 cm^3 conical flask. Start the stopwatch, **insert the stopper** and swirl the mixture thoroughly. Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You must not stop the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture

7. At approximately 4 minutes, using a 10.0 cm^3 pipette, remove a 10.0 cm^3 aliquot of the reaction mixture. **Immediately** transfer this aliquot into the boiling tube labelled **4 minutes** and swirl the mixture. Note the actual time when half of the reaction mixture has emptied from the pipette. Replace the stopper in the flask.
8. At each of your chosen times, repeat **step 7** but transfer each aliquot to its appropriately labelled boiling tube.

Titrations

9. Pour the whole of the contents of a boiling tube into a clean 250 cm^3 conical flask. Wash out the boiling tube and add the washings to the conical flask.
10. Titrate the iodine in this solution with **FA 4**. Add about 1 cm^3 of starch indicator when the colour of the solution turns pale yellow. The solution will turn blue–black. The end–point is reached when the dark blue–black colour just disappears. Record your results.
11. Empty the contents of this conical flask into the waste bottle. Wash this conical flask thoroughly with water.
12. Repeat **steps 9 to 11** for each of your boiling tubes.

(a) Results

[3]

(b) **(i)** On Fig 1.1, plot a graph of **volume of sodium thiosulfate, FA 4**, on the y–axis, against time, ***t***, on the x–axis. Start the x–axis at ***t*** = 0. You should choose a scale which will allow you to extrapolate your graph back to ***t*** = 0.

Draw the most appropriate best–fit line taking into account all of your plotted points.

Fig 1.1

[2]

(ii) Deduce the order of reaction with respect to the I_2 in reaction **1**. Explain your answer.

order..

explanation..

....

.... [1]

(c) **(i)** Write the rate equation for the iodination of propanone.

.... [1]

(ii) Calculate the gradient of the line you have drawn in Fig 1.1, showing clearly how you did this.

gradient = ...
[1]

(iii) Use your answer from **(c)(ii)** to determine the rate of change of amount of $S_2O_3^{2-}$ ions required in mol min^{-1}.

rate of change of amount of $S_2O_3^{2-}$ ions required = ... mol min^{-1}
[1]

(iv) Hence, deduce the rate of disappearance of I_2 in mol min^{-1}.

rate of disappearance of I_2 = ... mol min^{-1}
[1]

(v) Use your answer from **(c)(iv)** to calculate the rate of change of [I_2] in the reaction mixture.

rate of change of [I_2] in the reaction mixture = ...
[1]

(vi) Hence, calculate the value of the rate constant for this reaction.

rate constant = ...
[1]

(d) **Step 7** requires you to mix each aliquot immediately with an excess of sodium hydrogencarbonate solution, **FA 5**. Suggest a clear explanation for this requirement.

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………………………………………………………………………………………………….. [1]

(e) Explain why the concentration of iodine in **FA 3** is very much lower than the concentrations of propanone in **FA 1** and of H^+ ions in **FA 2**.

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………………………………………………………………………………………………….. [1]

(f) **Planning**

The Finkelstein reaction can be used to synthesise 1–iodopropane, a colourless liquid, from 1–bromopropane and sodium iodide. The reaction is carried out using dry propanone as a solvent.

$$CH_3CH_2CH_2Br + NaI \rightleftharpoons CH_3CH_2CH_2I + NaBr$$

(i) What *type of reaction* is the Finkelstein reaction?

…………………………………………………………………………………………………….. [1]

(ii) Explain why it is important for **dry** propanone to be used as a solvent for this reaction.

………………………………………………………………………………………………………

……………………………………………………………………………………………………… [1]

(iii) Table 1.1 shows the solubilities of sodium bromide and sodium iodide in propanone.

Table 1.1

compound	solubility at 25 °C in g / 100 g of propanone
sodium bromide	0.00841
sodium iodide	39.9

Use this information to explain why, although the reaction between $CH_3CH_2CH_2Br$ and NaI is reversible, the reaction produces a very high yield of $CH_3CH_2CH_2I$.

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……………………………………………………………………………………………………… [1]

Sodium iodide is a white crystalline solid.
1–bromopropane is a colourless liquid which has a density of 1.35 g cm^{-3}.

Table 1.2 gives the boiling points of 1–bromopropane, 1–iodopropane and propanone.

Table 1.2

compound	boiling point / °C
1–bromopropane	71.0
1–iodopropane	102.6
propanone	56.0

A 100% yield of pure 1–iodopropane is assumed to be obtained using the procedure described below:

1–bromopropane, an excess of sodium iodide and propanone solvent are mixed and then heated under reflux conditions for around thirty minutes.

The crude 1–iodopropane product is distilled to produce the pure 1–iodopropane.

[A_r: C, 12.0; H, 1.0; O, 16.0; Br, 79.9; I, 126.9; Na, 23.0]

(iv) Calculate the minimum volume of 1–bromopropane you would use to prepare 10 g of pure 1–iodopropane, showing your working.

[1]

(v) Write a plan for the preparation of about 10 g of pure 1–iodopropane.

In your plan you should:

- give a full description of the procedures you would use to prepare the crude 1–iodopropane;
- draw a labelled diagram of the assembled apparatus you would use to obtain the pure 1–iodopropane.

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.... [5]

[Total: 23]

2 Investigation of the dissolution of potassium iodide and lithium chloride in water

Both KI and LiC*l* can dissolve in water to give aqueous solutions.

$$KI(s) \rightarrow K^+(aq) + I^-(aq) \qquad \Delta H > 0$$

$$LiCl(s) \rightarrow Li^+(aq) + Cl^-(aq) \qquad \Delta H < 0$$

The temperature change when a mixture containing KI and LiC*l* dissolves in water is due to the summation of the temperature change when KI and LiC*l* dissolve separately in water.

FA 6 is a mixture containing **equal** masses of potassium iodide, KI, and lithium chloride, LiC*l*.

The ΔT per gram of LiC*l* dissolved in water 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 its dissolution. The temperature change when **FA 6** dissolves completely in water is then determined.

(a) Determination of the value of the decrease in temperature, ΔT_{KI}, for the dissolution of KI in water

(i) You will follow the instructions to perform the following experiment.

1. Weigh accurately about 2.0 g of KI 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 placed in a 250 cm^3 beaker.
3. Stir and measure the initial temperature of the water in the Styrofoam cup.
4. Add the KI in the weighing bottle into the water in the Styrofoam cup.
5. Stir the mixture continuously until it reaches its **minimum** temperature. Record this temperature.
6. Reweigh the weighing bottle.
7. In an appropriate format in the space below, record all measurements of mass and temperature.
8. Calculate the value of the decrease in temperature, ΔT_{KI}, for this experiment.

Results

[4]

(ii) Using the mass of KI and ΔT_{KI} obtained in **(a)(i)**, together with the data in Table 2.1, plot a graph of ΔT_{KI} against the mass of KI used on the grid in Fig 2.1.
Draw the most appropriate line, taking into account all of the plotted points.

Table 2.1

mass of KI / g	decrease in temperature, ΔT_{KI} / °C
4.00	4.1
6.00	6.2
8.00	7.8

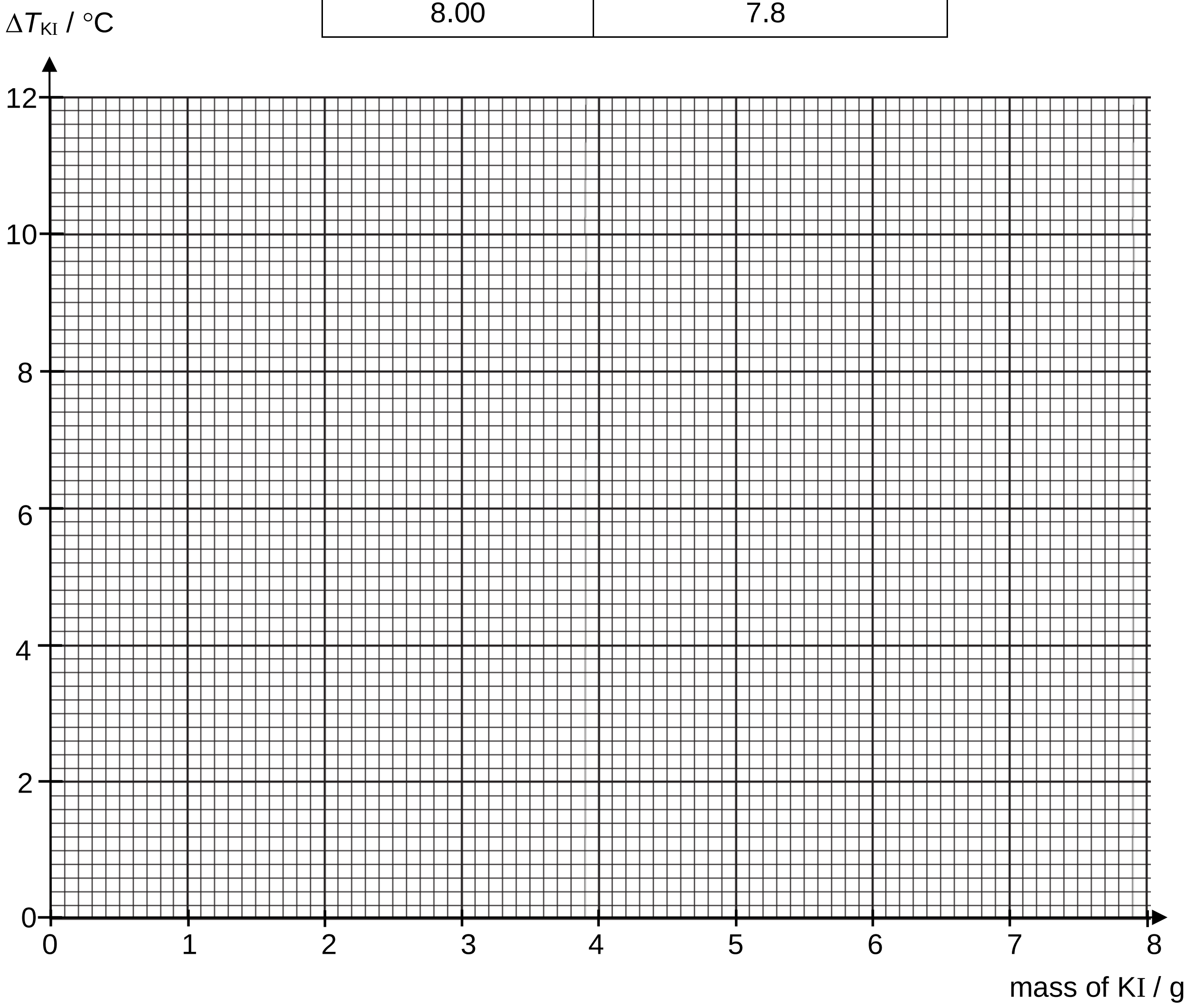


Fig 2.1

[1]

(b) **Determination of the maximum temperature change, ΔT_m, for the dissolution of FA 6 in water**

The maximum temperature change, ΔT_m, when **FA 6** dissolves completely in water was determined by measuring the temperature at timed intervals. The mass of **FA 6** used in the experiment was 6.020 g.

The results from this experiment are plotted on the grid in Fig 2.2 on Page 16.

Draw two best–fit lines, the first taking into account the points before the **FA 6** was added and the second taking into account the points after the reaction had finished.

Extrapolate both lines to four minutes.

Determine a value for the maximum temperature change, ΔT_m, at t = 4.0 min using the graph.

ΔT_m = ……………………………..°C

[2]

(c) **(i)** Using the graph in **(a)(ii)**, determine the change in temperature due to the dissolution of potassium iodide in **FA 6**.

ΔT_{KI} = ………………………°C

[1]

(ii) Using your results in **(b)** and **(c)(i)**, determine the change in temperature due to the dissolution of lithium chloride in **FA 6**.

$\Delta T_{\text{LiC}l}$= ……………………….°C
[1]

(iii) Hence, show clearly how the ΔT per gram of LiC*l* dissolved in water can be determined.

ΔT per gram of LiC*l* = …………………………….°C g^{-1}
[3]

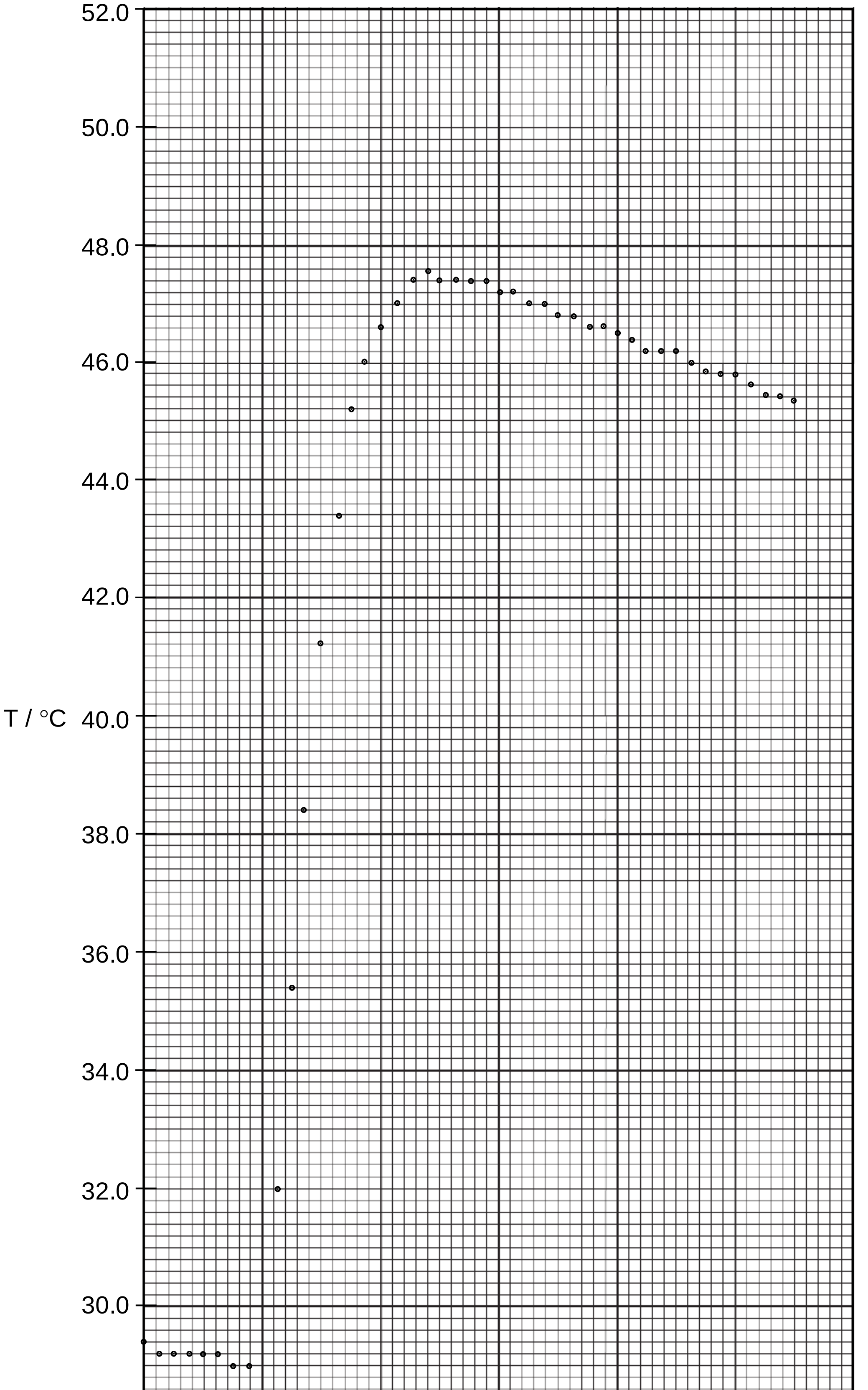

T / °C
52.0
50.0
48.0
46.0
44.0
42.0
40.0
38.0
36.0
34.0
32.0
30.0
28.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
22.0
24.0
t / min

Fig 2.2

(d) **Planning**

When solid hydrated barium chloride, $BaCl_2.\mathbf{x}H_2O$, dissolves in water, Ba^{2+}(aq) and Cl^{-}(aq) ions are formed.

The concentration of dissolved chloride ions in a solution can be determined by titration with aqueous silver nitrate of known concentration.

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$

Potassium chromate(VI), K_2CrO_4(aq), can be used as the indicator for the reaction. At the end–point of the titration, it forms a red precipitate in the presence of excess silver ions.

The solubilities, in mol dm^{-3}, of the various ionic solids at 20 °C are given in Table 2.2.

Table 2.2

	anion		
cation	Cl^{-}	CrO_4^{2-}	SO_4^{2-}
Ag^{+}	1.32×10^{-5}	6.63×10^{-5}	0.940
Ba^{2+}	1.72	1.10×10^{-5}	1.05×10^{-5}

E.g. the solubility of AgCl at 20 °C = 1.32×10^{-5} mol dm^{-3}

Sulfuric acid must be added to the solution to prevent the Ba^{2+}(aq) ions from interfering with the action of the potassium chromate(VI) indicator.

(i) How would Ba^{2+}(aq) ions interfere with the action of this indicator?

………

……… [1]

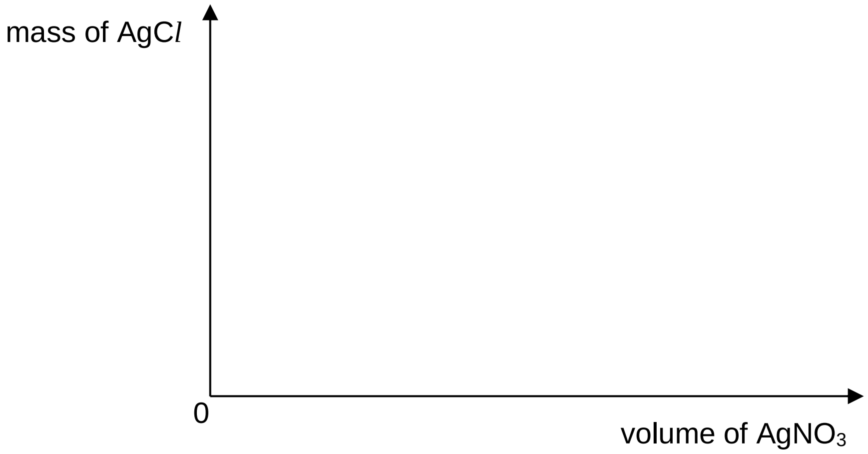
(ii) How does the addition of sulfuric acid prevent Ba^{2+}(aq) ions from interfering with the action of this indicator?

………

……… [1]

(iii) In an initial rough titration, excess silver nitrate solution is added so that the end–point is exceeded.

Draw a sketch graph to show how the mass of silver chloride varies with the volume of silver nitrate added.



[1]

You are provided with the apparatus normally used in a school laboratory and the following materials:

3.00 g of hydrated barium chloride, $BaCl_2.\mathbf{x}H_2O$
0.050 mol dm^{-3} aqueous silver nitrate
1.0 mol dm^{-3} potassium chromate(VI) solution
1.0 mol dm^{-3} sulfuric acid

(iv) Describe how you would prepare a solution of barium chloride that is suitable for use in your titration. You should give details of any apparatus used.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………….… [2]

(v) A known volume of the barium chloride solution you have prepared in **(d)(iv)** is transferred to a conical flask.

In what order should the other three solutions then be added to the flask?

first………………………………………………………………………………………………

second……………………………………………………………………………………………

third………………………………………………………………………………………………

[1]

[Total: 18]

3 **(a)** Carry out the following tests on **FA 7** which contains **two** cations and **one** anion from the following list: NH_4^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, CO_3^{2-}, NO_3^-, NO_2^-, SO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, I^-.

Carefully record your observations in the space provided in Table 3.1.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved.

Table 3.1

	test	observations
1.	Add 1 cm depth of **FA 7** to a test–tube. Add aqueous ammonia slowly, with shaking, until no further change is seen. Filter the mixture and add dilute nitric acid drop–wise to the filtrate, until no further change is seen. *(You may continue with test 2, while waiting for the filtration process to complete.)*	
2.	Add 1 cm depth of **FA 7** to a test–tube. Add aqueous barium nitrate, followed by dilute nitric acid.	

[3]

Summary

Identify the ions present in **FA 7**. Use evidence from your observations in Table 3.1 to support your deductions on the identification of the cations in **FA 7**.

FA 7 contains the cations …………………………… and ……………………………

evidence …………………………………………………………………………………..……….

……

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……

FA 7 contains the anion …………………………… [2]

FA 8 is an aqueous solution of $FeCl_3$.

(b) **(i)** Perform the tests described in Table 3.2, and record your observations in the table.

Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.2

	test	observations
1.	Add 1 cm depth of **FA 8** to a test–tube. Add **FA 4** slowly, with shaking, until no further change is seen. Leave it to stand.	
2.	Add 1 cm depth of **FA 8** to a test–tube. Add 1 cm depth of **FA 5**, with shaking, until no further change is seen.	
3.	Add 1 cm depth of **FA 8** to a test–tube. Add 1 cm depth of aqueous potassium iodide, with shaking, until no further change is seen.	

[2]

(ii) Explain your observation(s), in test 2 in Table 3.2, in terms of the chemistry involved.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

Table 3.3 gives some standard electrode potential values.

Table 3.3

electrode reaction	$E^{\ominus}$ / V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

(iii) Explain the observation(s), in test 3 in Table 3.2, in terms of the chemistry involved.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

(iv) Consider your observation(s) when aqueous potassium iodide was added to $FeCl_3$ solution in test 3 in Table 3.2. No such colour change was observed when aqueous potassium iodide was added to a solution containing $[Fe(CN)_6]^{3-}$ ions.

Use data from Table 3.3 to explain the observations and comment on the difference in observations in terms of the stability of the $[Fe(CN)_6]^{3-}$ ion and the iron–containing complex ion in $FeCl_3$.

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……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

(v) State what you would expect to observe when an equal volume of hexane is added to the mixture you have obtained in test 3 in Table 3.2.

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [1]

[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

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 SERANGOON JUNIOR COLLEGE

H2 Chemistry 9729 **2019 JC2 Prelim Exam Paper 1 Worked Solutions**

1 Answer: **C**

^{68}Ge has 32 protons and 36 neutrons.
When 'a proton changes into a neutron', ^{68}X contains 31 protons and **37 neutrons**.
X is gallium (Ga) which is in Group 13, i.e. has 3 valence electrons, only 1 of which is in the outer p orbitals.
Ga: [Ar] $3d^{10}$ $4s^2$ $4p^1$

2 Answer: **C**

X: The biggest jump in IE is between 4th to 5th electron hence, X has 4 valence electrons and belongs to Group 14.
Y: The biggest jump in IE is between 6th to 7th electron hence, X has 6 valence electrons and belongs to Group 16.

Possible covalent compounds formed are CO_2, CS_2 and SiO_2.

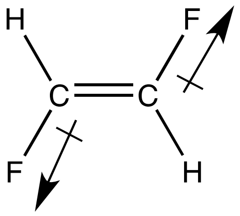
3 Answer: **C**

Notice that N^1 and N^3 only have two covalent bonds with carbon atoms. To fulfil octet, they need to gain one electron each from the central Mg atom to form N^-. Hence, N^1 and N^3 are involved in ionic bonding.

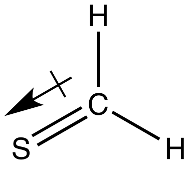
N^2 and N^4 have three covalent bonds with carbon atoms. They have one lone pair each, which interacts with the central Mg^{2+} ion via co–ordinate bonding.

4 Answer: **D**

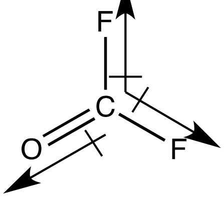
Dipole moments cancel out.



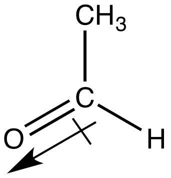
B: Dipole moment is smaller than that in D since S is less electronegative than O.



C: Dipole moment is smaller than that in D as the net dipole moment of C–F bonds reduces the dipole moment of C=O bond



D:



5 Answer: **C**

$$pV = nRT$$

$$pV = \frac{m}{M}RT$$

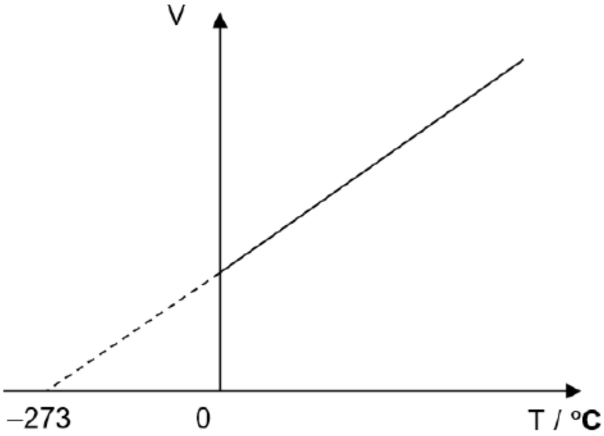
$$pM = \frac{m}{V}RT$$

$$pM = \rho RT$$

p is directly proportional to ρ. The graph should be a straight line that passes through the origin. Hence, A is wrong

*p*V = nRT
p is directly proportional to T / K. The graph should be a straight line that passes through the origin. Hence, B is wrong.

V is also directly proportional to T / K.



Hence, C is correct

*p*V = nRT
$\frac{1}{p} = \frac{V}{nRT}$: $\frac{1}{p}$ α V at constant *T*. The graph should be a straight line that passes through the origin. Hence, D is wrong.

6 Answer: **B**

The solution is one which is able to maintain the pH at about 5, hence it is an acidic buffer.
Only the mixture in option B can form an acidic buffer.

7 Answer: <u>**C**</u>

$H_2O \rightleftharpoons H^+ + OH^-$
$K_w = [H^+][OH^-]$

Since the stoichiometric coefficients of H^+ and OH^- ions are equal in the above equation, $[H^+] = [OH^-]$ at all temperatures. Hence, water is a neutral liquid at all temperatures. Option B is wrong.

When temperature of water increases, K_w also increases. This shows that the position of equilibrium has shifted to the right, i.e. the forward reaction is favoured, and more H^+ and OH^- ions are produced. Since the endothermic reaction is favoured when temperature increases, the dissociation of water (forward reaction) is an endothermic reaction. Option D is wrong.

The value of K_w does not provide any information about hydrogen bonding between water molecules. Option A is wrong.

8 Answer: <u>**C**</u>

A: Volatility of halogens (X_2) <u>decreases</u>: $F_2 > \mathrm{C}l_2 > Br_2 > I_2$
X_2 has simple molecular structure with weak id–id forces of attraction between molecules. Down the group, the number of electrons increases hence the electron cloud is bigger and more easily polarised resulting in stronger id–id forces of attraction. Thus, the boiling point increases down the group and the halogens become less volatile.

B: Bond energy of X–X bond <u>decreases</u> down group 17

molecule	bond energy of X–X (kJ mol^{-1})
F_2	+ 158
$\mathrm{C}l_2$	+ 244
Br_2	+ 193
I_2	+ 151

C: Down group 17, $E^{\ominus}_{(X2/X^-)}$ becomes less positive.
Γ ⇒ <u>increasing</u> tendency for X^- to be oxidised to X_2

D: Thermal stability of hydrogen halides <u>decreases</u> down group 17 as the bond energy of H–X bond decreases down the group.

molecules	bond energy of H–X (kJ mol^{-1})
H–F	562
H–C*l*	431
H–Br	366
H–I	299

9 Answer: <u>**A**</u>
There are 3 chlorine atoms in 1 molecule of trichloroisocyanuric acid.

No. of moles of trichloroisocyanuric acid in the pool = $\dfrac{2.50 \times 10^6 \times 1.50 \times 10^{-3}}{232.5}$ = 16.1
No. of moles of chlorine atoms = 3 x 16.1 = 48.38
No. of chlorine atoms = 48.38 x 6.02 x 10^{23} = <u>**2.91 x 10^{25}**</u>

10 Answer: **<u>B</u>**

No. of moles of H_2S = $\frac{720}{24000} = 0.03\ \text{mol}$

No. of moles of HNO_3 = $\frac{40}{1000} \text{ x } 0.500 = 0.02\ \text{mol}$

Mole ratio of H_2S: HNO_3 = 3 : 2
From the given half–equation,
1 mole of H_2S loses 2 moles of electrons → 3 moles of H_2S will <u>lose 6 moles of electrons</u>
2 moles of HNO_3 gain 6 moles of electrons → **<u>1 mole of HNO_3 will gain 3 moles of electrons</u>**

original oxidation state of N in HNO_3:
(+1) + x + 3(–2) = 0
x = +5
Since the nitrogen atom in HNO_3 gains 3 electrons,
+5 – 3 = +2

new oxidation state of N = **<u>+2</u>** (N in NO has an oxidation state of +2)

11 Answer: **<u>D</u>**

Q' (heat taken in by water) = 300 x 4.2 x T J

Q (heat evolved by the reaction) = $\frac{m}{46.0} \times 1371 \times 1000\ \text{J}$

% efficiency = $\dfrac{300 \times 4.2 \times T}{\frac{m}{46.0} \times 1371 \times 1000} \times 100\% = \dfrac{300 \times 4.2 \times T \times 46.0}{m \times 1371 \times 1000} \times 100\%$

12 Answer: **<u>A</u>**

To calculate enthalpy change of formation of $MgCO_3(s)$, use the following:

$$\Delta H_{rxn} = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$$

The enthalpy of combustion of C(s) is the same as the enthalpy change of formation of $CO_2(g)$. Hence, option A is correct.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

13 Answer: **<u>A</u>**

When a liquid boils, energy is needed to overcome the forces of attraction between liquid particles, hence ΔH is positive (i.e. endothermic).

When a liquid boils, the state changes from liquid to gaseous state, which is more disordered, hence ΔS is positive.

14 Answer: **B**

rate = $k[(CH_3)_3CCl]$ (first order reaction)

When $[(CH_3)_3CCl]$ is **doubled**, the **rate** is **doubled**.
Given that 20% of 0.02 mol dm^{-3} $(CH_3)_3CCl$ has reacted in 5 min, 0.004 mol dm^{-3} has reacted.
Hence, for 0.04 mol dm^{-3} $(CH_3)_3CCl$, 0.008 mol dm^{-3} would have reacted as rate has doubled.
% reacted = (0.008/0.04) x 100% = **20%**

15 Answer: **B**

.

expt no.	initial $[O_2]$ / mol dm^{-3}	initial [NO] / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	2.0	1.0	8.0
2	1.0	1.0	*s*
3	1.0	*t*	16.0
4	0.5	0.5	*u*

Given: rate = $k[O_2][NO]^2$

Comparing expt 1 & 2, in which initial [NO] is constant,
When $[O_2]$ is halved, rate will be halved $\Rightarrow s = 8.0/2 = \underline{\mathbf{4.0}}$

Comparing expt 2 & 3, in which initial $[O_2]$ is constant,
Since rate increases 4 times (from 4.0 to 16.0) and order of reaction w.r.t. NO is 2, [NO] must have doubled (from 1.0 to 2.0) $\Rightarrow t = \underline{\mathbf{2.0}}$

Alternatively,

$$\left(\frac{1.0}{1.0}\right)\left(\frac{t}{1.0}\right)^2 = \left(\frac{16.0}{4.0}\right)$$

$$t = 2.0$$

Comparing expt 3 & 4,

$$\left(\frac{0.5}{1.0}\right)\left(\frac{0.5}{2.0}\right)^2 = \left(\frac{u}{16.0}\right)$$

$$u = 0.5$$

16 Answer: **D**

1: The rate equation can be derived as follows:
Based on the slow step (rds): rate = $k\,[OH^+]\,[I^-]^2\,[H^+]$ ——— (1)

For the first step (fast step), $K_c = \dfrac{[OH^+]}{[H_2O_2][H^+]}$

$[OH^+] = K_c\,[H_2O_2]\,[H^+]$ ——— (2)

Substituting (2) into (1): rate = $k\,K_c\,[H_2O_2]\,[H^+]\,[I^-]^2\,[H^+]$

rate = $\mathbf{k_1\,[H_2O_2]\,[H^+]^2\,[I^-]^2}$

which is not consistent with the experimentally obtained rate equation.

2: The overall chemical equation obtained by summing up the 2 equations in the slow and fast steps is different from that given in the option.

$NO_2 + NO_2 \rightarrow \cancel{N_2O_3} + O$ (slow)
$\underline{\cancel{N_2O_3} + CO \rightarrow CO_2 + 2NO \text{ (fast)}}$

$\mathbf{CO + 2NO_2 \rightarrow CO_2 + 2NO + O}$

(given) $CO + NO_2 \rightarrow CO_2 + NO$

3: Based on the slow step (rds), the rate equation should be: **rate = k_3 [H_2]** which is not consistent with the experimentally obtained rate equation.

17 Answer: **<u>C</u>**

$\Delta G^\ominus < 0$ at points 1, 2 and 3.

When K_c is more than 1, it implies that the position of equilibrium lies more towards the right. This means that the forward reaction is spontaneous. Therefore, consider points where $\Delta G^\ominus < 0$.

18 Answer: **<u>C</u>**

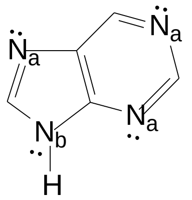
At ***t₁***: When NO_2 was removed, the position of equilibrium shifts right to produce more NO_2, causing the amount and hence pressure of NO_2Cl to decrease.
At ***t₂***: when the temperature was increased, the position of equilibrium shifts left to favour the endothermic reaction by absorbing more heat. This causes the pressure of NO_2Cl to increase.

At ***t₃***: when more NO_2Cl was added, it led to a sharp increase in pressure. The position of equilibrium then shifts right to counter act the change, leading to a decrease in the pressure of NO_2Cl.

19 Answer: **<u>D</u>**

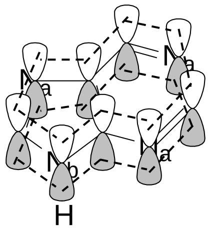
1. Gas produced suggests H_2 gas. $H_2 + Fe^{2+} \rightarrow Fe + 2H^+$ is <u>not spontaneous</u> as $E^\ominus_{cell} = -0.44\ V < 0$
2. $[Fe(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons Fe(OH)_2 + 6H_2O$
   This is an <u>acid–base reaction</u> since the OH^- accepts the H^+ from the water ligand to form H_2O.
3. $Fe^{2+}(aq)$ ion has a low charge density and hence can only hydrolyse in water to a small extent. It can only undergo a simple precipitation reaction with Na_2CO_3 to form $FeCO_3(s)$.

20 Answer: **A**

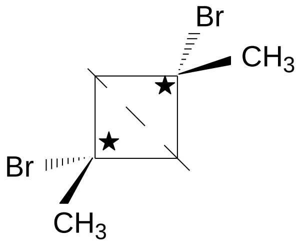


All the carbon atoms and nitrogen atoms labelled as N_a are sp^2 hydridised (3 electron regions).

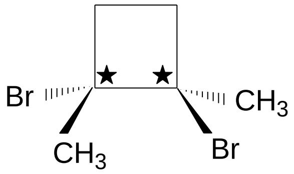
Although there are 4 electron regions around the nitrogen atom labelled as N_b, N_b is also sp^2 hybridised. This is because given that N_b is non–basic, its lone pair of electrons resides in the unhybridised p orbital and can be delocalised due to the overlapping of the p orbitals. Hence, the lone pair of electrons on N_b is not available to accept a H^+.



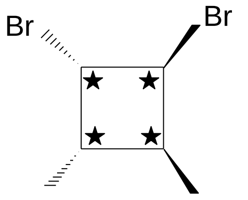
21 Answer: **C**



Option 1: has a plane of symmetry



Option 2: has no plane of symmetry, thus is optically active



Option 3: has no plane of symmetry, thus is optically active

22 Answer: **D**

The correct reagents should be:
Option 1: NaOH in ethanol
Option 2: NaCN in ethanol
Option 3: no reaction due to partial double bond character in the C–C*l* bond

23 Answer: **C**

–NO_2 and –$COCH_3$ groups are 3–directing, which explains why option A is wrong.
Option B is wrong as C–F bond is too strong for nucleophilic substitution to take place.
Option D is wrong as free–radical substitution (FRS) at a sp^2 hybridised C does not occur readily / FRS cannot be easily controlled (i.e. a mixture of products is obtained)

24 Answer: **A**

$NaBH_4$ can reduced ketone to 2^o alcohol but it not able to reduce carboxylic acid, alkenes or nitrobenzene

25 Answer: **D**

Since there is no reaction with Fehling's solution, **Z** is not an aliphatic aldehyde. Hence, option **B** is wrong.

1 mole of **Z** reacts with 2 moles of Na metal, hence there are two groups that can react (carboxylic acid, phenol or alcohol)

When PCl_5(s) is added to **Z,** it reacts with carboxylic acid in option **D** to from acyl chloride, which further reacts with the phenol group to form a sweet smelling ester.

26 Answer: **B**

Q hydrolyses readily in water to produce a strongly acidic solution of CH_3CO_2H and **H*Cl***. Hence, the resulting solution formed has the lowest pH.

P, **R** and **S** are weak acids which ionise partially in water.
The presence of electronegative atoms (C*l* and Br) on **R** and **S** exerts an electron–withdrawing effect on $ClCH_2CH_2COO^-$ and $BrCH_2CH_2COO^-$ respectively, which disperses the negative charge and stabilises the anion.
Since C*l* is more electronegative than Br, it exerts a stronger electron–withdrawing effect on $ClCH_2CH_2COO^-$ and hence stabilises the anion more. $ClCH_2CH_2COOH$ is more acidic than $BrCH_2CH_2CO_2H$. Hence, the resulting solution from **R** has a lower pH than **S**.

CH_3CH_2COOH contains an electron–donating alkyl group, which intensifies the negative charge of the anion. Thus, dissociation of CH_3CH_2COOH to give H^+ ions is least favourable. The resulting solution from **P** has the highest pH.

27 Answer: **D**

1: The empirical formula is $C_7H_{15}ON$. When the compound in option 1 is hydrolysed, it gives CH_3CO_2H, which has the empirical formula CH_2O.

2: The empirical formula is $C_8H_{17}ON$. When the compound in option 2 is hydrolysed, it gives $CH_3CH_2CH_2CO_2H$, which has the empirical formula C_2H_4O.

3: The empirical formula is $C_7H_{15}ON$. When the compound in option 3 is hydrolysed, it gives $(CH_3)_2CHCO_2H$, which has the empirical formula C_2H_4O.

28 Answer: **C**

1. The α–amino group should have a pK_a value of 9.0 because it is closer to the –COOH group which is electron–withdrawing in nature.
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**.
3. At point **C**, $H_2NCH(CO_2^-)(CH_2)_4NH_3^+$ is present, which is a zwitterion with no net charge.
4. At point **B**, $H_3N^+CH(CO_2^-)(CH_2)_4NH_3^+$ is present which has a net positive charge, hence will migrate to cathode(–).

29 Answer: **A**

1. When calculating the oxidation state (O.S), consider the bonds around the atom of concern.
   C bonded to O in quinone has 3 bonds: C=O and two C–C. Since O.S of O in C=O is –2, C is +2.
   Similarly, C bonded to O in quinol has 3 bonds: C–O and two C–C. O.S of O in C–O is –1, hence O.S of C is +1.

2. $E^\ominus_{cell} = +1.52 - (+0.70) = +0.82 \text{ V} > 0$

3. $E^\ominus_{cell} = +0.70 - (+0.17) = +0.53 \text{ V} > 0$ (reaction is spontaneous)

30 Answer: **A**

Q = current x time = n_eF
current α n_e since time and F are a constant

Electrolysis of aqueous sulfuric acid at the anode:
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Electrolysis of molten aluminium oxide at the cathode:
$Al^{3+} + 3e^- \rightarrow Al$

$$\frac{n_{O_2}}{n_{Al}} = \frac{0.01}{0.01}$$

$$\frac{n_{\text{electrons transferred for } O_2}}{n_{\text{electrons transferred for } Al}} = \frac{4}{3} = \frac{\text{current used in electrolysis 1}}{\text{current used in electrolysis 2}}$$

$$\frac{4}{3} = \frac{I}{\text{current used in electrolysis 2}}$$

$\Rightarrow$ current used in electrolysis 2 = $\frac{3}{4}I$.

ANDERSON SERANGOON JUNIOR COLLEGE

H2 Chemistry 9729 **2019 JC2 Prelim Exam Paper 2 Solutions**

1 **(a)** Reducing power of Group 2 elements increases [1] down the group.

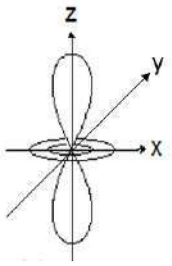
Number of (principal) quantum shell / electronic shell increases and valence electrons are further away and more shielded from the nucleus. Valence electrons are less strongly attracted to the nucleus and smaller amount of energy is needed to remove the valence electron so it is more easily oxidised. [1]

(b) **(i)** Copper can give up both 3d and 4s electrons for delocalisation whereas calcium can only give up 2 electrons. [1] Electrons act as mobile charge carriers [1] to conduct electricity.

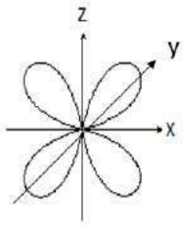
(ii) Cu has smaller atomic radius and higher atomic mass [1] compared to Ca.
Also, Cu has a more closely packed structure due to stronger metallic bonding as compared to Ca. [1]
Hence, Cu has a much higher density than Ca.

(c) **(i)** A
Each orbital can hold a maximum of 2 electrons of opposite spin.
Diagram B has a pair of electrons having the same spin.
[1] with explanation

(ii)



$3d_{z^2}$ [1]



$3d_{xz}$ [1]

Alternative answers: $3d_{x^2-y^2}$, $3d_{xy}$, $3d_{yz}$

(d) **(i)** Both silicon and silica have a giant molecular structure. [1]

(ii)
- From the data booklet:
  Si–Si BE: 222 kJ mol^{-1}
  Si–O BE: 460 kJ mol^{-1} [1]

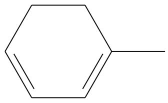
- Size of valence orbitals: Si > O
- Valence orbitals of Si are more diffused than that of O
- Overlap of orbitals is less effective in Si–Si than in Si–O

- The Si–O bond in silica is stronger than the Si–Si bond in silicon.
- Hence, bond energy: Si–Si < Si–O and more energy is required to break the Si–O bond than the Si–Si bond. [1]

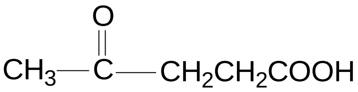
2 **(a)** **(i)** presence of carboxylic acid or –COOH group
presence of $CH_3CO–$ or methyl ketone
absence of chiral carbon

any 2 for [2]

(ii)



C



$CH_3—\overset{\overset{O}{\|}}{C}—CH_2CH_2COOH$

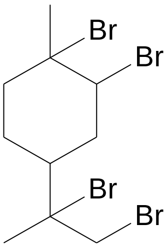
D

[1] each

(iii) **E**: $(CH_3)_2CO$; **F**: CH_3CH_2CHO [1] each

(iv) **G**: $CH_3CH{=}CHCH(CH_3)_2$ [1]

(b) **(i)**

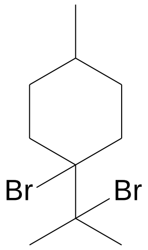


[1]

Orange–red / red–brown Br_2 decolourises / turns colourless. [1]

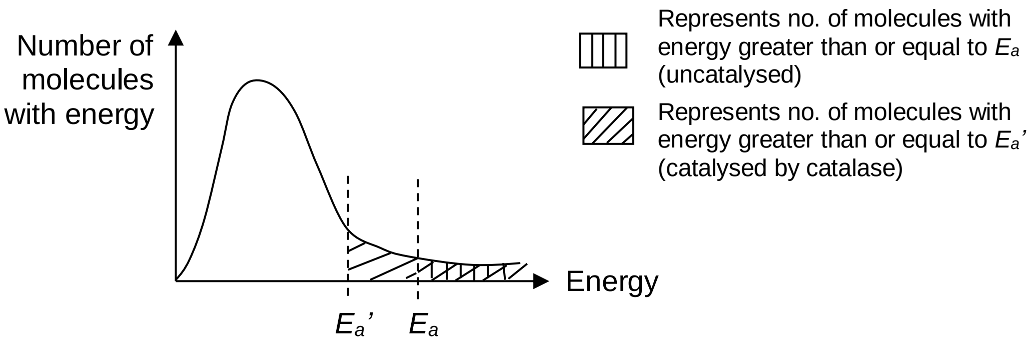
(ii) NaOH in ethanol, heat (under reflux) [1]

(iii)



[1]

3 **(a)** **(i)**



[1]: diagram

As shown on the diagram, in the presence of catalase, at a certain temperature T,
- Catalase provides a different pathway of a lower activation energy ($E_a' < E_a$).
- More molecules have energies greater than or equal to the lowered activation energy E_a'.
- This results in an increase in the frequency of effective collisions. [2]

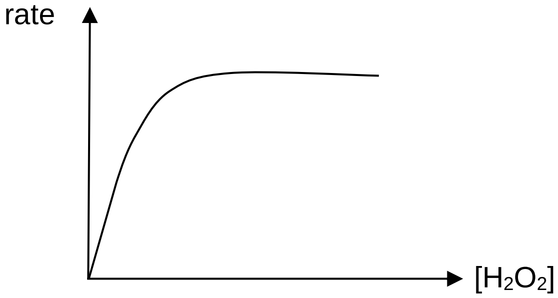
(ii) Repeat the experiment described but using varying volumes of H_2O_2 and topping it up with deionised water to keep the total volume constant at 50 cm^3 and add in 1 cm^3 of catalase. [1]

Record the time taken for 20 cm^3 of O_2 to form. [1]

As rate is inversely proportional to the time taken, plot a graph of 1/t against $[H_2O_2]$ / V_{H2O2}. [1]

Or find the product of $(V_{H2O2})^n t$ and determine the value of n when $(V_{H2O2})^n t$ becomes a constant.

(iii)



[1]: diagram

At low $[H_2O_2]$, rate is directly proportional to $[H_2O_2]$ (OR 1st order reaction) since active sites are not fully occupied.

At high $[H_2O_2]$, rate becomes constant (OR zero order reaction) since active sites are fully occupied. [1]

(b) **(i)** FeS is precipitated first.

(ii) When FeS is precipitates,
$[S^{2-}] = 3.7 \times 10^{-19} \div 0.100 = 3.70 \times 10^{-18}$ mol dm^{-3}

(iii) When MnS starts to precipitate,
$[S^{2-}] = 3.7 \times 10^{-13} \div 0.100 = 3.70 \times 10^{-12}$ mol dm^{-3} [1]
$[Fe^{2+}] = 3.7 \times 10^{-19} \div 3.7 \times 10^{-12} = 1.00 \times 10^{-7}$ mol dm^{-3}

(iv) % of Fe^{2+} remaining in solution = $1.00 \times 10^{-7} \div 0.1 \times 100\% = 0.0001\% << 1\%$
$\Rightarrow$ separation is effective

(v) As the pH increases, $[H^+]$ decreases, the positions of equilibrium (1) and (2) shift to the right, resulting in a higher $[S^{2-}]$.

For selective precipitation, the pH is increased such that the ionic product of FeS > K_{sp}(FeS) but ionic product of MnS < K_{sp}(MnS). Only FeS is precipitated.

[1] explain relationship between pH and $[S^{2-}]$ using LCP
[1] linking $[S^{2-}]$ to ionic product and hence K_{sp} to show sequence of precipitation

(c) **(i)** $2Cr_2O_3 + 3O_2 + 8OH^- \rightarrow 4CrO_4^{2-} + 4H_2O$ [1]

(ii) From yellow (CrO_4^{2-}) to orange ($Cr_2O_7^{2-}$) to green (Cr^{3+}) [1]

(iii) step **III**: acid–base reaction
complex ion in solution **P**: $[Cr(OH)_6]^{3-}$ (accept $[Cr(OH)_4]^-$ or $[Cr(OH)_4(H_2O)_2]^-$) [1]

(iv) $Na_3Fe(CN)_6$ [1]

4 **(a)** Ethylamine is a stronger base than phenylamine.

Ethylamine:
Ethyl group is electron–donating and increases the electron density around the N atom. This increases the availability of the lone pair of electrons on N atom to accept a proton. [1]

Phenylamine:
Lone pair of electrons on N atom in phenylamine is delocalised into the π electron cloud of the benzene ring. This decreases the availability of the lone pair of electrons on N atom to accept a proton. [1]

(b) **(i)** methyl orange
The working pH range of methyl orange lies within the range of rapid pH change of the titration curve which lies in the acidic pH region (equivalence pH < 7). [1]

(ii) At equivalence point:
$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$
$CH_3CH_2NH_3^+ + H_2O \rightleftharpoons CH_3CH_2NH_2 + H_3O^+$

$[H_3O^+]$ at equivalence point = $10^{-5.91}$ mol dm^{-3}

K_a of $CH_3CH_2NH_3^+ = 10^{-(14-3.35)} = 10^{-10.65}$

$$K_a = \frac{[H_3O^+][CH_3CH_2NH_2]}{[CH_3CH_2NH_3^+]} = \frac{[H_3O^+]^2}{[CH_3CH_2NH_3^+]}$$

$[CH_3CH_2NH_3^+]$ at equivalence point = $\dfrac{(10^{-5.91})^2}{(10^{-10.65})} = 0.0676 \text{ mol dm}^{-3}$ [1]

(iii) Let x cm^3 be the volume of HC*l* needed to neutralise ethylamine.

n(HC*l*) required to neutralise $CH_3CH_2NH_2$ = n($CH_3CH_2NH_3^+$)

$$= \frac{x}{1000} \times 0.2 = 0.0002x \text{ mol}$$

$[CH_3CH_2NH_3^+]$ at equivalence point = $\dfrac{0.0002x}{\dfrac{x+20}{1000}} = 0.0676 \text{ mol dm}^{-3}$

$x = 10.2$ cm^3 [1]

(iv) n($CH_3CH_2NH_2$) = 0.2 x 10.2/1000 = 0.00204 mol
$[CH_3CH_2NH_2] = \dfrac{0.00204}{\dfrac{20}{1000}} = 0.102 \text{ mol dm}^{-3}$ [1]

(v)
$$K_b = \frac{[OH^-][CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]} = \frac{[OH^-]^2}{[CH_3CH_2NH_2]}$$

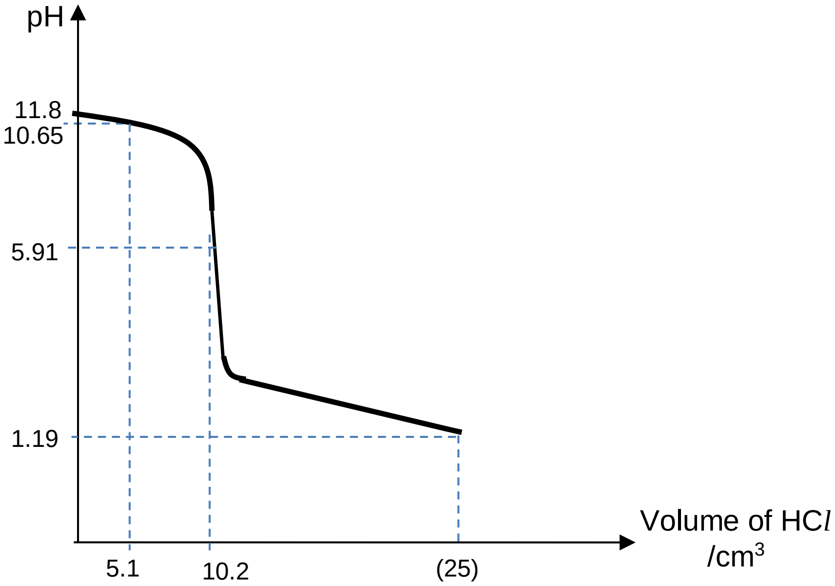
$[OH^-] = \sqrt{10^{-3.35} \times 0.102} = 0.0067499 \text{ mol dm}^{-3}$
pOH = –log 0.0067499 = 2.17
pH = 14 – 2.17 = 11.8 [1]

(vi) n(HC*l*) unreacted = $\dfrac{25 - 10.2}{1000} \times 0.2 = 0.00296$ mol

[HC*l*] after 25.00 cm^3 has been added = [H_3O^+] = $\dfrac{0.00296}{\frac{20+25}{1000}}$ = 0.06577 mol dm^{-3}

pH = –log 0.06577 = <u>1.18</u> [1]

(vii)



(c) **(i)** Initial amount of $C_6H_5NH_2$ = $\dfrac{200}{1000}$ x 0.15 = 0.03 mol

Initial amount of HC*l* = $\dfrac{100}{1000}$ x 0.2 = 0.02 mol

	$C_6H_5NH_2$ + HC*l* → $C_6H_5NH_3^+Cl^-$ + H_2O		
Initial mol	0.03	0.02	
Change in mol	–0.02	–0.02	+0.02
Final mol	0.01	0	0.02 [1]

$$K_b = \frac{[OH^-][C_6H_5NH_3^+]}{[C_6H_5NH_2]} = \frac{[OH^-](\frac{0.02}{0.3})}{(\frac{0.01}{0.3})} = 10^{-4.63}$$

[OH$^-$] = 1.1721 x 10^{-5} mol dm^{-3}
pOH = –log 1.1721 x 10^{-5} = 4.93
pH = 14 – 4.93 = <u>9.07</u> [1].

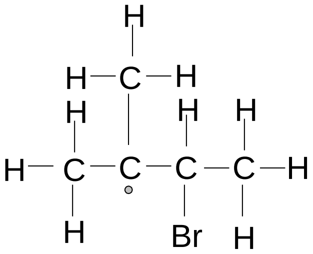
(ii) $C_6H_5NH_3^+$ + OH^- → $C_6H_5NH_2$ + H_2O [1]

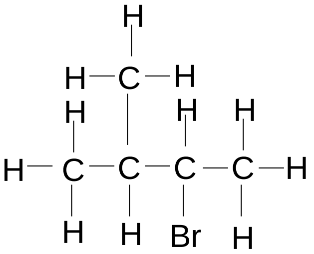
5 **(a)** A highly reactive atom or group of atoms with an unpaired electron. [1]


[1]

Break homolytically (shown in diagram with 2 half arrows) at the O–O single bond

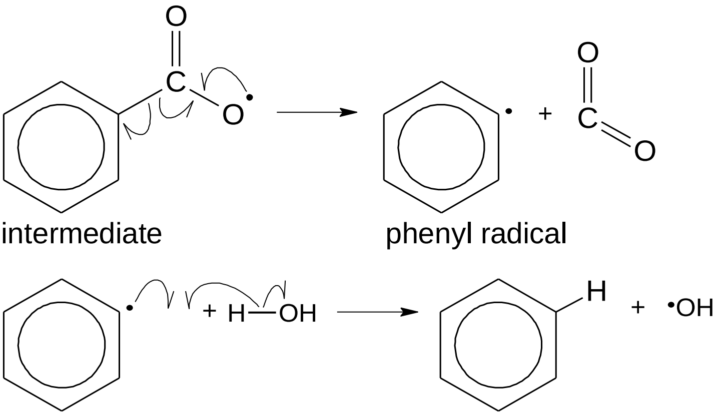
(b)


alkyl radical


organic product

[1] each

(c)



6 half arrows [2]
Identity of the 2 radicals [1]

(d) **(i)** Total energy in the coffee = (4.5 x 38) + (20 x 17) + (15 x 17) = 766 kJ [1]
No. of minutes = 766 / 7 = 109 min [1]

(ii) M_r of $C_{55}H_{98}O_6$ = 854.0
x = 38 x 854.0 = 32452 kJ mol^{-1} or 32500 kJ mol^{-1} [1]

(e) **A:** $(CH_3)_3CCH_2CHO$ [1]
B: $CH_3COC(CH_3)_3$ [1]

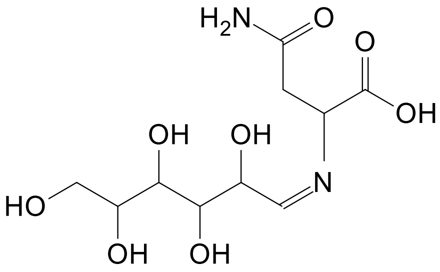
6 **(a)** **(i)** Since potatoes are boiled in water, the temperature is below 140 °C. Therefore, only a small amount of acrylamide is formed. [1]
(or words to the effect)

(ii) The Maillard reaction occurs largely on the surface of cooked food.
Since deep fried potato is cut into strips, there is an increased surface area to volume ratio for the formation of acrylamide compared to baked potato. [1]

(b) **(i)** At a lower pH, the amine group in asparagine is protonated. This prevents nucleophilic attack by the amine on the carbonyl group in glucose, preventing the formation of acrylamide. [1]

(ii) Glycine competes effectively with asparagine in the Maillard reaction, preventing the formation of the imine which leads to the formation of acrylamide. [1]
(or words to the effect)

(c)



imine [1]

(d) **(i)** The circled carbon atom is most susceptible to nucleophilic attack because it faces **<u>less steric hindrance</u>** than the other carbon atom in the epoxide group. [1]

(ii) This reaction **<u>decreases the amount of guanine</u>**, damaging the DNA structure such that it is not able to function normally, potentially leading to cancer. [1]

(iii) Since the **<u>lone pair</u>** on the N atoms in thymine is delocalised into the π bond of the adjacent C=O by resonance, it is **<u>not available</u>** to act as a nucleophile. [1]

(iv) The **<u>C=C double bond</u>** in phenylethene can be metabolised **<u>into an epoxide</u>** by the enzyme, just like the C=C double bond in acrylamide. [1]
This epoxide then follows the same mechanism as glycidamide, by reacting with guanine.
(or words to this effect)

ANDERSON SERANGOON JUNIOR COLLEGE

H2 Chemistry 9729 **2019 JC2 Prelim Exam Paper 3 Solutions**

1 (a) (i) $K_c = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$ [1]

units = $mol^{-1}\ dm^3$ [1]

(ii) $K_c = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

$4.99 \times 10^2 = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][5.00\times10^{-3}]}$

$\dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}]} = 2.495$ [1]

Let % of $Fe(SCN)^{2+}$ = x %, then % of Fe^{3+} = 100 – x,

$\dfrac{x}{100 - x} = 2.495$

$x = 249.5 - 2.495x$

$3.495x = 249.5$

$x = \dfrac{249.5}{3.495} = \underline{71.4\%}$ [1]

(iii) When temperature is increased (to 500 K), backward endothermic reaction is favoured, shifting the equilibrium position to the left to decrease the temperature by absorbing the extra heat. [1]

The red colour of the solution becomes less intense/fade. [1]

(b) Na, Mg and A*l* have giant metallic lattice structure with high melting points, as a large amount of energy is required to overcome the strong electrostatic forces of attraction between cations and sea of delocalised electrons. [1]

Melting point increases from Na to A*l* as the number of valence electrons for metallic bonding increases, and cationic radii decreases. Hence, metallic bond strength increases. [1]

Si has a giant molecular structure with high melting point as very large amount of energy is required to overcome the extensive covalent bonds between atoms in the three dimensional network structure. [1]
P_4, S_8 and Cl_2 have simple molecular structure with low melting points as small amount of energy is required to overcome the weak instantaneous dipole–induced dipole (id–id) attractions between the molecules. [1]

Melting point: $S_8 > P_4 > Cl_2$
- Number of electrons of $S_8 > P_4 > Cl_2$
- Hence, the strength of id–id attractions between the molecules decreases across the period from $S_8 > P_4 > Cl_2$

Amount of energy required to overcome the id–id attractions between the molecules decreases across the period from $S_8 > P_4 > Cl_2$ [1]

(c) (**B** and **C** could be metal oxides or chlorides due to the high melting points while **D** and **E** could be non–metal oxides or chlorides due to the low melting points.)

B is $\underline{SiO_2}$ (as it has a high melting point, insoluble in water and only reacts with hot concentrated NaOH.)

Reaction of B with hot NaOH:
$\underline{SiO_2 \text{ (s)} + 2OH^– \text{ (aq)} \rightarrow SiO_3^{2–} \text{ (aq)} + H_2O \text{ (l)}}$

C is $\underline{NaCl}$ *(*as it has a high melting point and dissolves in water to form a neutral solution. Due to low charge density of Na^+, NaC*l* will not hydrolyse in water.)

D has a low melting point and dissolves in water to give an acidic solution. In addition, the ratio of **D** to precipitated $Cl^–$ = 1: 5.

D is $\underline{PCl_5}$
$\underline{PCl_5 \text{ (s)} + 4H_2O(l) \rightarrow H_3PO_4\text{(aq)} + 5HCl\text{(aq)}}$

E is $\underline{SO_3}$
It has low melting point and dissolves readily in water to give a strongly acidic solution.
$\underline{SO_3 \text{ (g)} + H_2O \text{ (l)} \rightarrow H_2SO_4 \text{ (aq)}}$

(It is an acidic oxide that reacts with aqueous sodium hydroxide in the ratio of 1:2.)
$\underline{SO_3 \text{ (g)} + 2OH^– \text{ (aq)} \rightarrow SO_4^{2–} \text{ (aq)} + H_2O \text{ (l)}}$

[6]

2 **(a)** **(i)** pV = nRT

$$n_1 = \frac{125 \times 101325 \times 60 \times 10^{-3}}{8.31 \times (273 + 27)}$$
$= 304.8$ [1]

$$\frac{125}{n_1} = \frac{50}{n_2}$$

$$\frac{n_1}{n_2} = 2.5$$

$n_2 = 121.9$ (number of moles of He remaining in the tank)

Number of moles of helium used to fill up the balloons
= 304.8 –121.9
= 183 mol [1]

(ii) At constant temperature $P_1V_1 = P_2V_2$. (Boyle's law)
$50 \times 60 \times 10^{-3} = 1.2 \times V_2$
$V_2 = \underline{2.5 \text{ m}^3}$ [1]

Let n = number of balloons and V_b = the volume of each blown–up balloon.
$V_b = \frac{4\pi r^3}{3} = \frac{4\pi(0.15)^3}{3} = 1.414 \times 10^{-2} \text{ m}^3$
$n = V_2/V_b = 176.8$

The remaining gas in the tank can fill up <u>176</u> balloons. [1]

(iii) Helium behaves more ideally in balloons. [1]

Since the pressure is lower in the balloon (1.2 atm) as compared to in the tank (50 atm), the helium gas molecules will be further apart in the balloon.

The volume of the gas molecules therefore becomes insignificant compared to the volume of the balloon.

OR

The intermolecular forces of attraction are negligible. [1]

(b) **(i)**

$$\begin{tikzcd}
CH_3CH(OH)CH_3(l) + 9/2O_2(g) \arrow[rr, "?"] & & 3CO_2(g) & + \; 4H_2O(l) \\
 & 3C(s) + 4H_2(g) + 5O_2(g) \arrow[ul, "-318"] \arrow[ur, "3 \times (-394)"] \arrow[urr, "4 \times (-286)"'] & &
\end{tikzcd}$$

[1] for cycle

$\Delta H^\ominus_c = -(-318) + 3(-394) + 4(-286) = \underline{-2008}$ or $\underline{-2010}$ kJ mol^{-1} [1]

(ii)

Energy taken in during Bond breaking	Energy released during Bond forming
2 x C–C = 2 x 350 7 x C–H = 7 x 410 1 x C–O = 1 x 360 1 x O–H = 1 x 460 9/2 x O=O = 4.5 x 496	3 x 2 x C=O = 6 x 805 4 x 2 x O–H = 8 x 460
6622	8510

$\Delta H^\ominus_c = 6622 - 8510 = -1888$ kJ mol^{-1} [1]

$$\begin{tikzcd}
CH_3CH(OH)CH_3(g) + 9/2\,O_2(g) \arrow[r, "-1888"] & 3CO_2(g) + 4H_2O(g) \\
CH_3CH(OH)CH_3(l) + 9/2\,O_2(g) \arrow[r, "-2008"] \arrow[u, "\Delta H^\ominus_{vap}"] & 3CO_2(g) + 4H_2O(l) \arrow[u, "4 \times 41"']
\end{tikzcd}$$

$\Delta H^\ominus_{vap} = -2008 + 4 \times (41) - (-1888) = \underline{+44.0}$ kJ mol^{-1} [1]

(iii)
- ΔH for combustion is negative
- ΔS for combustion is positive as the number of gaseous particles increases. [1]

- $-T\Delta S$ is negative
- Since $\Delta G = \Delta H - T\Delta S$
  ⇨ ΔG will always be negative and the reaction is spontaneous at all temperatures. [1]

(c) **(i)**
- (least acidic) 2–methylpropan–2–ol, 2,2–dimethylpropanoic acid, 2–chloro–2–methylpropanoic acid, (most acidic) [1]

Compare alcohol with acids:

- Both 2–chloro–2–methylpropanoic acid and 2,2–dimethylpropanoic acid are more acidic than 2–methylpropan–2–ol as the negative charge on the carboxylate ion is distributed equally [1] between the two O atoms and hence stabilises the ion to a greater extent. The dissociation of the acid to release H^+ is highly favoured.

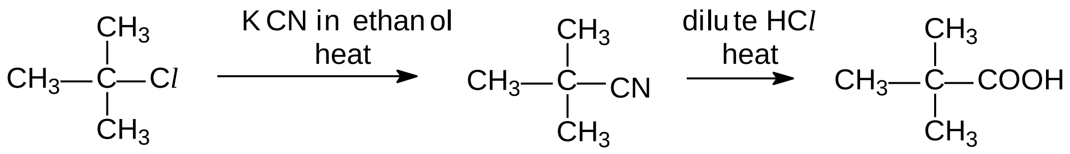
Compare 2,2–dimethylpropanoic acid with 2–chloro–2–methylpropanoic acid

- 2–chloro–2–methylpropanoic acid is the most acidic due to the presence of electron–withdrawing Cl atom, which disperses the negative charge on the carboxylate ion to an even greater extent [1] and stabilises it more.

OR

- 2,2–dimethylpropanoic acid is less acidic due to the presence of electron–donating alkyl (methyl) group, which intensifies the negative charge on the anion (carboxylate ion) and destabilises it. Therefore, the dissociation of this acid to release H^+ is less favourable.

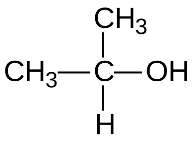
(ii)



[1] [1] [1]

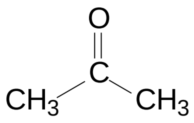
(iii) Step 1: aq. NaOH, heat [1]
Step 2: acidified $K_2Cr_2O_7$ or $KMnO_4$, heat [1]
Step 3: CH_3MgBr, followed by H_3O^+ [1]

G:



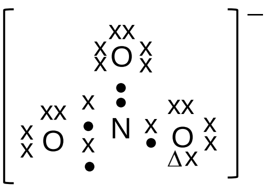
[1]

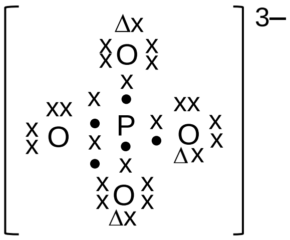
H:



[1]

3 **(a)** **(i)**





[1] each

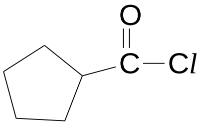
NO_3^- : trigonal planar
PO_4^{3-}: tetrahedral

both correct shapes [1]

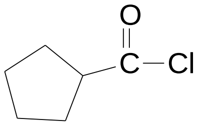
(ii) sp^2 [1]

(iii) The continuous overlap of p orbitals between the N and O atoms allow the lone pair / negative charge on the O atom to be delocalised into the N=O bond. [1]
As a result, all the N–O bonds have partial double bond character.
(or words to the same effect)

(b) **(i)** Step 1: CH_3COCl [1]
Step 2:

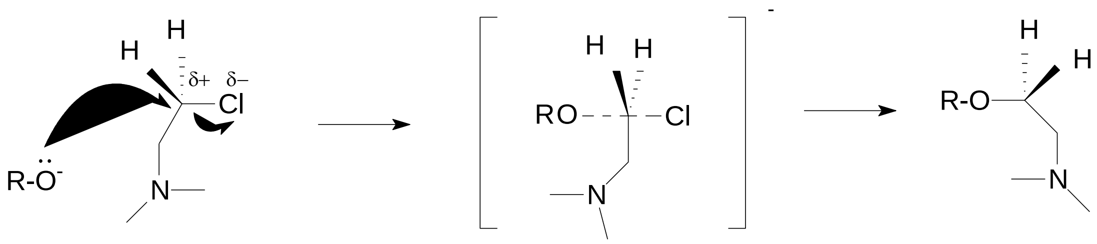
$AlCl_3$ and 

[1]

(ii) If step 2 is carried out first,  can react with phenylamine via nucleophilic substitution, triggering an unwanted reaction. [1]

(iii) Sodium ethoxide is added as a base to deprotonate the phenol to generate a stronger nucleophile.

(iv) nucleophilic substitution (S_N2)

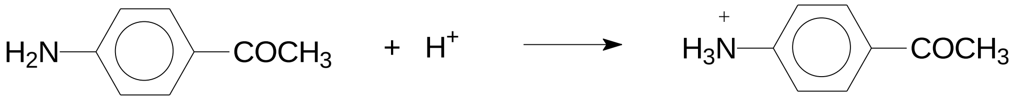


[3]

(v) Rate is ¼ times the original rate [1]

(vi) Phenol is more reactive towards electrophilic substitution. C=O attached to the benzene in K is electron–withdrawing [1] due to the more electronegative O atom. This will reduce the electron density of the benzene ring, making it less susceptible to be attacked by an electrophile/for electrophilic substitution [1].

(c) **(i)**



4–aminoacetophenone undergoes acid–base reaction with HC*l* [1] to form an anion salt. Being ionic, it can form favourable ion–dipole interactions with water molecules [1], making it soluble in water.

Acetanilide has a neutral amide functional group and will not undergo acid–base reaction with HC*l*. Hence, it exists as molecular form which is insoluble in water due to non–polar benzene ring. [1]

(ii) 1. Dissolve the mixture in aqueous mineral acid such as dilute HC*l* or H_2SO_4.
2. Filter the mixture to recover the solid acetanilide.
3. Add excess aq NaOH to the filtrate (aqueous solution) until the solid reappears
4. Filter the mixture to recover the solid 4–aminoacetophenone.

[2]

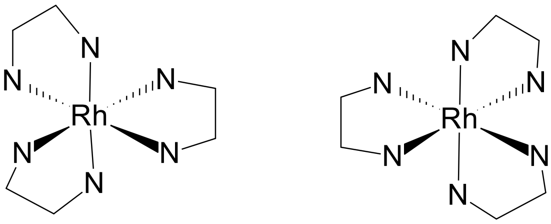
4 **(a)** **(i)** A ligand is a neutral molecule or an anion that has at least one lone pair of electrons to be used in forming a dative bond to the central metal atom or ion. [1]

(ii) +1 [1]

(iii) **M** is a catalyst since it is reacted/consumed in step 1 and regenerated in step 4 of the mechanism. [1]

N is an intermediate since it is formed in step 2 and reacted/consumed in step 3 of the mechanism. [1]

(v)



Either structure [1]

(b) **(i)** $[V(H_2O)_6]^{2+}$ has an oxidation number of +2, with 3 electrons in the 3d subshell. $[V(H_2O)_6]^{3+}$ has an oxidation number of +3, with 2 electrons in the 3d subshell.

The different electronic configurations OR different number of d electrons cause magnitude of the energy gap (ΔE) to be different. [1]

Since the ΔE is different in the different complex ions, the colours of the complex ions are different.

(ii) $NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O \quad E^\ominus = +0.96$ V
$V^{3+} + e \rightleftharpoons V^{2+} \quad E^\ominus = -0.26$ V

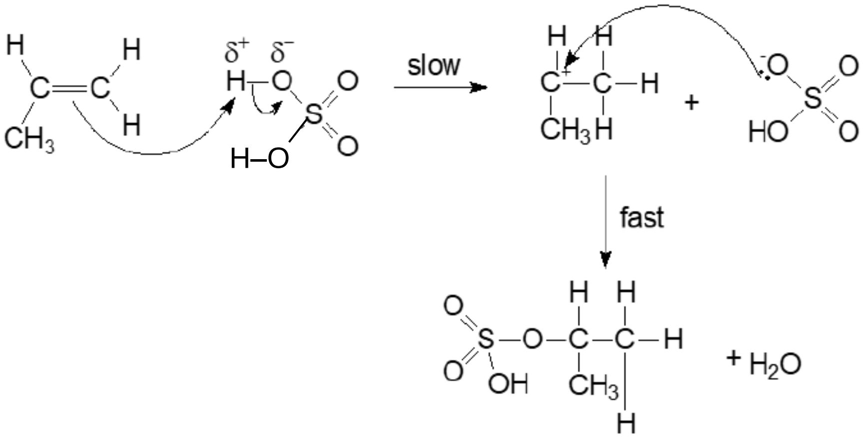
$E^\ominus_{cell} = +0.96 - (-0.26) = +1.22 \text{ V} > 0$

$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O \quad E^\ominus = +0.96$ V
$VO^{2+} + 2H^+ + e \rightleftharpoons V^{3+} + H_2O \quad E^\ominus = +0.34$ V

$E^\ominus_{cell} = +0.96 - (+0.34) = +0.62 \text{ V} > 0$
Products: VO^{2+}, NO and H_2O [1]

Overall equation: $3V^{2+} + 2NO_3^- + 2H^+ \longrightarrow 3VO^{2+} + H_2O + 2NO$ [1]

(c) **(i)**



[1] displayed formula of H_2SO_4
[2] mechanism

(ii) A more substituted (secondary) carbocation intermediate, which is more stable is produced in the first step. (since a 2° C^+ has more electron–donating alkyl groups bonded to the C^+ to disperse the positive charge). [1]

(d) **(i)** $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1]

(ii) $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad E^\ominus = +1.33\text{ V}$

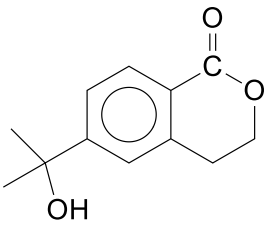
$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e \quad E^\ominus = +0.17\text{ V}$

$E^\ominus_{cell} = +1.33 - (+0.17) = \underline{+1.16\text{ V}}$ [1]

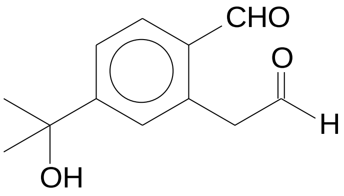
$$\begin{aligned}\Delta G^\ominus &= -nFE^\ominus_{cell}\\ &= -6(96500)1.16\\ &= \underline{672\,000\text{ J mol}^{-1}} \quad \text{OR} \quad \underline{-672\text{ kJ mol}^{-1}}\end{aligned}$$ [1]

(iii)

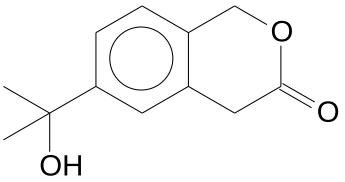
P:



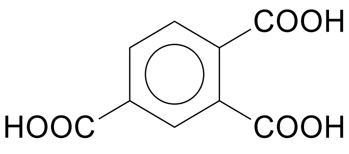
OR



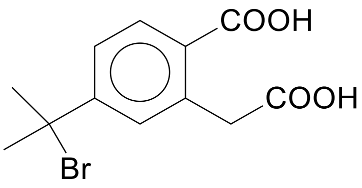
OR



Q:



S:



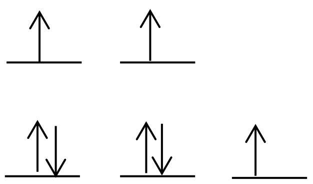
[1] each

(iv) C*l* 2 is more reactive than C*l* 1 [1]

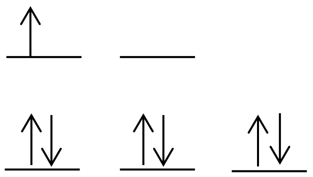
The C atom of the acyl group is highly electron–deficient, since it is bonded to two highly electronegative atoms, O and C*l*, while the C atom bonded to C*l* in alkyl chloride is only bonded to one electronegative atom, C*l*. [1]

OR nucleophile approaching the planar sp^2 carbon in acyl chloride experiences less steric hindrance than the tetrahedral sp^3 carbon in alkyl chloride.

5 **(a)** **(i)**



high spin state



low spin state

[1] each

(ii) The <u>high</u> spin state as it has a <u>greater</u> number of unpaired electrons. [1]

(iii)

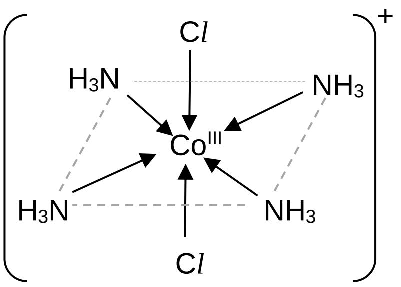
	Co	N	H	C*l*
% by mass	25.2	24.1	5.1	45.6
A_r	58.9	14.0	1.0	35.5
$\%/A_r$	0.428	1.72	5.1	1.28
simplest ratio	1	4	12	3

Empirical formula: $CoN_4H_{12}Cl_3$ [1]

(iv) $\text{nAgC}l = \frac{1.43}{107.9 + 35.5} = 9.97 \times 10^{-3}$ mol $\approx$ 0.01 mol

no. of moles of Ω: AgC*l* = 1 : 1

Hence, the six ligands around the cobalt ion are 4 NH_3 and 2 Cl^- ligands.



or the 2 Cl^- ligands placed diagonally to each other at the equatorial positions [2]

(b) **(i)** Cathode: $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Overall: $2NiO(OH) + 2H_2O + Cd \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

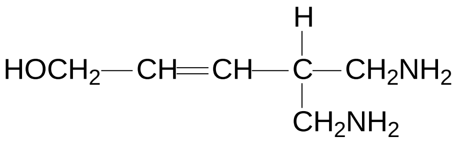
[1] for each equation (no need state symbols)

(ii) Mass of Cd to be restored = 100/86 x 5.5 = 6.395 g
n(Cd) = 6.395 / 112.4 = 0.0569 mol
n(electron) involved = 2 x 0.0569 = 0.1138 mol
Amount of charge required = 0.1138 x 96500 = 10982 C

Q = I x t
$\Rightarrow$ 10982 = 2.0 x t
time = 5491 s = <u>1.53 h</u>

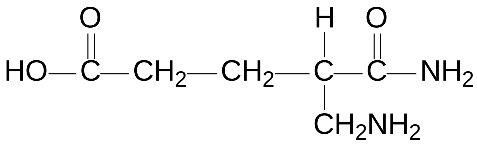
[1]: n(electron) required
[1]: charge required
(scaling to 100% can be done at any point before calculating the time)
[1]: answer expressed in hours

(c)



$HOCH_2-CH=CH-C(H)(CH_2NH_2)-CH_2NH_2$

I



$HO-C(=O)-CH_2-CH_2-C(H)(CH_2NH_2)-C(=O)-NH_2$

J

[1] each

(d)

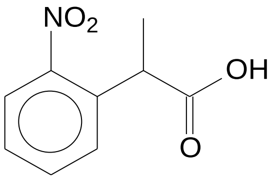
- W contains a chiral carbon since it rotates plane polarised light.
- W contains a nitrobenzene as it undergoes reduction with tin and concentrated HC*l* to form X which is a phenylamine.
- X contains a –COOH group since it undergoes acid–base reaction with sodium hydrogencarbonate to give carbon dioxide.
- X undergoes electrophilic substitution with Br_2(aq) to give compound Y, $C_9H_9NO_2Br_2$

  → Since only 2 Br are substituted, one of the 2, 4, 6 positions relative to $-NH_2$ group on benzene has another substituent.
- The –COOH in X undergoes nucleophilic (acyl) substitution with PCl_5 to give –COC*l*
- which then undergoes intramolecular nucleophilic (acyl) substitution to form Z.

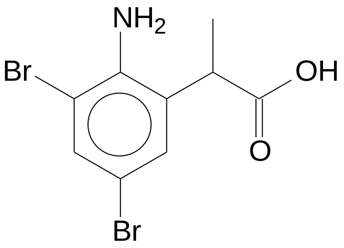
  ($-NH_2$ group in X attacks the electron deficient acyl C in the –COC*l* group)

  → $-NH_2$ and –COOH groups on benzene ring are at positions 1 and 2 / next to each other.

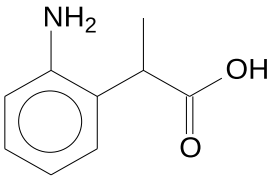
W:



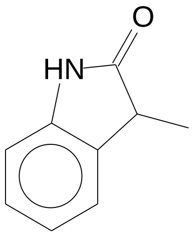
Y:



X:



Z:



[1] for each structure
[1] for every 2 correct deductions (max 3)

ANDERSON SERANGOON JUNIOR COLLEGE

H2 Chemistry 9729 **2019 JC2 Prelim Exam Paper 4 Solutions**

1 (a) Results

Chosen time/min	Actual time	t/min	Initial burette reading/cm^3	Final burette reading/cm^3	Volume of FA 4 used/cm^3
4	4 min 6s	4.1	0.00	15.90	15.90
8	8 min 3s	8.1	15.90	30.30	14.40
12	12 min 3s	12.1	0.00	12.90	12.90
16	15 min 56s	15.9	12.90	24.40	11.50
20	19 min 59s	20.0	24.40	34.50	10.10

***[1]**: Tabulates initial and final burette readings, volume of FA 4 added, chosen time, actual time and decimal time with correct headers and units*
***[1]**: record all volumes to 0.05 cm^3, actual time in min and s, correct calculation of t to 1 dp*
***[1]**: 5 sets of titration results and each aliquot is taken within ±0.5 min from the chosen time*

(b) (i)

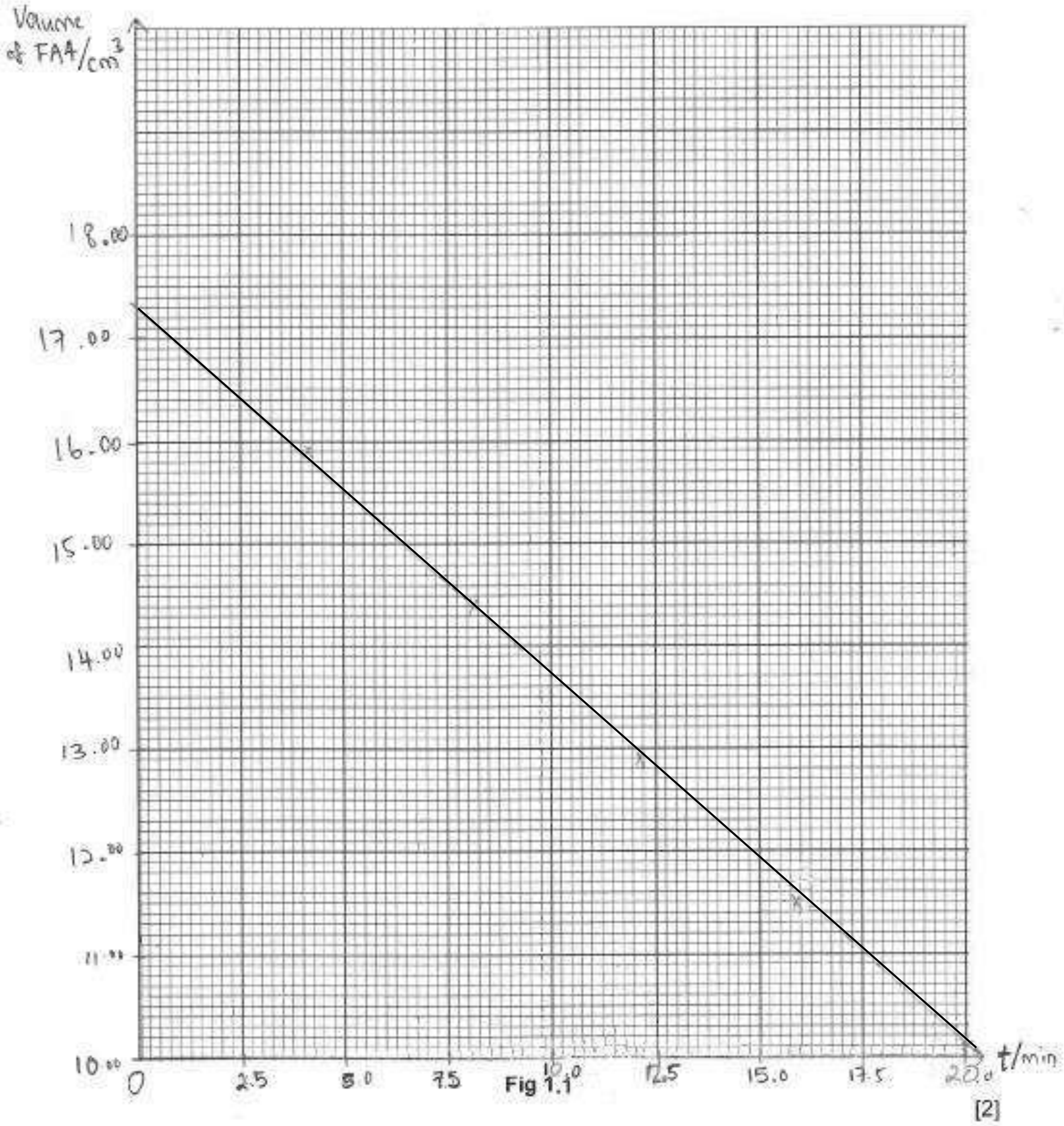


Fig 1.1

[2]

***[1]:** Both axes are correctly labelled + Scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions (taking into consideration the extrapolation) + no odd scale*
***[1]:** One plotted point is within ±½ small square*

(ii) Order of reaction is zero with respect to I_2 because it is straight line with constant gradient / rate of reaction is independent of $[I_2]$ / $[I_2]$ decreases linearly with time / $[I_2]$ does not affect rate / $[I_2]$ decreases at a constant rate. **[1]**

(c) **(i)** Rate = $k\,[CH_3COCH_3][H^+]$ **[1]**

(ii) Gradient = $\frac{y2-y1}{x2-x1} = \frac{9-14.8}{18.75}$ = -0.309 $cm^3\ min^{-1}$ (3 s.f with units) **[1]**

Show coordinates on the graph or in the working

(iii) rate of change = (c)(ii) x 0.01/1000
= 0.309 x 0.01/1000
= 3.09×10^{-6}
= 3.09×10^{-6} mol min^{-1} (3 s.f.) **[1]**

(iv) $I_2 \equiv 2S_2O_3^{2-}$

rate of disappearance of I_2 = $\frac{1}{2}$ x (c)(iii)
= $\frac{1}{2}$ x 3.09×10^{-6}
= 1.545×10^{-6}
= 1.55×10^{-6} mol min^{-1} (3 s.f.) **[1]**

(v) rate of change of $[I_2]$ = (c)(iv) ÷ 10/1000
= 1.545×10^{-6} ÷ 10/1000
≈ 1.55×10^{-4} mol dm^{-3} min^{-1} (3 s.f with units) **[1]**

(vi) (c)(v) = $k[CH_3COCH_3][H^+]$
$1.545 \times 10^{-4} = k\,[CH_3COCH_3][H^+]$
$1.545 \times 10^{-4} = k\,(1.00 \times \frac{1}{4})(1.00 \times 2 \times \frac{1}{4})$
$k = 1.24 \times 10^{-3}$ $mol^{-1}\ dm^3\ min^{-1}$ (3 s.f with units) **[1]**

(d) It is added to react with acid catalyst so that the reaction will stop / It is to quench the reaction by reacting with the acid catalyst. **[1]**

(e) The low concentration of iodine means that very little propanone and acid are reacted away from the reaction mixture and hence the concentration of propanone and acid remain effectively constant. Hence, the order of reaction with respect to iodine can be determined because any change in the rate is due to the change in concentration of iodine. **[1]**

(f) **(i)** nucleophilic substitution **[1]**

(ii) To prevent reaction of $CH_3CH_2CH_2Br$ with water/hydrolysis (if wet) **[1]**

(iii) Due to the low solubility of NaBr in propanone, NaBr formed gets precipitated out. Position of equilibrium shifts to the right. **[1] or**

Since sodium bromide is not soluble in water, there will not be sufficient Br^- ions to attack the electrophilic C attached to I, hence position of equilibrium favors right **or**

Since NaI is much more soluble than NaBr, [NaI] is >> [NaBr]. Forward rate is much greater than the backward rate. Hence, the reaction favors right.

(iv) Since 100% yield of pure 1–iodopropane is obtained and sodium iodide is used in excess,

n($CH_3CH_2CH_2Br$) required = n($CH_3CH_2CH_2I$) obtained
= 10 / 169.9 = 0.05886 mol

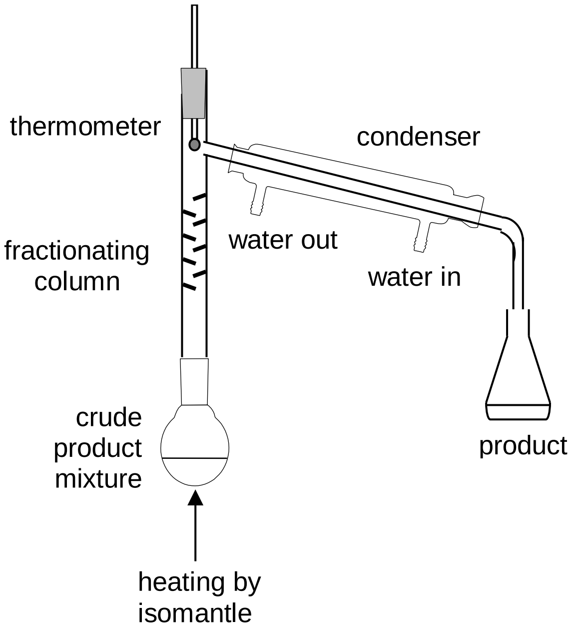
mass of $CH_3CH_2CH_2Br$ = 0.05886 x 122.9 = 7.234 g

minimum volume of $CH_3CH_2CH_2Br$ = 7.234 / 1.35 = 5.36 cm^3 **[1]**

(v) Minimum mass of sodium iodide required = 0.05885 x 149.9 = 8.82 g
Since sodium iodide is added in excess, mass of sodium iodide to be used > 8.82 g

Preparation of crude 1–iodopropane

1. Weigh accurately about 10 g of sodium iodide in a 50 cm^3 round–bottomed flask.
2. Using a 10 cm^3 measuring cylinder, transfer 6 cm^3 of 1–bromopropane to the flask.
3. Using a 50 cm^3 measuring cylinder, transfer 25 cm^3 of propanone to the flask.
4. Swirl the flask to ensure even mixing.
5. Add boiling chips (anti–bumping granules) to the mixture.
6. Using a water bath / isomantle, gentle heat the flask fitted with a reflux condenser for about 30 minutes.
7. Cool down the flask by removing the water bath / isomantle.
8. Remove the flask and fractionally distil the mixture to obtain the pure 1–iodopropane at its boiling point of 102.6 °C.
(Note: solid NaI and NaBr will remain in the flask)



*max. **[2]** for labelled diagram (fractionating column, thermometer, condenser, heating by isomantle clearly labelled)*

***[1]**: Sound quantities of 1–bromopropane, sodium iodide and propanone chosen for preparation of crude 1–iodopropane*
***[1]**: General procedure for preparation of crude 1–iodopropane*
***[1]**: Apparatus used for measurements (measuring cylinders) & reflux (round–bottomed flask, reflux condenser, hot water bath / isomantle)*

2 (a) (i) Results

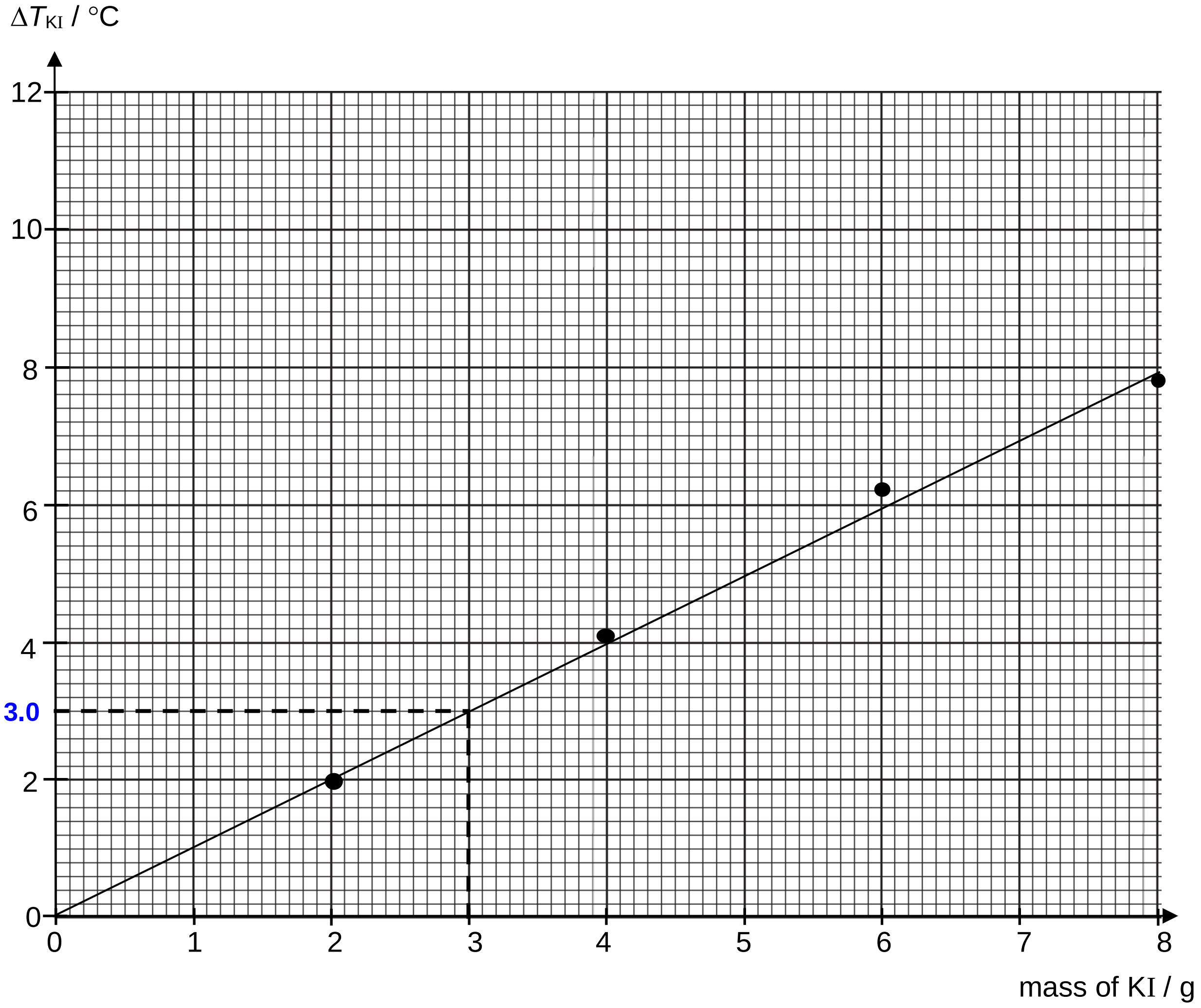
mass of empty weighing bottle / g	
mass of weighing bottle + KI / g	
mass of weiging bottle + residual KI / g	
mass of KI used / g	**2.013**

initial temperature of water / °C	
minimum temperature reached / °C	
ΔT_{KI} / °C	**2.0**

[1]: *Both tables have correct headers and units*
[1]: *Weighs between 1.950 g to 2.050 g of KI* ***and*** *correctly calculates mass of KI used and correctly calculates* ΔT_{KI}

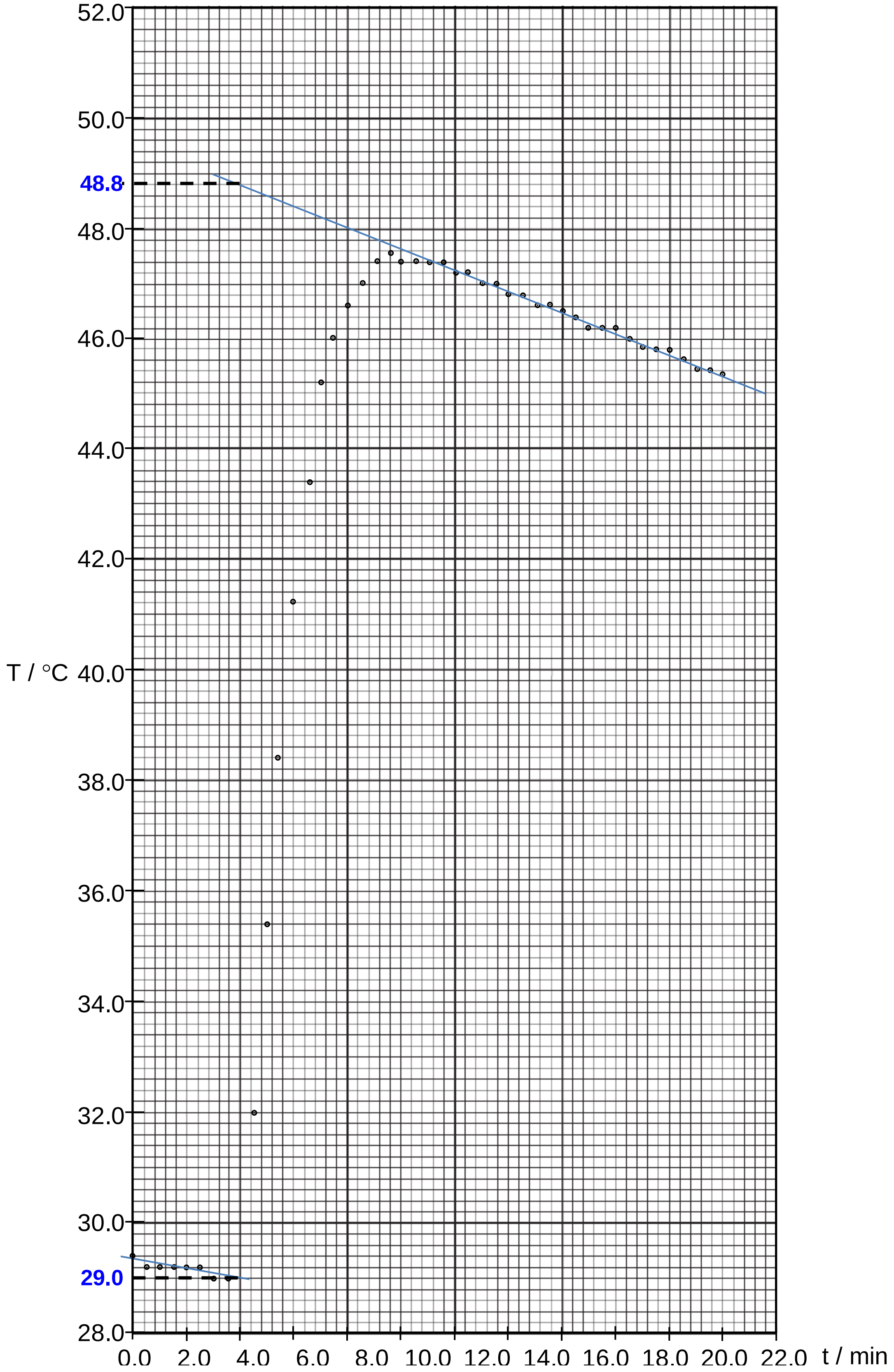
Final mass of KI dissolved may be out of range, but initially weighed mass must be within range.
[1]*: All temperature recorded and calculated* ΔT_{KI} *value are to 0.1 °C,* ***and*** *all mass recorded calculated mass of KI used are to 3 d.p.*
[1]*: Accuracy: how close the point is to the teachers' result (2 small square from teachers result)*

(ii)



[1]: *Correctly plots all points and draws line of best–fit which passes through the origin*

(b)



ΔT_m = 48.8 – 29.0 = <u>19.8 °C</u> *(read T_{max} and T_{min} correctly to ±½ small square, i.e. to 0.1 °C (1 d.p)*

[1]: *Draws best–fit line (instead of horizontal line) for the points before* ***FA 6*** *was added.*
[1]: *Correctly calculates ΔT_m (allow ±0.4 °C difference from teachers' value because of 1 small square (±0.2 °C) allowance for each temperature reading).*

(c) **(i)** ***[1]:*** *Correctly reads off ΔT_{KI} for m g of potassium iodide from plotted graph at the point*

$$m = \frac{\text{mass of FA 6 used}}{2} = \frac{6.020}{2} = 3.010 \text{ g}$$

Or correctly calculates using ΔT per gram of KI by finding gradient
Working on the graph, e.g. dotted lines or otherwise, must be shown.

(ΔT_{KI}: read to ±½ small square, i.e. to 0.1°C (1 d.p))

(ii) ***[1]****: Correctly calculates change in temperature due to lithium chloride,*
$\Delta T_m - \Delta T_{KI} = \Delta T_{LiCl}$ (to 0.1°C (1 d.p))

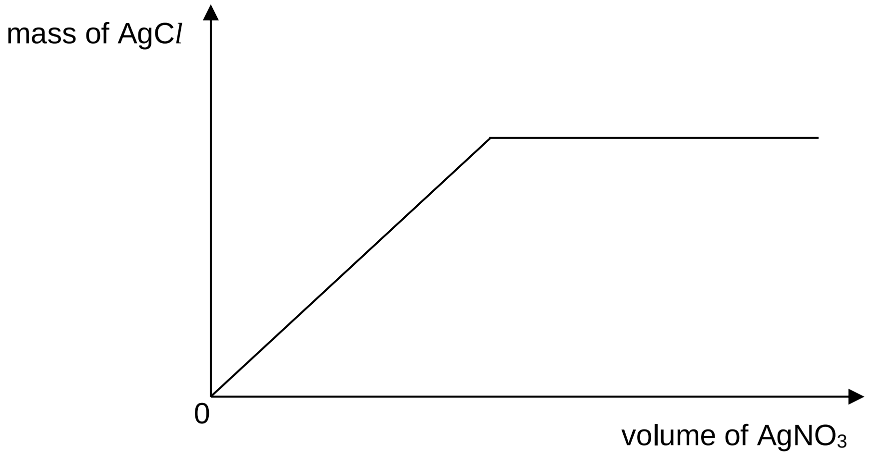
(iii) ***[1]****: Correctly calculates the value of change in temperature of water per gram of lithium chloride =* $\frac{\Delta T_{LiCl}}{(6.020 \div 2)}$ *(3 s.f)*

[1]*: Correct significant figures for 1(c)(ii) to (c)(vi); 2(b), (c)(i) to (c)(iii)*
[1]*: Correct units for 1(c)(ii),(v),(vi)*

(d) **(i)** Insoluble barium chromate is formed. **[1]**

(ii) The formation of insoluble barium sulfate will ensure that insoluble barium chromate is not formed during titration. **[1]**

(iii)



Straight line through origin ***and*** *reaches a plateau* ***[1]***

(iv)
1. Weigh accurately about 3.00 g of $BaCl_2.xH_2O$ in a pre–weighed weighing bottle, using a weighing balance (or electronic balance)
2. Dissolve this solid in a beaker with 30 cm^3 of *water*.
3. Transfer the solution and washings into a 250 cm^3 graduated flask and make up to the mark with deionised water
4. Shake the solution to obtain a homogeneous solution.
5. Reweigh the emptied weighing bottle.

[1]*: Sound procedure for standard solution preparation (weigh solid, dissolve in water, transfer, make up to the mark)*
[1]*: Ensures accuracy and reliability for preparation of standard solution (use of graduated flask, transfer washings, shake, reweigh if solid not completely transferred to graduated flask)*

(v) First: sulfuric acid
Second: potassium chromate(VI)
Third: silver nitrate

3 **(a)**

	test	observations
1.	*Add 1 cm depth of **FA 7** to a test–tube.* *Add aqueous ammonia slowly, with shaking, until no further change is seen.* *Filter the mixture and add dilute nitric acid drop–wise to the filtrate, until no further change is seen.* *(You may continue with test 2, while waiting for the filtration process to complete.)*	(Off) white ppt, insoluble in excess NH_3 Filtrate is colourless Residue is brown in colour White ppt reappears, soluble in excess acid
2.	*Add 1 cm depth of **FA 7** to a test–tube.* *Add aqueous barium nitrate to **FA 7**,* *followed by dilute nitric acid.*	White ppt formed White ppt insoluble in acid

[3]

FA 7 contains the cations Mn^{2+} and Zn^{2+}.

identity	evidence
FA 7 contains cation: **Mn^{2+}**	Off white ppt, insoluble in excess NH_3 Brown ppt formed on standing
FA 7 contains cation: **Zn^{2+}**	White ppt soluble in excess NH_3 White ppt reforms when dilute acid is added dropwise

FA 7 contains the anion SO_4^{2-}. **[2]**

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(b) (i)

	test	observations
1.	*Add 1 cm depth of **FA 8** to a test–tube.* *Add **FA 4** slowly, with shaking, until no further change is seen.* *Leave it to stand.*	Yellow solution turns brown/reddish brown/dark orange/violet Yellow solution reforms
2.	*Add 1 cm depth of **FA 8** to a test–tube.* *Add 1 cm depth of **FA 5**, with shaking, until no further change is seen.*	Orange/red–brown ppt. Effervescence observed. Colourless gas evolved gives a white ppt with $Ca(OH)_2$/ limewater.
3.	*Add 1 cm depth of **FA 8** to a test–tube.* *Add 1 cm depth of aqueous potassium iodide, with shaking, until no further change is seen.*	Yellow solution turns brown.

[2]

(ii) Fe^{3+} has a high charge density. Hence, the cation can polarise the water molecules, giving rise to an acidic solution.

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

The acidic solution undergoes acid–base reaction with $NaHCO_3$ to give CO_2 and a red–brown ppt of $Fe(OH)_3$.

(iii)
- Fe^{3+} is an oxidising agent. Fe^{3+} oxidises I^- to brown I_2 **[1]**
- Reaction between $[Fe(H_2O)_6]^{3+}(aq)$ and I^-:
  $E^\ominus_{cell} = +0.77 - 0.54 = +0.23\ V > 0$ ⇒ reaction is feasible **[1]**

(iv) Reaction between $[Fe(CN)_6]^{3-}$ and I^-:
$E^o_{cell} = +0.36 - 0.54 = -0.18\ V < 0$ ⇒ reaction is not feasible.

***[1]**: Correct calculation of $E^\ominus_{cell}$ ($E^\ominus$ values quoted)*

CN^- ligands stabilise Fe^{3+} more than Fe^{2+}, thus $E^o([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-})$ is less positive than $E^o(Fe^{3+}/Fe^{2+})$. $[Fe(CN)_6]^{3-}$ is less easily reduced / is a weaker oxidising agent than $Fe^{3+}(aq)$. **[1]**

(v)
- Purple organic layer
- Yellow / Brown aqueous layer **[1]**

Note: Both layers are immiscible.

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

18 September 2019
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.

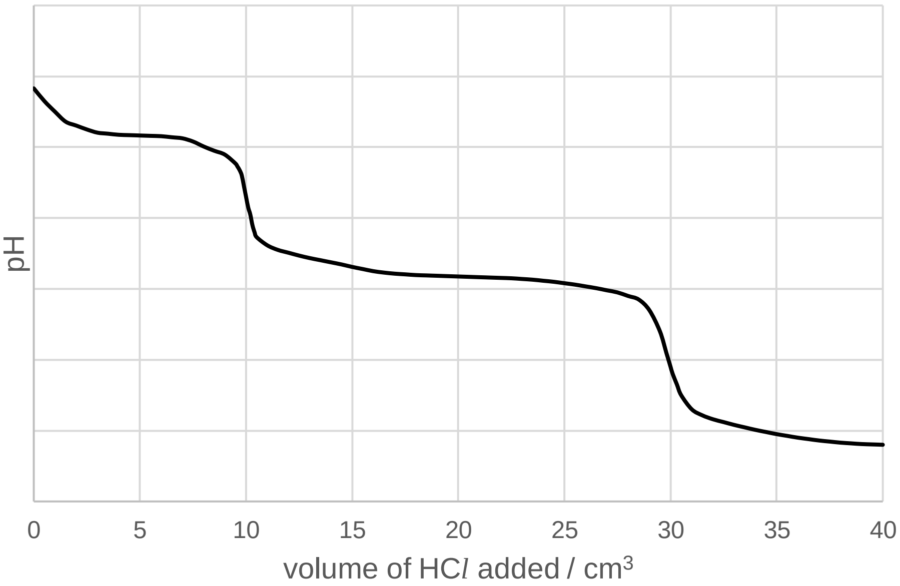
Any rough working should be done in this booklet.

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

This document consists of **18** printed pages.

1 An aqueous mixture of sodium carbonate and sodium hydrogencarbonate was titrated with hydrochloric acid and the pH was recorded.

What is a suitable indicator to use for detecting the first end point and the ratio of sodium carbonate to sodium hydrogencarbonate in the mixture?



	indicator	ratio
A	methyl orange	1:1
B	methyl orange	1:2
C	thymol blue	1:1
D	thymol blue	1:2

2 The most common oxidation state of americium, Am, in aqueous solution is +3.

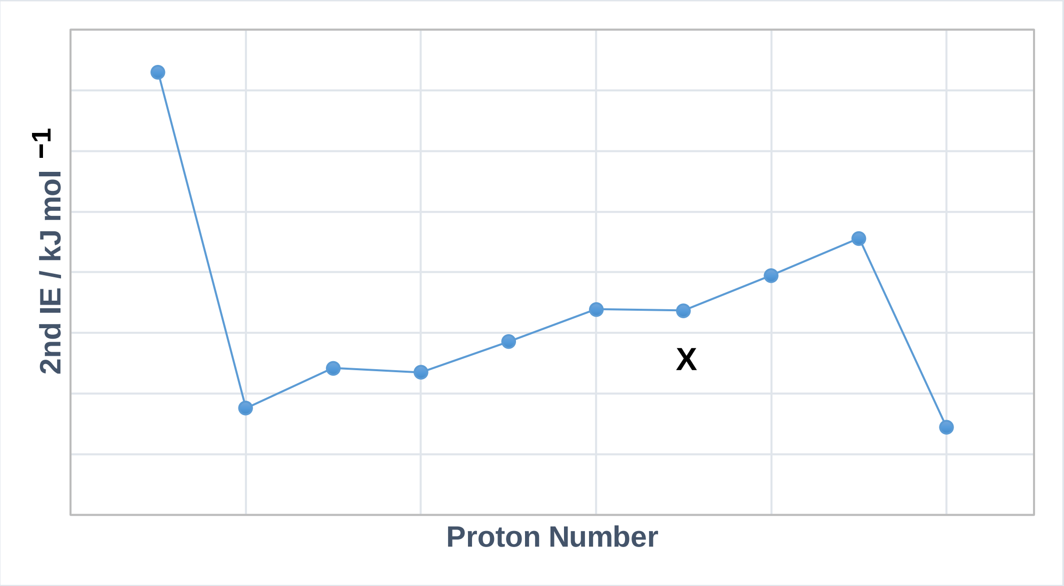
Recently, Cu^{3+} has been shown to quantitatively oxidise Am^{3+}(aq) in dilute HNO_3, while itself is reduced to Cu^{2+}.

In an experiment, 20.0 cm^3 of 0.0120 mol dm^{-3} Am^{3+}(aq) was found to require 24.00 cm^3 of 0.0300 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium-containing species formed?

A AmO^+ **B** AmO^{2+} **C** AmO_2^{2+} **D** $Am_2O_2^{2+}$

3 The graph shows the second ionisation energies for ten consecutive elements.

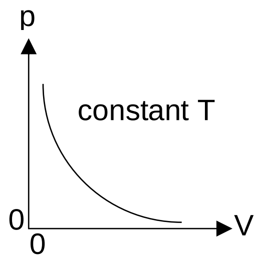


Which of the following could be **X**?

A oxygen **B** fluorine **C** neon **D** sodium

4 Which of the following graphs are correct about a fixed amount of an ideal gas?

1



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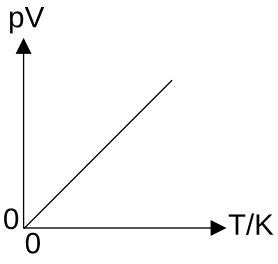

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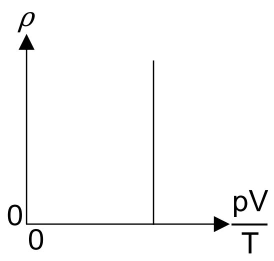


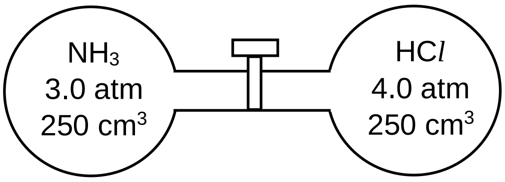
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D all of the above

5 Two single-neck round-bottomed flasks were evacuated and insulated from the surroundings. They were filled separately with gaseous ammonia and gaseous hydrogen chloride at room temperature and connected with a gas tap joint.



When the gas tap joint is opened, the two gases are allowed to mix.

What is the final pressure of the resultant gas mixture?

A more than 3.5 atm but less than 7.0 atm

B exactly 3.5 atm

C more than 0.5 atm but less than 1.0 atm

D exactly 0.5 atm

6 When 1.00 g of ethanol was burned under a beaker of water, it was found that 100 cm^3 of water was heated from 15 °C to 65 °C. The process was known to be only 70% efficient.

Use these data and values from the *Data Booklet* to calculate the enthalpy change of combustion of ethanol.

A -209 kJ mol^{-1}

B -673 kJ mol^{-1}

C -1373 kJ mol^{-1}

D $+1373$ kJ mol^{-1}

7 Some standard enthalpy changes are given below.

	$\Delta H^{\ominus}$ / kJ mol^{-1}
$Ca^{2+}(g) + aq \longrightarrow Ca^{2+}(aq)$	-1650
$Cl^-(g) + aq \longrightarrow Cl^-(aq)$	-364
$Ca^{2+}(g) + 2Cl^-(g) \longrightarrow CaCl_2(s)$	-2258

What is the standard enthalpy change of solution of calcium chloride?

A $+244$ kJ mol^{-1}

B -120 kJ mol^{-1}

C -2378 kJ mol^{-1}

D -4636 kJ mol^{-1}

8 Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

In the investigation of this reaction, the following results were obtained.

initial concentrations of reactants / mol dm^{-3}			initial rate of formation of iodine / mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^-]$	$[H^+]$	
0.01	0.01	0.10	2.0×10^{-6}
0.03	0.01	0.10	6.0×10^{-6}
0.03	0.02	0.10	1.2×10^{-5}
0.03	0.02	0.20	1.2×10^{-5}

Which of the following statements are correct?

1 The rate equation can be written as: rate = k $[H_2O_2][I^-]$.

2 The reaction is second order with respect to H^+.

3 The value of the rate constant is 0.2.

A 1 only

B 2 only

C 1 and 2

D 1, 2 and 3

9 Phosphorus(V) chloride, PCl_5, is a white solid which sublimes at 160 °C.

When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

Rate constant, k_b, applies for the backward reaction and equilibrium constant, K_c, applies for the overall process.

How will the values of k_b and K_c change when the equilibrium is established at a higher temperature than before?

	k_b	K_c
A	increase	increase
B	increase	decrease
C	decrease	increase
D	decrease	decrease

10 When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

0.0200 moles of phosphorus(V) chloride was vaporised completely in a 2.0 dm^3 container. The amount of chlorine gas detected at equilibrium was found to be 0.00400 moles.

What is the value of K_c at this temperature?

A 1.0×10^{-3}

B 8.0×10^{-4}

C 5.0×10^{-4}

D 4.0×10^{-4}

11 The value of pK_w at 40 °C is 13.54.

What is the pH of an aqueous solution of 0.05 mol dm^{-3} $Ba(OH)_2$ at 40 °C?

A 12.23

B 12.54

C 12.70

D 13.00

12 In which of the following solutions will solid calcium phosphate, $Ca_3(PO_4)_2$, be the least soluble at 25 °C? The numerical value of K_{sp} of $Ca_3(PO_4)_2$ is 2.07×10^{-33}.

A 0.3 mol dm^{-3} $Ca(NO_3)_2$ (aq)

B 0.3 mol dm^{-3} Na_3PO_4 (aq)

C 0.6 mol dm^{-3} HNO_3 (aq)

D water

13 A cell diagram is written as follows:

$$\text{Ti(s)} \mid \text{Ti}^{2+}\text{(aq)} \parallel \text{H}_2\text{SO}_4\text{(aq)} \mid \text{SO}_2\text{(g)} \mid \text{Pt(s)}$$

Use relevant data from the *Data Booklet*, and the following electrode potential

$$\text{Ti}^{2+}\text{(aq)} + 2\text{e}^- \rightleftharpoons \text{Ti(s)} \qquad E^\ominus = -1.63\text{V}$$

to calculate the standard Gibbs free energy change of the cell in kJ mol^{-1}.

A −37 **B** −157 **C** −282 **D** −347

14 *Use of the Data Booklet is relevant to this question.*

The standard reduction potentials of some vanadium species are tabulated below.

half-reaction	$E^\ominus$ / V
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34

Which of the following metals, when added in excess, will reduce VO^{2+} to V^{3+}?

1 Sn

2 Zn

3 Pb

A 1 and 3

B 2 and 3

C 1 only

D 2 only

15 *Use of the Data Booklet is relevant to this question.*

Impure copper containing traces of cobalt, iron and silver was purified via electrolysis.

Which cations of the trace metals can be found in solution?

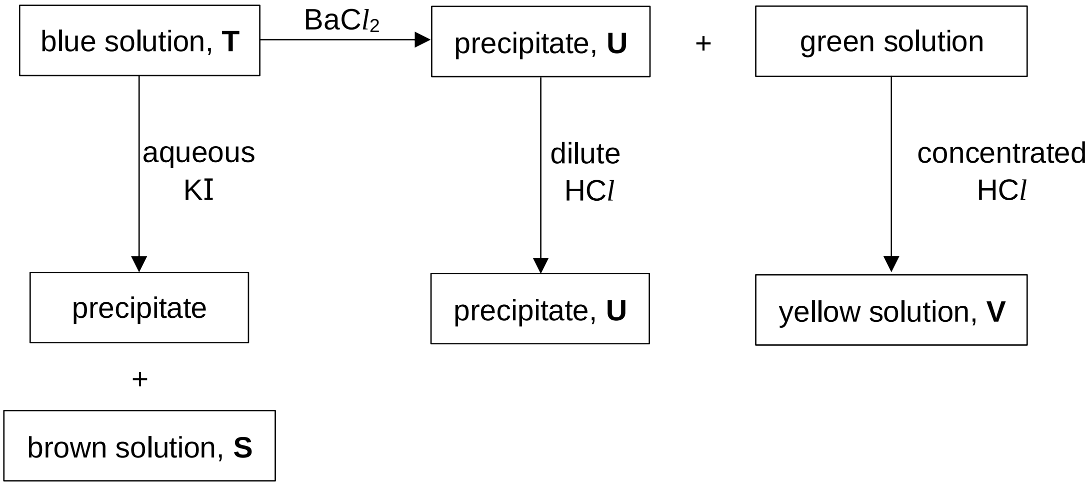
A Ag^+ only

B Ag^+ and Fe^{2+}

C Co^{2+} and Fe^{2+}

D Co^{3+} and Fe^{3+}

16 An aqueous transition metal compound, **T**, was subjected to a series of reactions.



Which statements are correct?

1 The anion in **S** is I^-.

2 The anion in **U** is SO_3^{2-}.

3 The anion in **V** is $CuCl_4^{2-}$

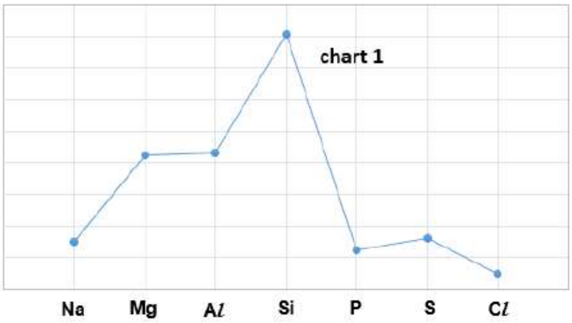
A 1 and 2

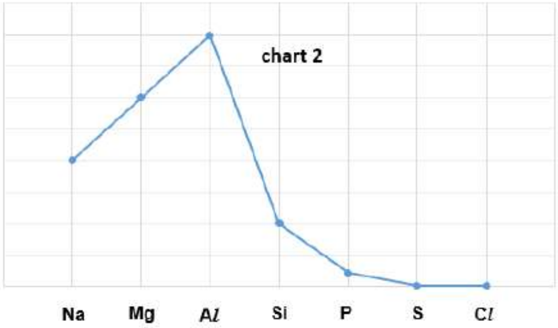
B 2 and 3

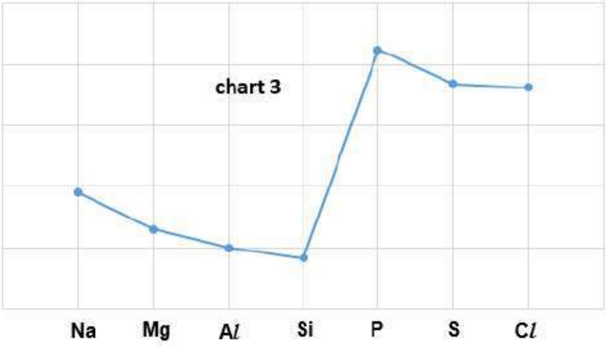
C 1, 2 and 3

D 3 only

17 Three charts below show the variation of three physical properties for the Period 3 elements.







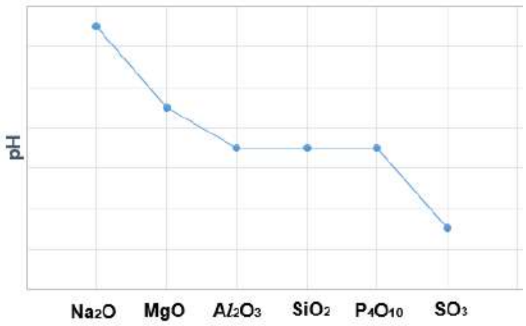
Which of the following is correct?

	chart 1	chart 2	chart 3
A	ionic radius	electrical conductivity	melting point
B	electrical conductivity	melting point	ionic radius
C	melting point	ionic radius	electrical conductivity
D	melting point	electrical conductivity	ionic radius

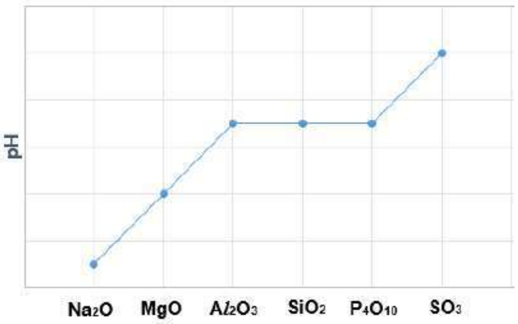
18 The highest oxides of the elements sodium to sulfur are added separately to water.

Which of the following diagrams best represents the pH of the solutions produced?

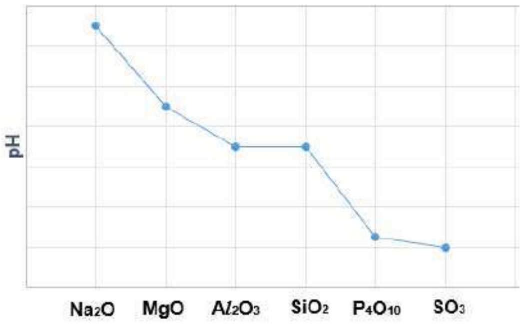
A



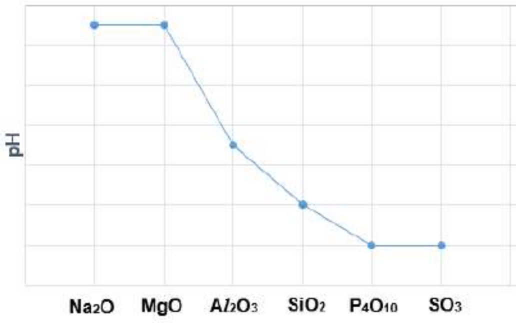
B



C



D



19 Stability constants and colours are given in the following table for this reaction.

$$Fe(H_2O)_6^{3+} + L^- \rightleftharpoons Fe(L)(H_2O)_5^{2+} + H_2O$$

ligand	lg K_{stab}	colour of $Fe(L)(H_2O)_5^{2+}$
SCN^-	2.1	blood red
F^-	5.4	colourless

What would be observed when the following reagents are added to a solution of iron(III) nitrate?

- potassium fluoride
- followed by potassium thiocyanate

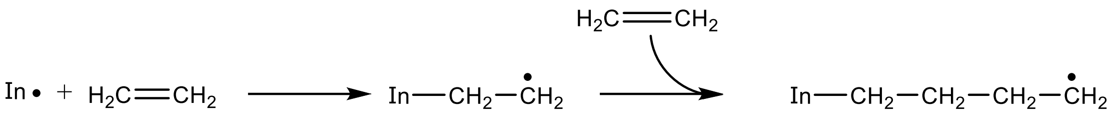
A Solution turns from green to colourless, and then blood red.

B Solution turns from green to colourless, and then remains colourless.

C Solution turns from yellow to colourless, and then to blood red.

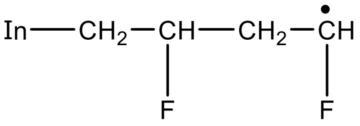
D Solution turns from yellow to colourless, and then remains colourless.

20 Free radical addition is a mechanism used in the synthesis of some addition polymers. Alkene monomers will polymerise in the presence of a radical initiator (In•). For instance, the synthesis of polyethene begins as such.

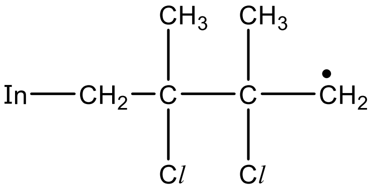


Which of the following chains could **not** have arisen from free radical addition?

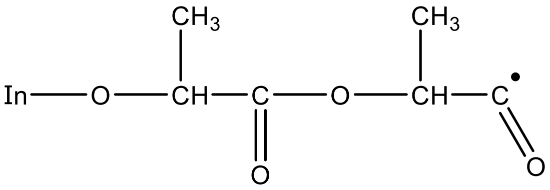
A



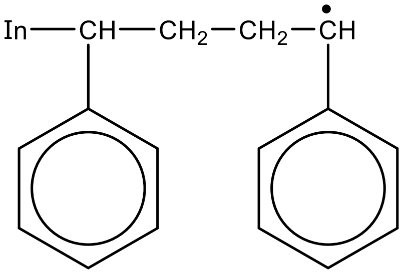
B



C



D



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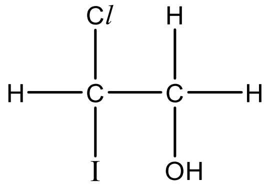
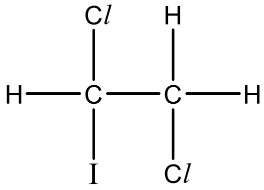
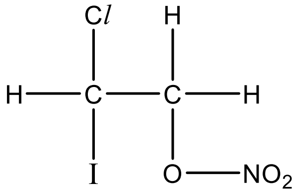
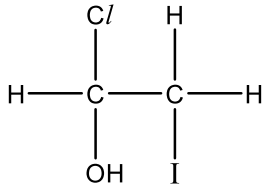
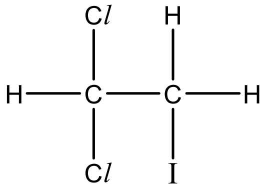
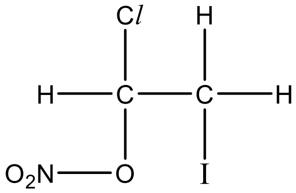
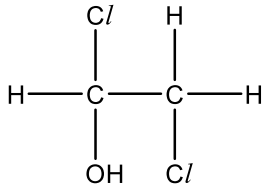
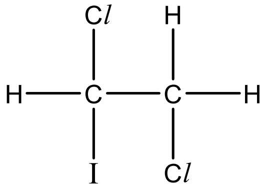
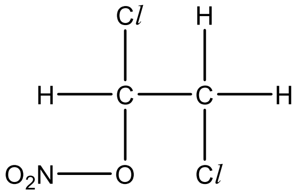
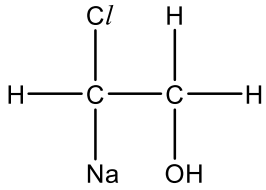
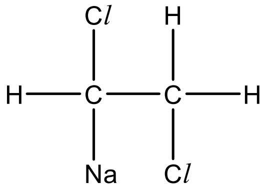
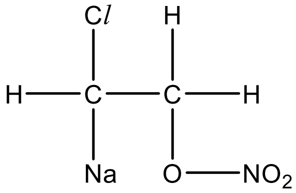
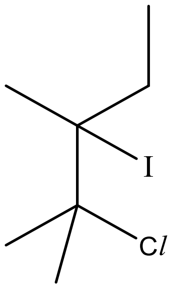
21 Chloroethene is reacted with iodine monochloride in the presence of aqueous sodium nitrate.

Which are the major and minor products?

	major product	minor products
A		 
B		 
C		 
D		 

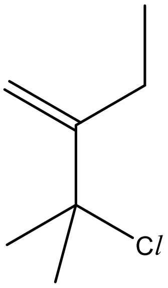
22 The following compound **Y** is reacted with ethanolic sodium hydroxide.



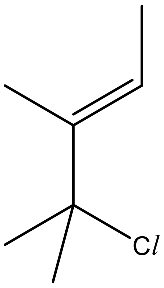
Compound **Y**

Which of the following is the **major** product?

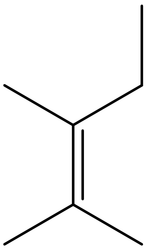
A



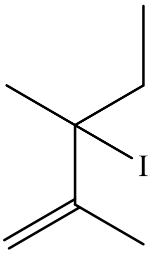
B



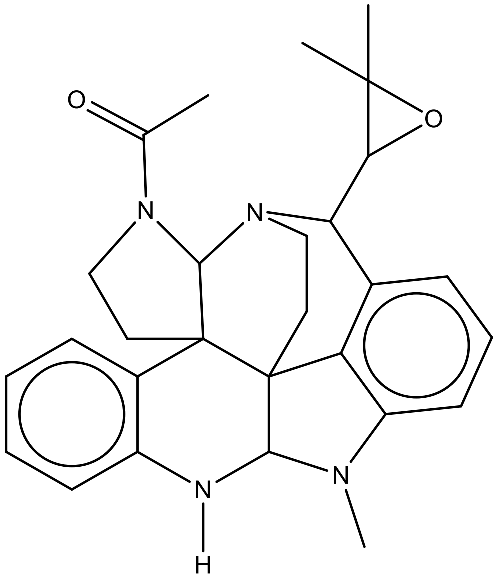
C



D



23 Communesin A is a natural product.



Which of the following statements about communesin A is correct?

A Communesin A gives a yellow precipitate when warmed with alkaline iodine solution.

B There are three tertiary amines in communesin A.

C It is a planar molecule.

D One of the oxygen atoms is sp^3 hybridised; the other is sp^2 hybridised.

24 Compound **B**, $C_6H_{12}O_6$, is an important biomolecule abundant in the brain as it mediates cell signal transduction in response to a variety of hormones and neurotransmitters.

All the atoms (besides the hydrogen atoms) in **B** are sp^3 hybridised.

On adding excess sodium to **B**, hydrogen gas is liberated.

Which of the following statements about compound **B** is true?

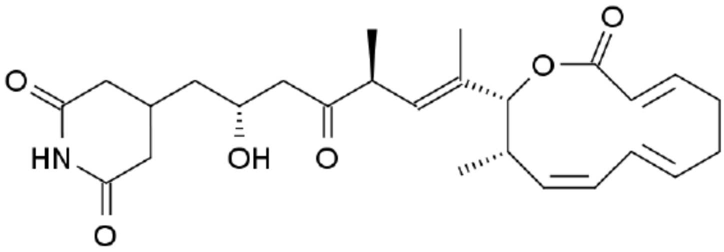
A Compound **B** forms a purple colouration with neutral iron(III) chloride solution.

B Compound **B** forms a yellow precipitate with warmed alkaline iodine solution.

C Compound **B** forms a bright orange precipitate with 2,4-dinitrophenylhydrazine.

D Compound **B** forms a brick-red precipitate with Fehling’s solution.

25 Lactimidomycin is an antibiotic with anti-viral and anti-cancer properties.



Which statements about lactimidomycin are correct?

1 One mole of lactimidomycin reacts completely with four moles of 2,4-dinitrophenylhydrazine.

2 On reacting lactimidomycin with hot acidified $KMnO_4$, there is no gas evolved.

3 On heating lactimidomycin with KOH(aq), there is ammonia gas evolved.

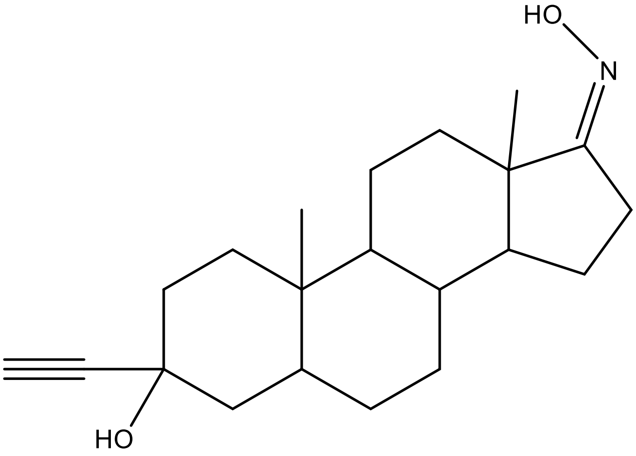
A 1 and 2

B 2 and 3

C 1 only

D 3 only

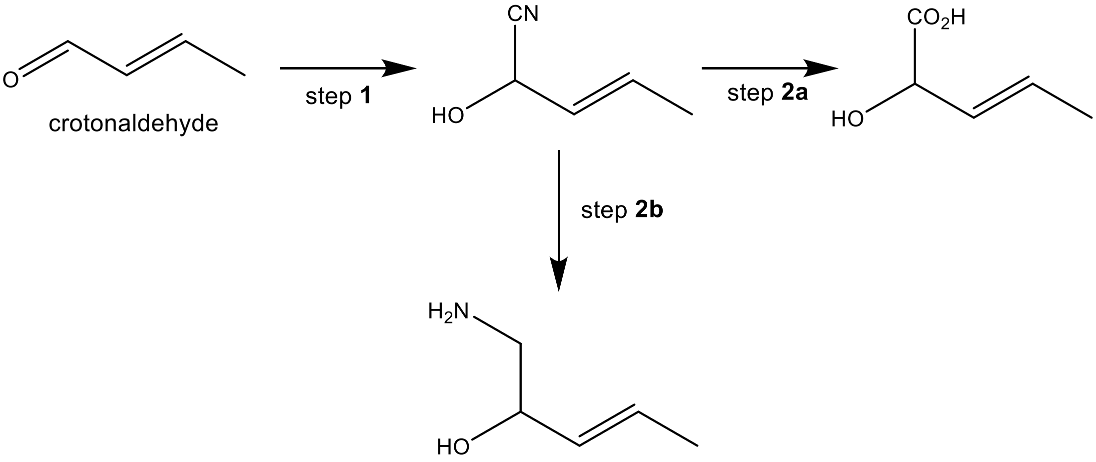
26 Golexanolone is a drug currently being studied for the treatment of hypersomnia.



What is the total number of stereoisomers exhibited by golexanolone?

A 512 **B** 256 **C** 128 **D** 64

27 Crotonaldehyde is an important biomolecule.



Which of the following statements is true about the above synthetic scheme?

A The reaction of crotonaldehyde with hot acidified $KMnO_4$ produces only one organic product.

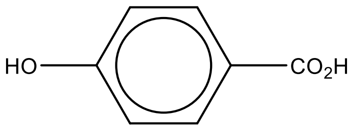
B Step **1** involves heating crotonaldehyde with NaCN in ethanol.

C Step **2a** involves the oxidation of crotonaldehyde because it gained oxygen atoms.

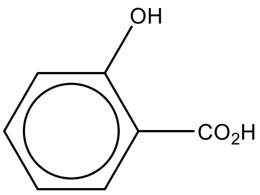
D $NaBH_4$ is the reagent used in step **2b**.

28 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde share the same molecular formula.

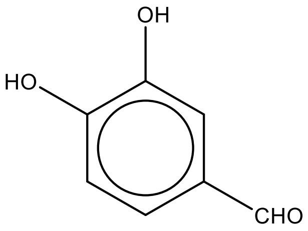
The standard enthalpy changes of formation for 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde are –481 kJ mol^{-1}, –493 kJ mol^{-1} and –392 kJ mol^{-1} respectively.



4-hydroxybenzoic acid



2-hydroxybenzoic acid



3,4-dihydroxybenzaldehyde

Which of the following statements is correct?

1 The thermodynamic stability of these three compounds decrease in the order:
2-hydroxybenzoic acid > 4-hydroxybenzoic acid > 3,4-dihydroxybenzaldehyde

2 3,4-dihydroxybenzaldehyde and 4-hydroxybenzoic acid are positional isomers.

3 The magnitude of the standard enthalpy change of combustion of these three compounds increase in the order:
3,4-dihydroxybenzaldehyde < 4-hydroxybenzoic acid < 2-hydroxybenzoic acid

A 1 only

B 2 only

C 1 and 3

D 2 and 3

29 Chloroethane can be used to make sodium propanoate.

$$\text{chloroethane} \longrightarrow \textbf{Z} \longrightarrow \text{sodium propanoate}$$

The intermediate, **Z**, is treated with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, **Z**, from chloroethane?

A potassium cyanide in ethanol

B hydrogen cyanide

C sodium hydroxide in ethanol

D alkaline $KMnO_4$

30 A polypeptide is subjected to hydrolysis by cyanogen bromide and two digestive enzymes.

- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide.
- The enzyme chemotrypsin hydrolyses a peptide bond at the carboxylic end of tryptophan (trp) to give two dipeptides and a tripeptide.
- The enzyme trypsin, which hydrolyses a peptide bond at the carboxylic end of lysine (lys) to give 2 tripeptides and gly.

What is the sequence of the amino acids in this polypeptide?

A ser-trp-lys-trp-met-lys-gly

B ser-trp-lys-met-trp-lys-gly

C gly-lys-met-trp-lys-trp-ser

D gly-lys-trp-met-lys-trp-ser

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY 9729/02
Higher 2

Paper 2 Structured Questions

26 August 2019
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 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	**/ 7**
2	**/ 21**
3	**/ 15**
4	**/ 7**
5	**/ 11**
6	**/ 14**
TOTAL	**/ 75**

This document consists of **22** printed pages.

1 **(a)** The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*.

(i) Explain the meaning of the word “amphoteric”. [1]

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Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer’s disease.

(ii) Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed. [1]

……………………………………………………………………………

(iii) By considering the nature of calcium oxide, explain why adding too much of it would increase the risk of contracting Alzheimer’s disease.

Write an equation to illustrate how “aluminium-containing ions remains in (drinking water)” as a result of adding too much calcium oxide. [2]

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1 **(b)** Beryllium oxide (BeO) is amphoteric, just like A*l*(OH)$_3$.

(i) Beryllium oxide reacts with sodium hydroxide according to the equation,

$$2NaOH + BeO \longrightarrow Na_2BeO_2 + H_2O$$

Given the position of beryllium in the Periodic Table, explain how this reaction illustrates the amphoteric nature of beryllium oxide. [2]

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(ii) To further illustrate its amphoteric nature, at 500 °C, BeO reacts with Na_2O to form compound **F** as the **sole product**. The molar masses of all three compounds are tabulated below.

compound	**molar mass / g mol^{-1}**
BeO	25
Na_2O	62
F	149

Write a balanced equation of the above reaction. [1]

……………………………………………………………………………………

[Total: 7]

2 **(a)** In the laboratory, there are three bottles labelled **X**, **Y** and **Z**. Each bottle contains one of the following reagents:

KI(aq), Cl_2(aq), and NaBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

test	procedure	observations
1	mix reagent in bottle **X** with reagent in bottle **Z**	no change in colour
2	mix reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown
3	mix reagent in bottle **Y** with reagent in bottle **X**	mixture turns reddish-brown

(i) By comparing relevant standard reduction potential values from the *Data Booklet*, explain how it can be deduced that **Y** is aqueous chlorine. There is **no** need for calculations. [1]

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(ii) Tests 2 and 3 were executed to determine the reagents in bottles **X** and **Z**.

Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand.

State the observations that will indicate whether the bottles contained KI(aq) or NaBr(aq) initially. [2]

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2 **(b)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure.

SCl_2 is formed from S_8 and Cl_2.

(i) Explain why S_8 exists as a solid while Cl_2 exists as a gas at room temperature. [2]

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(ii) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps.

The first step involves disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write the equation of the second step. [1]

……………………………………………………………………………………

Some chemists speculate that the intermediate is not disulfur dichloride but **K**.
K shares the same elemental mass percentages as sulfur dichloride and has a molar mass of 206.2 g mol^{-1}.

(iii) State the molecular formula of **K**. [1]

……………………………………………………………………………………

(iv) All the chlorine atoms in **K** are terminal.
There are only two central atoms in **K**.
The bond angles about each central atom are different.

State the shape around each central atom and the respective bond angles. [2]

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2 **(c)** Sulfuryl chloride, SO_2Cl_2, is commonly confused with thionyl chloride, $SOCl_2$.

The properties of these two sulfur oxychlorides are quite different. SO_2Cl_2 is a source of chlorine while $SOCl_2$ is a source of chloride ions for various organic reactions.

When heated, sulfuryl chloride decomposes endothermically as follows:

$$SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$$

In an experiment, 1.00 mol of SO_2Cl_2 vapour was heated in a closed 4.00 dm^3 flask at 500 K until equilibrium was established. The flask was then rapidly cooled to liquefy SO_2Cl_2.

After removing gaseous SO_2 and Cl_2, excess water was then carefully added to the liquid SO_2Cl_2, causing the following reaction to occur.

$$SO_2Cl_2\,(l) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + 2HCl\,(aq)$$

The resulting solution was made up to 250 cm^3 in a standard graduated flask.

20.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH. 40.00 cm^3 of NaOH was required for complete neutralisation.

(i) Write an expression for K_c for the equilibrium above and state its units. [2]

(ii) Calculate the equilibrium amount of SO_2Cl_2, SO_2, and Cl_2 in the original equilibrium at 500 K. Hence calculate a value for the K_c for the equilibrium. [4]

2 **(c)** **(iii)** A student suggested to carry out the decomposition process at a higher temperature and high pressure to decrease the time required for the process. Discuss the effects of the proposed changes on the rate and the yield. [2]

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2 **(d)** SO_2Cl_2 is widely used as a reagent in chlorination of the hydrocarbons. Such reactions occur under free radical conditions using H_2O_2 as an initiator.

For example, methylbenzene undergoes free radical substitution with SO_2Cl_2 to give benzyl chloride, $C_6H_5CH_2Cl$.

The mechanism of this reaction involves three stages:
I. Initiation
II. Propagation
III. Termination

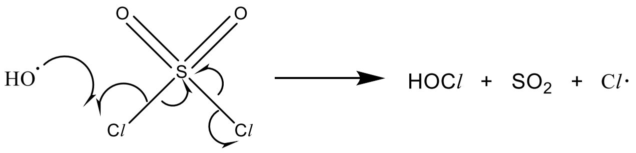
- The **initiation** stage is unique as it involves two successive steps.

(i) In the first step, there is an initial homolytic breaking of the peroxide bond in hydrogen peroxide forming two hydroxyl radicals.

Using curly arrows, show the mechanism for this step.

[1]

The second initiation step involves the reaction between the hydroxyl radical and SO_2Cl_2 to give SO_2, HOC*l* and a chlorine radical. It has been drawn for you below.



After these two initiation steps,

- The chlorine radical then reacts with methylbenzene in two **propagation** steps to form benzyl chloride and regenerating the hydroxyl radicals.
- The chain reaction **terminates** when two radicals combine to give stable compounds.

2 **(d)** **(ii)** Complete the mechanism by writing the steps for the **propagation** and **termination** stages.

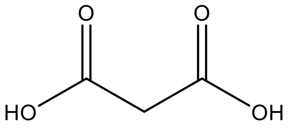
[3]

Propagation

Termination

[Total: 21]

3 Malonic acid is an important precursor to some polyesters.



(a) Malonic acid can be synthesised in more than one way.

(i) Suggest a three-step synthetic route from ethene to malonic acid. [5]

(ii) Malonic acid can be made by reacting two moles of **L** with a mole of carbon suboxide.

[1]

$$O{=}C{=}C{=}C{=}O$$

carbon suboxide

Identify **L**.

………………………………………………………………………………………

3 **(b)** Malonic acid behaves as a diprotic acid. The values of its K_{a1} and K_{a2} are 1.51×10^{-3} mol dm^{-3} and 2.00×10^{-6} mol dm^{-3} respectively.

In an experiment, 15.0 cm^3 of a 0.100 mol dm^{-3} solution of malonic acid was titrated against 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH. [1]

(ii) Calculate the volume of NaOH required for the first equivalence point. [1]

(iii) Write an equation to explain why the second equivalence point is above 7. [1]

……………………………………………………………………………………

(iv) Calculate the second equivalence pH. [2]

A buffer is obtained after the addition of 12.00 cm^3 of NaOH solution.

3 **(b)** **(v)** Write an equation for the reaction that occurs when a drop of HNO_3 is added to this buffer. [1]

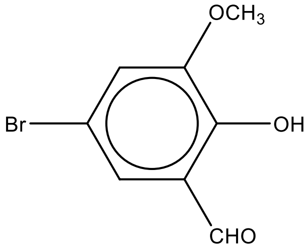
…………………………………………………………………………………

(vi) Calculate the pH of this buffer. [2]

(vii) Another buffer is obtained after the addition of 22.50 cm^3 of NaOH solution. Calculate its pH. [1]

[Total: 15]

4 **V** is a mono-brominated derivative of *ortho*-vanillin. *Ortho*-vanillins are used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals.



V

(a) Define the term "constitutional isomerism".

[1]

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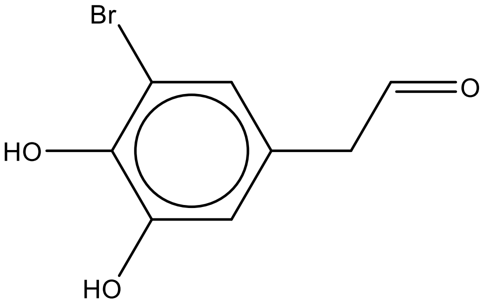
(b) **U** is a constitutional isomer of **V**.



U

State a simple chemical test to distinguish between **U** and **V**. State the observations.

[2]

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The structures you draw from 4(c) to 4(e) must contain one benzene ring.

4 **(c)** Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by cold $AgNO_3$ solution. State the observations. [2]

(d) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by warm alkaline iodine. [1]

(e) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself via 2,4-dinitrophenylhydrazine but not neutral iron(III) chloride solution nor sodium metal. [1]

[Total: 7]

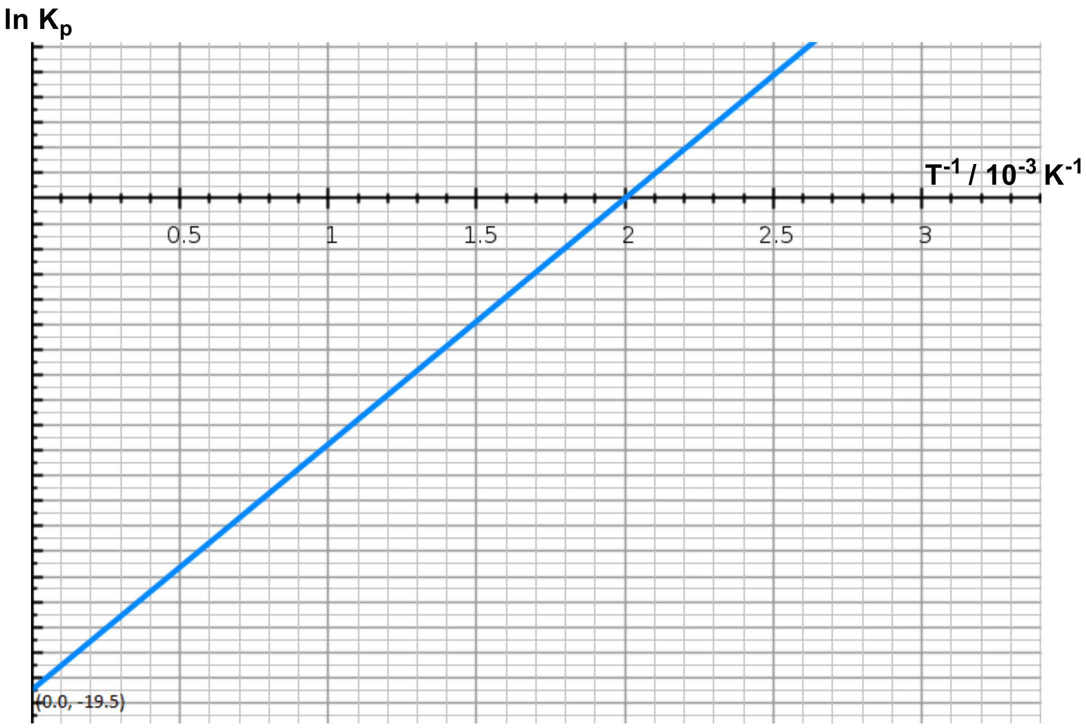
5 Space-suits need to be designed in such a way to supply oxygen to astronauts and to remove the carbon dioxide exhaled by them.

(a) Metal oxides like silver oxide, Ag_2O, are used to get rid of the carbon dioxide.

Ag_2O reacts reversibly with carbon dioxide, as described in the equilibrium equation,

$$Ag_2O\ (s) + CO_2\ (g) \rightleftharpoons Ag_2CO_3\ (s)$$

The van't Hoff plot shows how the equilibrium constant, K_p, of this reaction varies with temperature.



(i) From the above graph, deduce the relationship between K_p and T. [1]

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(ii) Hence, explain whether the reaction between silver oxide and carbon dioxide is exothermic or endothermic. [2]

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5 **(a)** **(iii)** Given that the straight line graph for ln K_p versus T^{-1} is described by the equation

$$\ln K_p = \left(\frac{-\Delta H^0}{R}\right)\frac{1}{T} + \frac{\Delta S^0}{R}$$

Calculate the standard entropy change of this reaction and explain the significance of its sign with respect to the reaction. [2]

After absorbing carbon dioxide for some time, most if not all of the silver oxide would have been depleted. To **recharge** the system, heat is applied into the system to form Ag_2O again.

(iv) ΔG^0 and K_p are mathematically related by the equation

$$\Delta G^0 = -RT \ln K_p$$

Using the graph, estimate the minimum temperature at which the **recharging** of this system becomes spontaneous. [1]

5 **(b)** Silver carbonate (relative formula mass = 275.8) is a sparingly soluble salt. At 25 °C, its solubility is 0.032 g dm^{-3} of water.

(i) Show that the value of the K_{sp} of silver carbonate at 25 °C is 6.25×10^{-12}. [1]

(ii) Calculate the solubility of silver carbonate in 0.100 mol dm^{-3} silver nitrate at 25 °C. [1]

(iii) 1.00 cm^3 of a 1.20×10^{-5} mol dm^{-3} silver nitrate solution was mixed with 3.00 cm^3 of a 7.45×10^{-5} mol dm^{-3} sodium carbonate solution.

Determine whether there would be precipitation of silver carbonate. [2]

5 **(c)** Silver carbonate can be reacted with ammonia to form silver fulminate, AgCNO, a powerful primary explosive.

$$4\ Ag_2CO_3 + 4\ NH_3 \rightarrow 4\ AgCNO + 6\ H_2O + 4\ Ag + O_2$$

Draw the dot-and-cross diagram of the fulminate ion given that the N is the central atom and the negative charge is on the carbon.

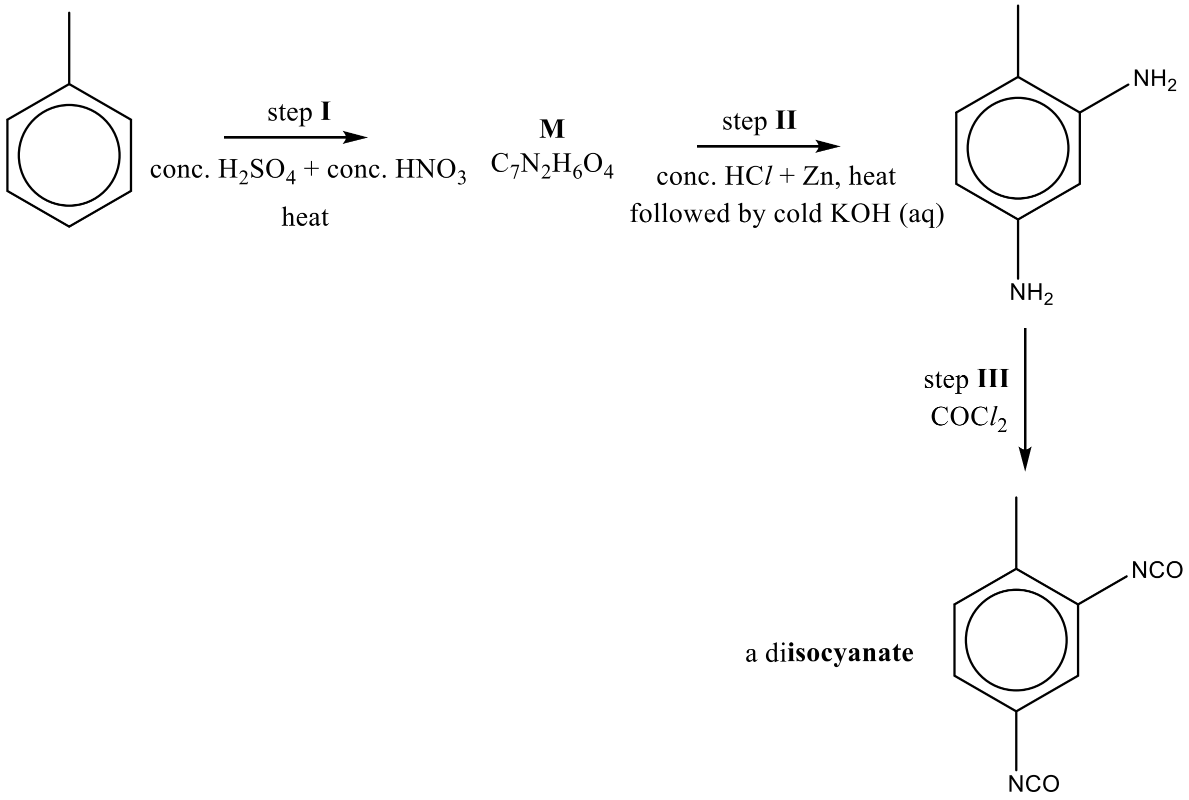
[1]

[Total: 11]

6 The isocyanate functional group is a constitutional isomer of the fulminate, which was mentioned in question **5(c)**. The isocyanate has the carbon atom instead of nitrogen atom as the central atom.

Isocyanates are important industrial chemicals; they react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

(a) This part is about the synthesis of a diisocyanate from methylbenzene.



(i) State the type of reaction in step **I**. [1]

....

(ii) Draw the structure of **M**. [1]

6 **(a)** **(iii)** Draw the structure of the isomer of **M** which is formed as a side-product in step **I**. [1]

(iv) Explain the purpose of KOH in step **II**. [1]

……………………………………………………………………………………

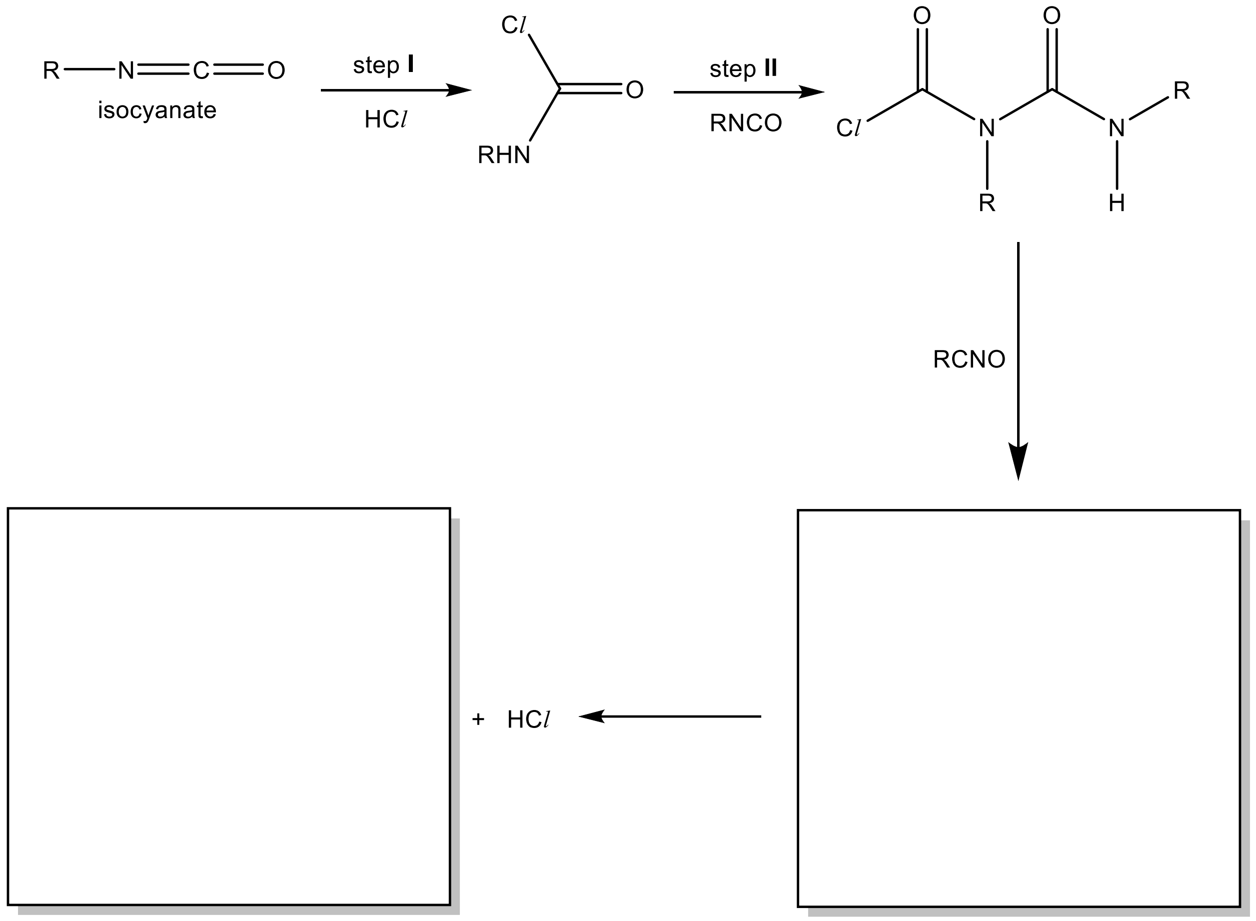
……………………………………………………………………………………

(v) Write a balanced equation for the overall reaction in step **II**. You are to use [H] to balance the equation. [1]

(vi) State the type of reaction in step **III**. [1]

……………………………………………………………………………………

6 **(b)** Examine the synthetic route below.



cyclic trimer **T**
$R_3C_3N_3O_3$

Q
$R_3C_3N_3O_3HCl$

(i) Draw the skeletal formulae of **Q** and the cyclic trimer **T** in the boxes provided. [2]

(ii) Step **I** is an electrophilic addition reaction. Draw the mechanism of step **I**. [3]

6 **(c)** When heated with HC*l* (aq), organic isocyanates (RNCO) are hydrolysed to the amine salt ($RNH_3^+Cl^-$) and carbon dioxide.

$$RNCO + HCl + H_2O \rightarrow RNH_3^+Cl^- + CO_2$$

A 1.13 g sample of an organic isocyanate was treated in this way, and the carbon dioxide produced was absorbed in an excess of aqueous $Ba(OH)_2$, according to the equation shown.

$$Ba(OH)_2\,(aq) + CO_2\,(g) \longrightarrow H_2O\,(l) + BaCO_3\,(s)$$

The mixture was filtered and the residue $BaCO_3$ washed and dried thoroughly. The mass of the residue was 1.97 g.

(i) Show that the molecular mass of the organic isocyanate is 113 g mol^{-1}. [1]

(ii) The R group in RNCO and $RNH_3^+Cl^-$ contains only carbon and hydrogen.

Use the molecular mass mentioned in **(i)** to suggest the molecular formula of the organic isocyanate. [1]

(iii) Given that a pure sample of this organic isocyanate rotates plane-polarised light, draw a possible stereochemical formula of it. [1]

[Total: 14]

~ End of Paper ~

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 9729/03

Paper 3 Free Response

2 September 2019
2 hours

Candidates answer on separate paper.

Additional Materials: Cover Page
Answer Paper
Insert

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 page of writing paper.
Fasten the insert in front of all writing paper at the end of the examination.

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.

This document consists of **14** printed pages.

Section A

Answer **all** the questions from this section.

1 **(a)** *Use of the insert is necessary for this question.*
Fasten the insert in front of all writing paper at the end of the examination.

An iodoalkane, RI, is hydrolysed by aqueous sodium hydroxide. The results obtained from two experiments are plotted on the insert. In each experiment, the overall [NaOH(aq)] remained virtually constant at the value given beside each graph.

(i) Use the graphs on the insert to determine the following. Show all workings clearly.

I Use the half-life method to deduce the order of reaction with respect to the iodoalkane.

II Use the initial rates method to deduce the order of reaction with respect to sodium hydroxide.

III Construct a rate equation for the reaction and use it to calculate a value for the rate constant. Include its units. [7]

(ii) Hence draw a fully labelled energy profile diagram of the reaction. [3]

(b) Silver(I) iodide and iodine are two solids which have low solubility in water. However when both are mixed together with water and left to stand, they dissolve completely to give a coloured solution of silver(I) triiodide.

(i) State the expected colour of the silver(I) triiodide solution. [1]

(ii) Write three relevant equilibria equations and use them to explain how the two solids can completely dissolve when mixed with water. [3]

(c) Another triiodide compound, nitrogen triiodide, NI_3 is a simple covalent molecule that is very sensitive to shock and will decompose rapidly. A touch of a feather or even alpha particles from radioactive decay can trigger an explosion.

$$2NI_3(s) \longrightarrow N_2(g) + 3I_2(g) \qquad \Delta H = -290 \text{ kJ mol}^{-1}$$

76.5 kJ mol^{-1} of energy is needed to convert solid NI_3 to gaseous NI_3.

Use the above information and relevant information from the *Data Booklet* to calculate the N–I bond energy. [2]

(d) Alpha particles, ${}^{4}_{2}He^{2+}$ are produced from the radioactive decay of certain isotopes. An example of one is from the decay of Americium-241.

$$ {}^{241}_{95}Am \rightarrow {}^{4}_{2}He^{2+} + \mathbf{M} $$

(i) Use the *Data Booklet* to identify species **M** that is formed. [1]

(ii) Calculate the angle of deflection for **M** in a uniform electric field if the angle of deflection for ${}^{4}_{2}He^{2+}$ is +7.11°. [1]

Americium is often used in smoke detectors as the compound AmO_2 and is made from the thermal decomposition of americium(III) ethanedioate, $Am_2(C_2O_4)_3$.

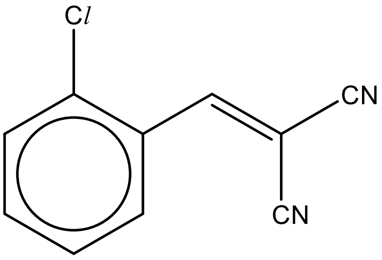
$$ Am_2(C_2O_4)_3 \longrightarrow 2AmO_2 + 4CO + 2CO_2 $$

(iii) Explain why the thermal decomposition is a redox reaction in terms of oxidation state changes. [2]

[Total: 20]

2 **(a)** On 12 June 2019, Hong Kong police fired tear gas into the crowds as many took to the streets to protest against a proposed extradition Bill.

The active compound in tear gas is 2-chlorobenzalmalononitrile.

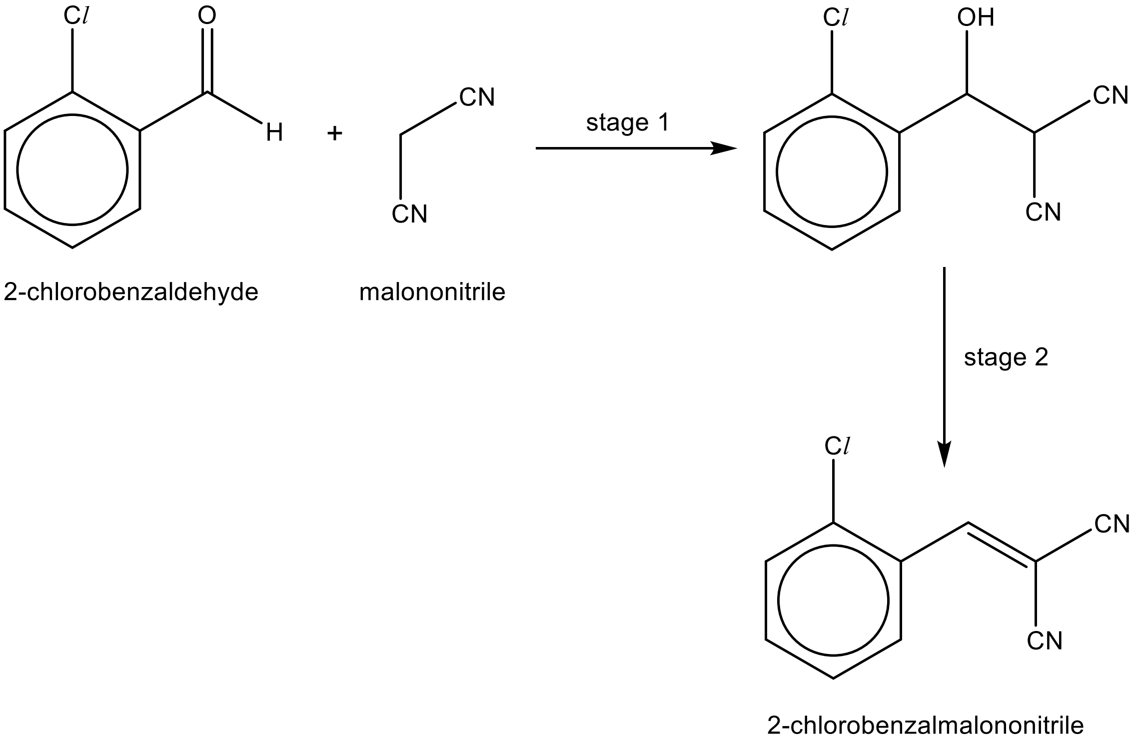


2-chlorobenzalmalononitrile

2-chlorobenzalmalononitrile is a solid at room temperature and is dispersed as an aerosol dissolved in a suitable organic solvent, typically dichloromethane, CH_2Cl_2. Its effects are felt when the solvent evaporates in air and the dry powder touches the eyes, nose and mouth.

(i) Suggest, with reasoning, two physical properties that make dichloromethane a suitable solvent. [2]

2-chlorobenzalmalononitrile can be synthesised via the 2-stage Knoevenagel condensation.

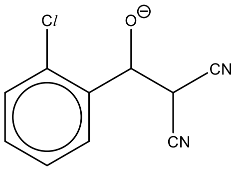


(ii) State the type of the reaction in stage 2. [1]

(iii) Instead of purchasing malononitrile as a starting reagent, it can be made from dichloromethane.

Suggest the reagent and conditions needed to convert dichloromethane to malononitrile. [1]

The following 3-step mechanism illustrates stage 1.

- Malononitrile is deprotonated by a weak base, R_2NH to form its conjugate base, $(NC)_2CH^-$.
- The conjugate base of malononitrile undergoes nucleophilic addition with 2-chlorobenzaldehyde to give  as an intermediate.
- The conjugate acid of R_2NH is deprotonated by the intermediate.

(iv) Describe the 3-step mechanism illustrated above.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(v) Suggest another role of the weak base, R_2NH. [1]

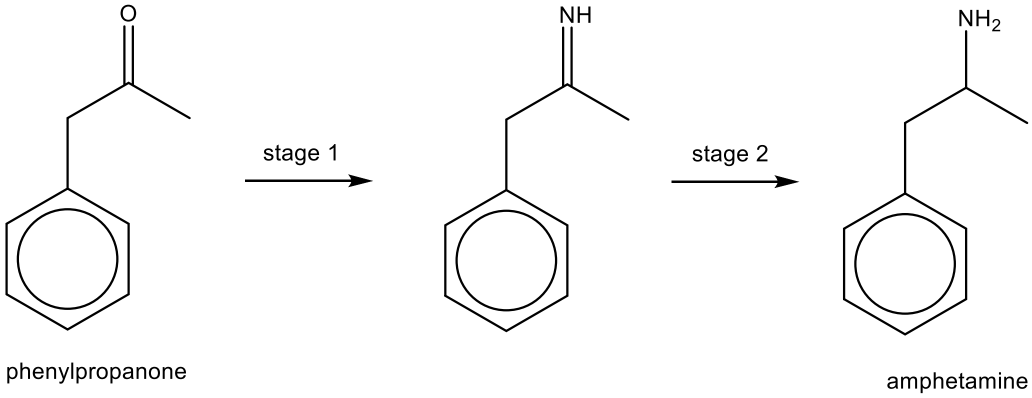
(vi) Compare, and explain, the relative acidities of dichloromethane and malononitrile. [2]

(vii) Draw the **only two** organic products formed when 2-chlorobenzalmalononitrile is heated with acidified potassium manganate(VII). [2]

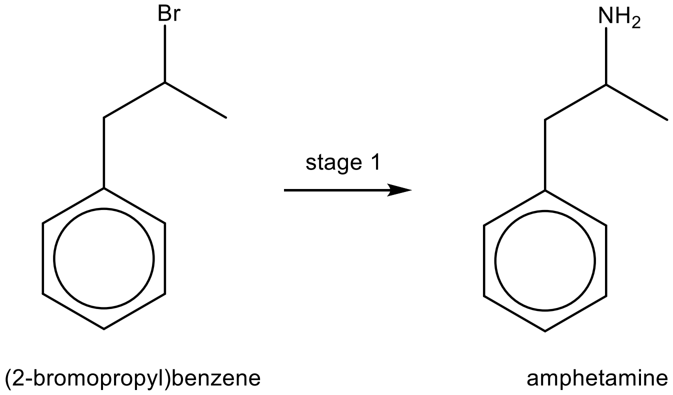
(b) During World War II, amphetamine pills were issued to the German army as they promoted alertness and self-confidence while reducing pain, hunger and the need for sleep.

Study the two methods of synthesis and answer the questions below.

Method 1



Method 2



(i) State the reagent used in stage 1 for both methods of synthesis. [1]

(ii) One would think that Method 2 would give better yield of amphetamine during synthesis since it only involves one stage as compared to two stages in Method 1, but this is not true.

Suggest why the yield of amphetamine via Method 2 would be poor. [1]

(iii) Only half of the product formed via Method 1 was biologically active in the body.

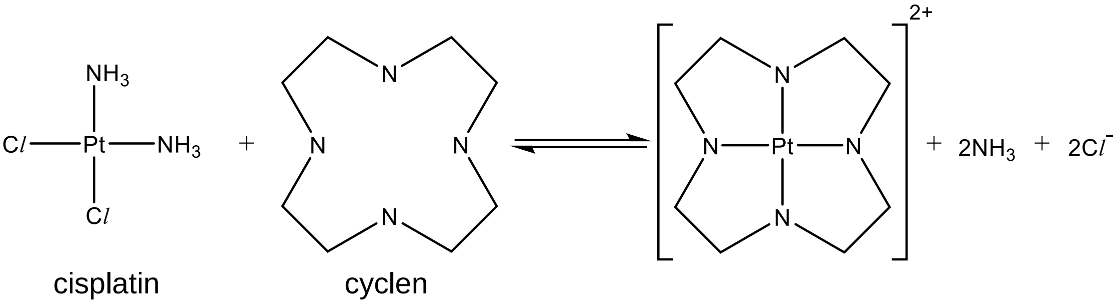
Account for this observation. [2]

(iv) Stage 2 of Method 1 employs the use of platinum metal as a catalyst.

State the type of catalysis involved and briefly outline the stages involved in the reaction. [3]

(v) Explain why transition metals are useful as catalysts. [1]

(c) Cisplatin is an anti-cancer drug containing a platinum centre and appears as a light yellow powder. When cisplatin is dissolved in water and allowed to react with the cyclen *ligand*, the position of equilibrium lies strongly to the right hand side.



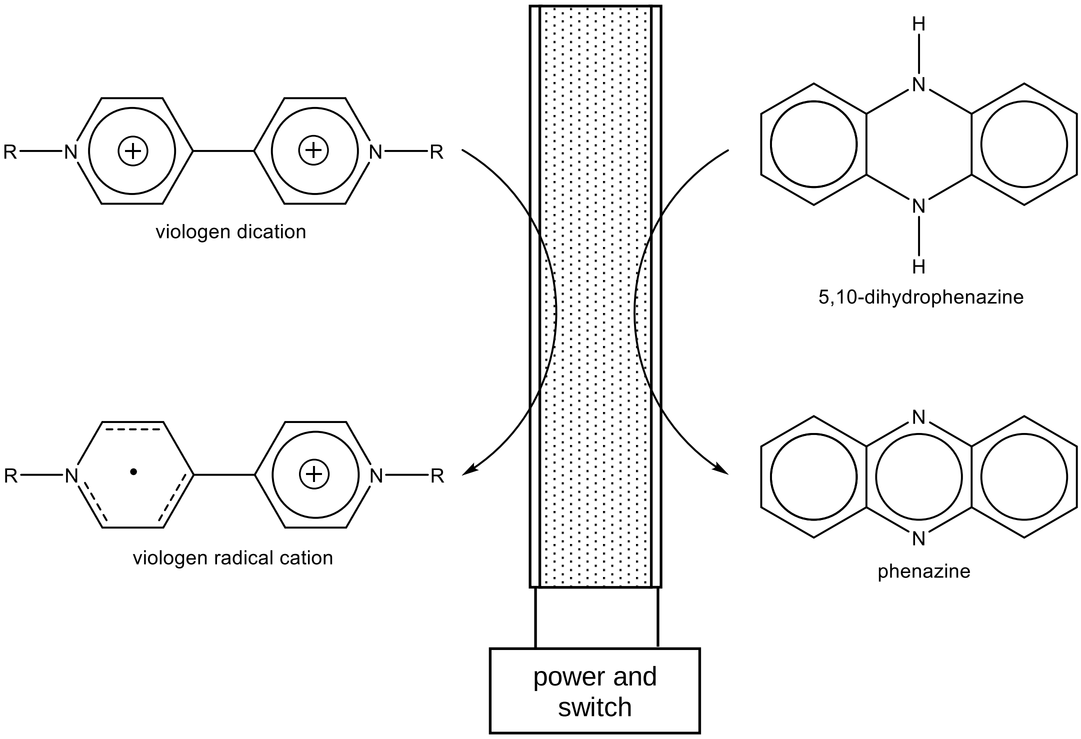
(i) Define the term *ligand*. [1]

(ii) Suggest signs for the enthalpy change of reaction and entropy change of reaction for the forward reaction, and comment on the spontaneity of the reaction across different temperatures. [2]

(iii) Explain why transition metal compounds are coloured. [2]

[Total: 25]

3 **(a)** Boeing 787-9 Dreamliners are equipped with electronically dimmable windows. When a constant current is applied, electrochemical reactions happen within a panel and the conversion of colourless viologen dication to viologen radical cation forms an intense dark purple that shields out sunlight. A simplified diagram together with the chemical changes is shown.



The viologen dication and phenazine are aromatic species. Hückel's rule states that planar cyclic species with 4n+2 pi electrons, where n = 0, 1, 2 ..., are considered aromatic.

(i) State the hybridisation of the nitrogen atoms in the viologen dication. [1]

(ii) State the number of pi electrons in phenazine. [1]

(iii) State the electrode at which the conversion of 5,10-dihydrophenazine to phenazine occurs. [1]

(iv) Write the half-equation for the reaction of 5,10-dihydrophenazine to phenazine in alkaline medium. You may write the names of both compounds respectively. [1]

(v) 0.0300 g of 5,10-dihydrophenazine is finely coated on to one side of the panel.

Calculate the time needed to react all of the coated 5,10-dihydrophenazine to completely darken a window panel, given that a constant current of 0.150 A is supplied. [4]

(b) It is mandatory for all aircrafts to provide an inflatable life vest for every passenger. One particular model of life vests uses a rapid inflation system of compressed CO_2 in a canister.

A student read that the canisters typically pack 11.0 g of CO_2 and commented that the amount of CO_2 present will inflate a life vest fully to 6.00 dm^3 in capacity.

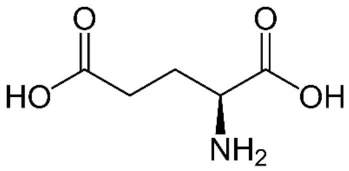
(i) Show how the student obtained 6.00 dm^3 as the capacity of the life vest and state the assumption made in the calculation. [2]

(ii) State two assumptions of the ideal gas law which allowed the student to make the calculations. [2]

(c) Passengers on planes often find that they are more drawn to *umami*-rich flavours as the sweet and salty tastes are dulled due to changes in altitude.

Monosodium glutamate (MSG) is one compound responsible for providing *umami* flavouring and it is the monosodium salt of glutamic acid.

The pK_a values associated with glutamic acid are 2.19, 4.25 and 9.67.



glutamic acid

(i) Draw the structure of glutamic acid at pH 1 and assign the three pK_a values. [2]

(ii) Draw the structure of monosodium glutamate. [1]

[Total: 15]

Section B

Answer **one** question from this section.

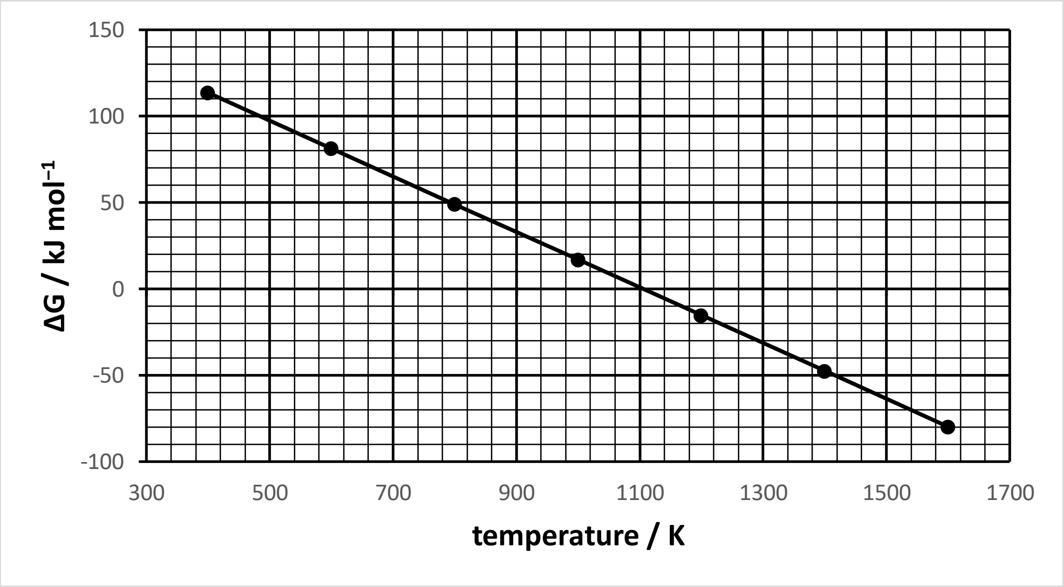
4 **(a)** The thermal decomposition reactions for calcium ethanoate and calcium methanoate are given as follows:

$Ca(HCOO)_2 \rightarrow CaCO_3 + HCHO$

$Ca(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

Predict the organic product, other than propanone and methanal, when a mixture of calcium methanoate and calcium ethanoate undergoes thermal decomposition. [1]

(b) The following Ellingham diagram shows the variation of Gibbs free energy change with temperature for the thermal decomposition of calcium carbonate.



(i) State the range of temperatures where solid calcium carbonate would decompose upon heating. [1]

(ii) Calculate the entropy change of the reaction. [1]

(iii) Hence, calculate the enthalpy change of the reaction. [1]

(c) Dolomite consists of $CaCO_3$ and $MgCO_3$ with the formula $CaMg(CO_3)_2$. It can be added to soil or marine aquarium as a pH buffer.

(i) Write a balanced equation for the action of heat on dolomite. [1]

(ii) Each carbonate is heated separately.

Predict and explain the difference in the thermal decomposition temperatures of the two carbonates. [3]

(iii) Explain why Li_2CO_3 decomposes in a similar way compared to these two carbonates. [1]

(d) **(i)** Predict and explain the difference in melting points of calcium oxide and magnesium oxide. [2]

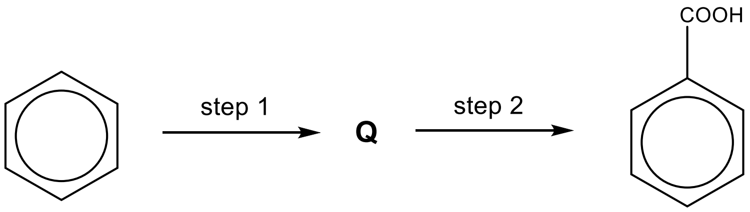
(ii) In power plant or trash incineration plant, large quantities of sulfur dioxide gas are produced. Calcium oxide can be used to remove sulfur dioxide from these exhaust gases in a process called flue-gas desulfurisation.

$$CaO + SO_2 \rightarrow CaSO_3$$

State the type of reaction for the above reaction. [1]

(e) Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Its salts are also used as food preservatives.

(i) Benzoic acid can be made from benzene by a two-step synthesis.



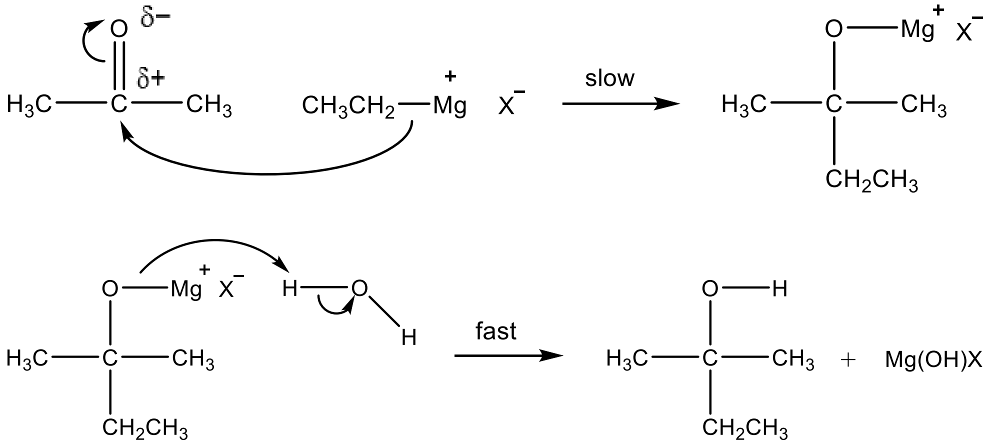
For steps 1 and 2, state the
- reagents and conditions, and
- type of reaction. [4]

(ii) Group 2 elements are known to form organometallic compounds. One example is the Grignard reagent with general formula RMgX. It is produced by reacting an alkyl halide or aryl halide with magnesium.

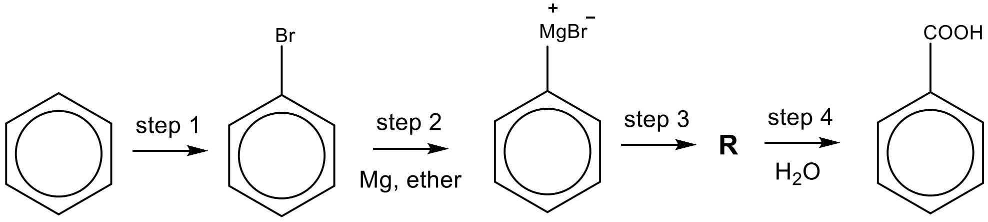
$RX + Mg \rightarrow R\text{–}Mg^+ X^-$ where X can be C*l* or Br.

The carbon-magnesium covalent bond is polarised as such; $\overset{\delta-}{C}\text{−}\overset{\delta+}{Mg}$.

Grignard reaction is important in making a new C–C bond. The mechanism for the reaction of ethylmagnesium bromide with propanone is shown as follows.



Benzoic acid can also be made from benzene by a four-step synthesis, using the Grignard reagent.



For step 3, state the reagent and intermediate **R**.

For steps 3 and 4, state the type of reaction. [4]

[Total: 20]

5 **(a)** **(i)** A compound **X** consists only of carbon, hydrogen and oxygen. During the complete combustion of 4 g of the compound, 8 g of carbon dioxide and 3.273 g of water were produced.

Determine the empirical formula of the compound **X**. [2]

(ii) Another 4 g sample of compound **X** was vaporised at 160 °C and 101 kPa, and found to occupy a volume of 1620 cm^3.

Determine the relative molecular mass of this compound. [1]

(iii) Hence determine the molecular formula of compound **X**. Show your working clearly. [1]

(b) Butanoic acid is used in the preparation of various esters. These esters have pleasant aromas or tastes. As a consequence, they are used as food and perfume additives.

(i) Biological methods have been developed to produce methane from waste organic matter using bacteria.

Based on the changes in oxidation numbers of carbon, construct a balanced equation for the disproportionation of **aqueous** butanoic acid to produce methane and carbon dioxide only. [1]

(ii) Given the following data,

- Enthalpy change of combustion of butanoic acid is −2184 kJ mol^{-1}.
- Enthalpy change of combustion of methane is −890 kJ mol^{-1}.

Calculate the enthalpy change for the reaction in **(b)(i)** for **liquid** butanoic acid instead of aqueous butanoic acid. [1]

(iii) Given that

$CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2CH_2COOH(aq)$ $\Delta H^{\ominus}_{soln} = -16.7$ kJ mol^{-1}

Use you answer in **(b)(ii)** to calculate the enthalpy change of reaction in **(b)(i)**. [2]

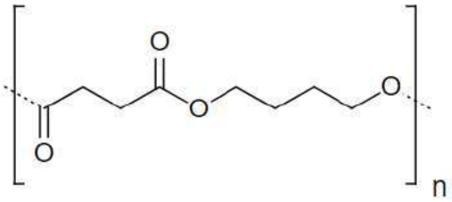
(iv) Butanoic acid boils at 117.7 °C. During boiling, the liquid phase is at equilibrium with the gas phase.

Calculate the entropy change of vaporisation of butanoic acid, given that the enthalpy change of vaporisation of butanoic acid is +52.0 kJ mol^{-1}. [1]

(v) Trouton's Rule states that the entropy change of vaporisation of many liquids, such as benzene and propanone, is about +88 J mol^{-1} K^{-1}.

Compare and explain the calculated result in **(b)(iv)** in relation to Trouton's Rule. [1]

(c) Polybutylene succinate (PBS) is a polyester used in packaging. It is receiving renewed interest due to increased demand for biodegradable polymers.



Polybutylene succinate

Hydrolysis of PBS produces two monomers **E** and **F**.

E can be reduced to **F**.

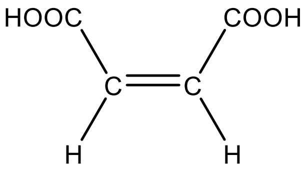
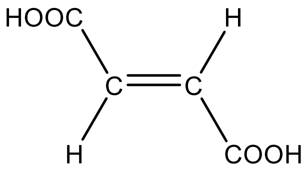
When an organic compound **D**, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.

G produces a yellow precipitate on warming with iodine in aqueous sodium hydroxide, and rotates the plane of polarised light.

Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** to **H**, and explain the observations described above. [7]

(d) Maleic acid and fumaric acid are two isomers with the same molecular and structural formulae, but with very different physical properties.

	 <u>maleic acid</u>	 <u>fumaric acid</u>
melting point / °C	130	287
pKa$_1$	1.9	3.0
pKa$_2$	6.5	4.5

(i) Give two reasons to explain why maleic acid has a lower melting point than fumaric acid. [2]

(ii) Explain why maleic acid has a lower pKa$_1$ value than fumaric acid. [1]

[Total: 20]

End of Paper

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2

9729/03

Paper 3 Free Response

2 September 2019
2 hours

Insert

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.

The insert is for use in **Question 1(a)**.
Fasten the insert in front of all writing paper at the end of the examination.

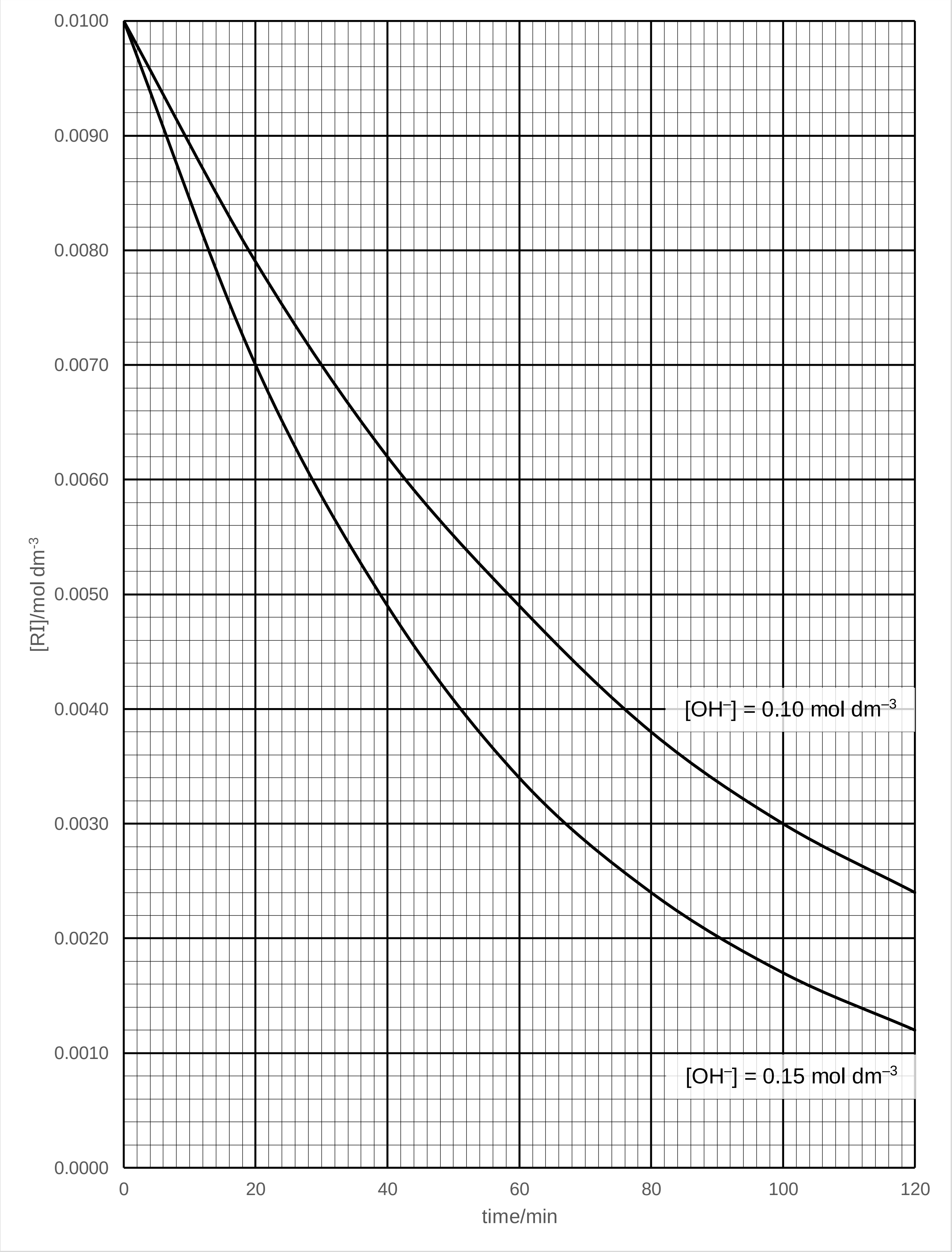
This document consists of **2** printed pages.

[Turn over

○

Index No.	Name	Form Class	Tutorial Class	Subject Tutor
			2CH________	

For use in Question 1(a)



1 Determination of solubility product, K_{sp}, of magnesium carbonate

Magnesium carbonate is basic and sparingly soluble in water, resulting in its use as drying agents in sports and antacids.

You are to carry out a titrimetric analysis to determine the solubility product of magnesium carbonate.

A saturated solution of magnesium carbonate can be prepared by dissolving excess solid magnesium carbonate into a measured volume of water. The mixture will be left to stand for some time before filtering. The filtrate can then be analysed through titration with a standard solution of hydrochloric acid.

The saturated solution of magnesium carbonate, FA 1, has been prepared for you, according to the procedure in **(a)**.

(a) Preparation of FA 1

1. Use a measuring cylinder to transfer 50 cm^3 of deionised water into a 100 cm^3 beaker.
2. Use a spatula to add solid magnesium carbonate into the same beaker, a little at a time with stirring until no more can dissolve.
3. Leave to stand for five minutes.
4. Filter the mixture to obtain the filtrate in a 250 cm^3 conical flask. Ensure that the filtrate is clear. Do not wash the residue.
5. The filtrate is **FA 1**.

You are provided with:
FA 1 saturated solution of magnesium carbonate
FA 2 0.0300 mol dm^{-3} hydrochloric acid solution
Methyl orange indicator

(b) (i) Dilution of FA 2

The concentration of **FA 2** is too high to be used in the titration. You will dilute **FA 2** before using it in **(c)**.

1. Pipette 25.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Top up to the mark with deionised water.
3. Stopper and shake thoroughly.

(b) **(ii)** Calculate the concentration of hydrochloric acid in **diluted FA 2**.

[HC*l*] in **diluted FA 2** = ………………………………… [1]

(c) **(i)** **Titration of FA 1 against diluted FA 2**

1. Fill the burette with **diluted FA 2** from **(b)**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 100 cm^3 conical flask.
3. Add 1 – 2 drops of methyl orange indicator into the conical flask.
4. Run **diluted FA 2** from the burette into this flask until the appropriate colour change is observed.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 1 to 5 until consistent results are obtained.

Results

[3]

(c) **(ii)** From your titrations, obtain a suitable volume of **diluted FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

Volume of **diluted FA 2** = …………………………………. [3]

(d) **(i)** Calculate the concentration of carbonate ions in **FA 1**, using your answers in **(b)(ii)** and **(c)(ii).**

[CO_3^{2-}] in **FA 1 =** …………………………………. [2]

(ii) Hence, calculate the solubility product of magnesium carbonate. State its units.

K_{sp} of magnesium carbonate = …………………………………….

units …………………………………. [1]

(e) In **(a)**, it was instructed that the filtrate had to be clear and that the residue should not be washed.

(i) State and explain the effect on titre volume if the filtrate was **not** clear.

effect on titre volume ……………………………………………………………………

explanation ……………………………………………………………………………

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…………………………………………………………………………………………… [1]

(ii) Explain why the residue should not be washed.

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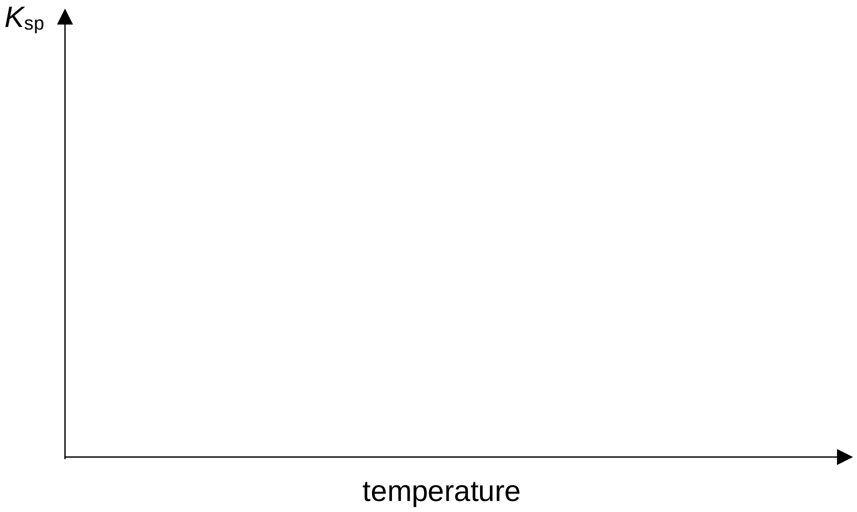
…………………………………………………………………………………………… [1]

(f) The dissociation of magnesium carbonate in water is endothermic.

Sketch a graph to show how the solubility product of magnesium carbonate varies with temperature. Explain your answer.



explanation ……………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

(g) **Planning**

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(i) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:
- 0.400 mol dm^{-3} sodium carbonate solution
- 0.400 mol dm^{-3} magnesium nitrate solution
- apparatus and equipment normally found in a school laboratory

In your plan you should include brief details of:
- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements you would make to allow for gravimetric analysis.

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…………………………………………………………………………………………… [4]

(ii) Show how the measurements recorded in **(g)(i)** can be used to calculate the concentration of Mg^{2+} and CO_3^{2-}, in mol dm^{-3}, in the saturated solution.

[2]

[Total: 20]

2 Determination of the concentration of $NaHCO_3$ and the value for the enthalpy change of reaction of $NaHCO_3$ and NaOH

FA 3 is a solution of sodium hydrogencarbonate, $NaHCO_3$, of unknown concentration.
FA 4 is 1.50 mol dm^{-3} sodium hydroxide, NaOH.

In this experiment, you will perform a thermometric titration to determine the equivalence point for the reaction of **FA 3** and **FA 4**, where maximum heat is evolved, without the use of an indicator.

You will follow the reaction by measuring the temperature as volumes of **FA 4** are added in regular portions from a burette to a fixed volume of **FA 3** placed in a Styrofoam cup.

The data obtained will allow you to determine the temperature change and then analyse your results graphically in order to determine the equivalence point of the reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 4**:

- Total volume of **FA 4** added from the burette, starting from 0.00 cm^3, up to the point in time
- Total volume of solution in the cup, V_{total}
- Temperature measured, T

In the same table, you also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 3**
- ($V_{total} \times \Delta T$) to 3 significant figures

State clearly the units of each parameter on the header of the column.

Procedure

1. Fill the burette to the 0.00 cm^3 mark with **FA 4**.

2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup.

3. Use a measuring cylinder to transfer 40.0 cm^3 of **FA 3** into the cup.

4. Measure and record the initial temperature of **FA 3**, T_0.

5. Run 3.00 cm^3 of **FA 4** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.

6. Immediately run a further 3.00 cm^3 of **FA 4** from the burette into the cup, stir and record the maximum temperature as before.

7. Continue the addition of **FA 4** in 3.00 cm^3 and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Results

[3]

(a) **(ii)** Plot a graph of ($V_{total} \times \Delta T$) against total volume of **FA 4** added.

Draw two best-fit straight lines for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq}
- maximum value of ($V_{total} \times \Delta T$)

V_{eq} = ……………………………………

Value of ($V_{total} \times \Delta T$) = …………………………….. [5]

(b) **(i)** Write down the chemical equation, with state symbols, for the reaction of $NaHCO_3$ and NaOH.

…………………………………………………………………………………………. [1]

(ii) Calculate the concentration of $NaHCO_3$ in **FA 3**.

$[NaHCO_3]$ in **FA 3** = ………………………………… [2]

(iii) Given that the heat capacity of solution is 4.2 J K^{-1} cm^{-3}, calculate the enthalpy change of the reaction of $NaHCO_3$ and NaOH, ΔH_r.

ΔH_r = ………………………………… [2]

(c) You plotted a graph of ($V_{total} \times \Delta T$) against total volume of **FA 4** added in **(a)(ii)**. Suggest, with explanation, whether plotting a graph of ΔT against total volume of **FA 4** instead is likely to yield a more accurate result for the equivalence point.

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…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………. [2]

(d) Performing the same experiment using a burette instead of a measuring cylinder to transfer **FA 3** into the Styrofoam cup is **not** expected to improve the accuracy of the results obtained. Suggest a reason why is this so.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………. [1]

(e) You are provided with methyl orange indicator in **Question 1**.

Explain whether methyl orange indicator can be used to determine the end-point of the titration of $NaHCO_3$ against NaOH instead of performing thermometric titration.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

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……………………………………………………………………………………………..

……………………………………………………………………………………………. [2]

[Total: 18]

3 Qualitative Analysis and Planning

You are provided with four different compounds labelled **FA 5**, **FA 6**, **FA 7** and **FA 8**. Each of these four bottles contains one of the following:

primary alcohol   aldehyde   monocarboxylic acid   metal halide

You will identify **FA 5**, **FA 6**, **FA 7** and **FA 8** by carrying out the prescribed experiments, as well as planning and conducting your own experiments.

For the prescribed experiments, record your observations in Table 3.1 below carefully. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You are advised to carry out the experiments in test (a) and (b) on each unknown compound one at a time. You are not required to carry out experiments in test (c) as the results are provided.

Table 3.1

Test		*Observations*			
		FA 5	**FA 6**	**FA 7**	**FA 8**
(a)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of sodium nitrite. **Test and determine if any gas is evolved.**				
(b)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of dilute sulfuric acid, followed by 5 drops of potassium manganate(VII) solution. Place the test-tube in the hot water bath. **Test and determine if any gas is evolved.**				

(c)	To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained. Then add 3 drops of the unknown into the same test-tube. Place the test-tube in the hot water bath.	No yellow precipitate	No yellow precipitate	Yellow precipitate obtained	Yellow precipitate obtained

[4]

(d) **Identifying unknown metal halide**

(i) From your observations in Table 3.1, suggest which one of the unknown compounds is the metal halide.

FA …………

explanation ……………………………………………………………………………..

…………………………………………………………………………………………

………………………………………………………………………………………. [1]

(ii) Suggest the reagent and carry out the test to confirm the identity of the halide in the metal halide.

reagent ……………………………..……………………………………………….

observations ……………………………………………...

…………………………………………………………………………..………………

FA ………… contains …………………….. anion. [2]

(d) **(iii)** In Table 3.2 below, describe two tests that will allow you to identify the cation in the metal halide. Perform the tests and record the observations in the same table. Use only bench reagents provided.

Table 3.2

Test	*Observations*
	FA …………

The cation in metal halide is ..………………………… [3]

(iv) The nature of the cation of the metal halide in aqueous solution accounts for its observations in test **(a)**. Describe and explain the nature of the cation by means of an equation.

equation ……………………………………………………………………………..

explanation …………………………………………………………………………..

………………………………………………………………………………………

…………………………………………………………………………………….. [2]

(e) **Identifying organic liquids**

(i) The three unknown organic compounds are primary alcohol, aldehyde and monocarboxylic acid.

Based on your observations in tests **(a)** and **(b)**, identify which is the monocarboxylic acid. Suggest the identity of the monocarboxylic acid and support your answer by giving the evidence.

FA …………

The identity of monocarboxylic acid is ……………………………………….

evidence ……………………………………………………………………………….

……………………………………………………………………………………….

……………………………………………………………………………………… [2]

(ii) Describe how you would conduct a chemical test, using only the bench reagents provided, to distinguish between the remaining two unknown organic compounds.

Carry out the chemical test.

With aid of your observations and results provided in test **(c)**, identify which is the primary alcohol and the aldehyde.

chemical test ………………………………………………………………………...

……………………………………………………………………………………………

observations ………………………………………………………………………….

……………………………………………………………………………………………

The primary alcohol is **FA** …………

The identity of the primary alcohol is ……………………………………….

The aldehyde is **FA** …………

The identity of the aldehyde is ………………………………………. [3]

[Total: 17]

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 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

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/01**
Higher 2

Paper 1 Multiple Choice

18 September 2019
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.

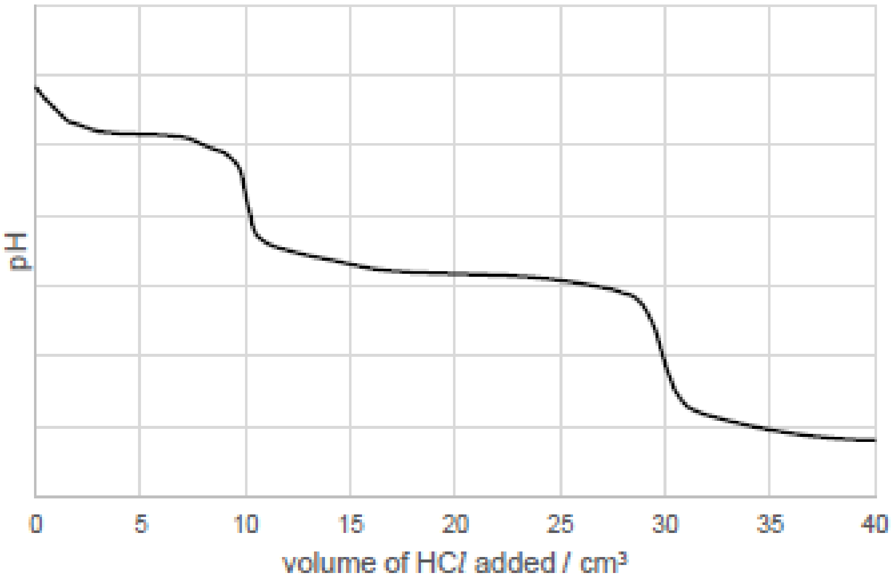
Any rough working should be done in this booklet.

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

This document consists of **18** printed pages.

1 An aqueous mixture of sodium carbonate and sodium hydrogencarbonate was titrated with hydrochloric acid and the pH was recorded.

What is a suitable indicator to use for detecting the first end point and the ratio of sodium carbonate to sodium hydrogencarbonate in the mixture?



	indicator	ratio
A	methyl orange	1:1
B	methyl orange	1:2
✓ C	thymol blue	1:1
D	thymol blue	1:2

Solution

The working range of methyl orange is between pH 3.1 to 4.4 and thus is not suitable for detecting the first end point between carbonate and H^+ at a pH that is above 7. Thus thymol blue is a more suitable choice.

$CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

$HCO_3^- + H^+ \longrightarrow H_2CO_3$

If 10 cm³ of H^+ is needed to react with the carbonate ions present in solution, then the same volume of H^+ is needed to react with the hydrogencarbonate produced after the first end point, i.e. 10 cm³. Thus the other 10 cm³ portion of H^+ is used to react with the initial hydrogencarbonate present. Hence ratio of carbonate to hydrogencarbonate is 1:1.

Comment: Students who were not careful erroneously chose D because of the convenient 1:2 ratio that they see from the graph.

2 The most common oxidation state of americium, Am, in aqueous solution is +3.

Recently, Cu^{3+} has been shown to quantitatively oxidise Am^{3+}(aq) in dilute HNO_3, while itself is reduced to Cu^{2+}.

In an experiment, 20.0 cm^3 of 0.0120 mol dm^{-3} Am^{3+}(aq) was found to require 24.00 cm^3 of 0.0300 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium-containing species formed?

A AmO^+ **B** AmO^{2+} **C** AmO_2^{2+}✓ **D** $Am_2O_2^{2+}$

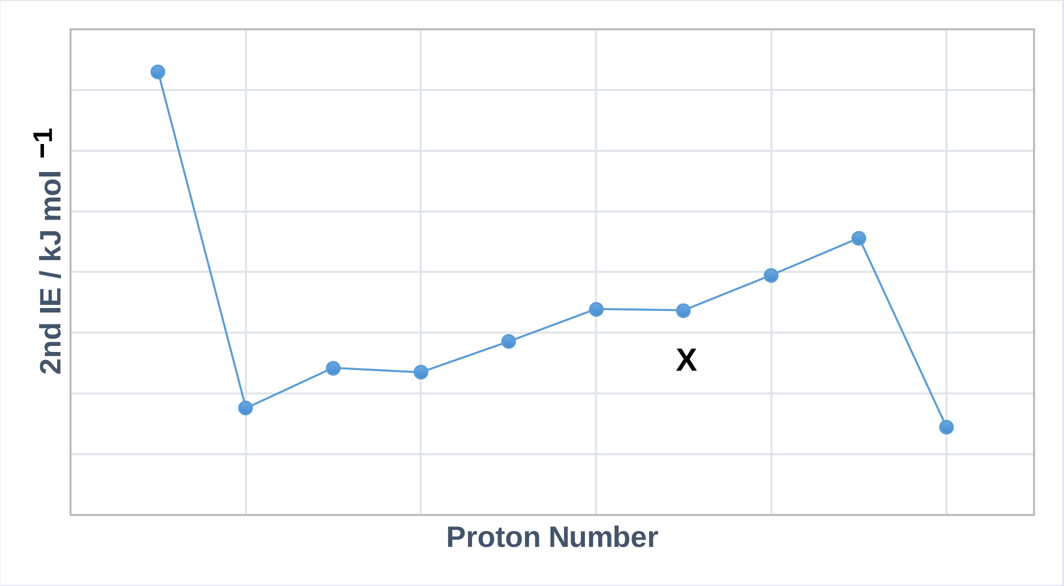
Solution

n(electrons) = n(Cu^{3+}) = 7.20 X 10^{-4}

change in oxidation state of Am = (7.20 X 10^{-4}) / (20.0 X 0.0120 / 1000) = +3

Initial oxidation state of Am = +3 +3 = +6

3 The graph shows the second ionisation energies for ten consecutive elements.



Which of the following could be **X**?

A oxygen **B** fluorine✓ **C** neon **D** sodium

Solution

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

1st Dip is for this case: $1s^2\ 2s^2$ to $1s^2\ 2s^2\ 2p^1$ (2p electron further away)

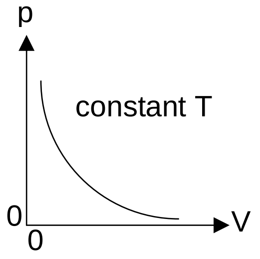
2nd Dip is for this case: $1s^2\ 2s^2\ 2p^3$ to $1s^2\ 2s^2\ 2p^4$ (inter-electron repulsion)

X^+(g) has this electronic configuration: $1s^2\ 2s^2\ 2p^4$

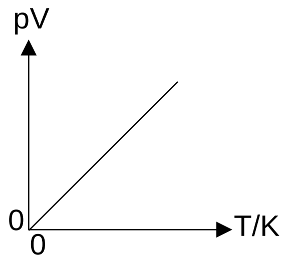
Hence X is $1s^2\ 2s^2\ 2p^5$. X is Fluorine.

4 Which of the following graphs are correct about a fixed amount of an ideal gas?

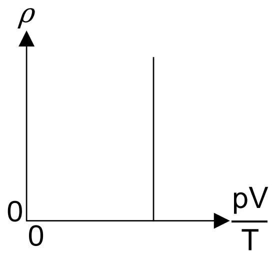
1



2



3



A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

✓ **D** all of the above

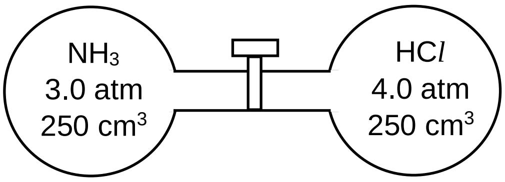
Solution

Using the ideal gas equation, pV = nRT, p=$\frac{nRT}{V}$. Since n, R and T are constant for (1), then p has an inverse relationship with V producing a "y=1/x" graph in (1).

pV has a direct positive relationship T as seen in the ideal gas equation and thus produces a "y=x" graph in (2).

$\frac{pV}{T}$=nR, where nR is a constant. Thus we expect to see a "x = k" graph in (3).

5 Two single-neck round-bottomed flasks were evacuated and insulated from the surroundings. They were filled separately with gaseous ammonia and gaseous hydrogen chloride at room temperature and connected with a gas tap joint.



When the gas tap joint is opened, the two gases are allowed to mix.

What is the final pressure of the resultant gas mixture?

A more than 3.5 atm but less than 7.0 atm

B exactly 3.5 atm

✓ **C** more than 0.5 atm but less than 1.0 atm

D exactly 0.5 atm

Solution

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$
All the $NH_3(g)$ will react with $HCl(g)$ to produce $NH_4Cl(s)$ which will deposit on the walls/bottom of the flasks. The solids' volume is negligible compared to the volume of the flasks.

That supposedly leaves us with 0.5 atm of $HCl(g)$ in a combined volume of 500 cm^3. But the reaction is exothermic and heat is given off. Since the flasks are insulated, the system will heat up and we expect the pressure of the system to be higher than 0.5 atm.

Comment: This question was poorly done with approximately half the cohort having chosen B, thinking that it was a simple mixing of the two gases.

6 When 1.00 g of ethanol was burned under a beaker of water, it was found that 100 cm^3 of water was heated from 15 ºC to 65 ºC. The process was known to be only 70% efficient.

Use these data and values from the *Data Booklet* to calculate the enthalpy change of combustion of ethanol.

A −209 kJ mol^{-1} **B** −673 kJ mol^{-1}

✓ **C** −1373 kJ mol^{-1} **D** +1373 kJ mol^{-1}

Solution

Heat absorbed by water = $mc\Delta T$ = (100)(4.18)(65 – 15) = 20,900 Joule

Heat given out by combustion = Heat absorbed by water ÷ 0.70 = 29,857 Joule

ΔH_c(ethanol) = − Heat / Amount of Limiting Reagent
= − 29,857 / (1 ÷ 46.0)
= −1,373,000 J mol^{-1}

7 Some standard enthalpy changes are given below.

	$\Delta H^\ominus$ / kJ mol^{-1}
$Ca^{2+}(g) + aq \longrightarrow Ca^{2+}(aq)$	–1650
$Cl^-(g) + aq \longrightarrow Cl^-(aq)$	–364
$Ca^{2+}(g) + 2Cl^-(g) \longrightarrow CaCl_2(s)$	–2258

What is the standard enthalpy change of solution of calcium chloride?

A +244 kJ mol^{-1}

✓ **B** –120 kJ mol^{-1}

C –2378 kJ mol^{-1}

D –4636 kJ mol^{-1}

Solution

$\Delta H_{soln} = \sum \Delta H_{hyd}(Ca^{2+} + 2Cl^-) - LE$

$= -1650 + 2(-364) - (-2258)$

$= -120$ kJ mol^{-1}

Students would have chosen A if they had only taken the ΔH_{hyd} for 1 mole of Cl^-.

Students would have chosen C if they misinterpret ΔH_{soln} as the summation of ΔH_{hyd} values.

Option D is just a summation of all three given enthalpy changes, factoring in ΔH_{hyd} for 2 moles of Cl^-.

8 Hydrogen peroxide reacts with acidified iodide ions, liberating iodine.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O$$

In the investigation of this reaction, the following results were obtained.

initial concentrations of reactants / mol dm^{-3}			initial rate of formation of iodine / mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^-]$	$[H^+]$	
0.01	0.01	0.10	2.0 x 10^{-6}
0.03	0.01	0.10	6.0 x 10^{-6}
0.03	0.02	0.10	1.2 x 10^{-5}
0.03	0.02	0.20	1.2 x 10^{-5}

Which of the following statements are correct?

1 The rate equation can be written as: rate = k $[H_2O_2][I^-]$.

2 The reaction is second order with respect to H^+.

3 The value of the rate constant is 0.2.

✓ **A** 1 only

B 2 only

C 1 and 2

D 1, 2 and 3

Solution

Compare Expt 1 and 2, keeping $[I^-]$ and $[H^+]$ constant, triple $[H_2O_2]$, rate triple.
Order of reaction wrt H_2O_2 is ONE.

Compare Expt 2 and 3, keeping $[H_2O_2]$ and $[H^+]$ constant, double $[I^-]$, rate double.
Order of reaction wrt I^- is ONE.

Compare Expt 3 and 4, keeping [H_2O_2] and [I^-] constant, double [H^+], rate constant.
Order of reaction wrt H^+ is ZERO.

Rate = k [H_2O_2] [I^-]

Using Expt 1 data, 2.0×10^{-6} = k (0.01) (0.01)
Therefore k = 0.02 $mol^{-1}\ dm^3\ s^{-1}$

9 Phosphorus(V) chloride, PCl_5, is a white solid which sublimes at 160 °C.

When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

Rate constant, k_b, applies for the backward reaction and equilibrium constant, K_c, applies for the overall process.

How will the values of k_b and K_c change when the equilibrium is established at a higher temperature than before?

		k_b	K_c
✓	**A**	increase	increase
	B	increase	decrease
	C	decrease	increase
	D	decrease	decrease

Solution

Increasing temperature will lead to an increase in rate of reaction because of increased frequency of effective collisions thus k_b will increase.

As the reaction is endothermic, ∆H > 0, increasing temperature will favour the endothermic process to absorb the heat and thus position of equilibrium will shift to the right. POE shifting right increases K_c.

Comments: This question was poorly done, with more than half the cohort having chosen C thinking that with POE going right, k_b will decrease with no regard for the increase in temperature.

10 When gaseous phosphorus(V) chloride is heated in a closed container, the following equilibrium is established.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

0.0200 moles of phosphorus(V) chloride was vaporised completely in a 2.0 dm^3 container. The amount of chlorine gas detected at equilibrium was found to be 0.00400 moles.

What is the value of K_c at this temperature?

A 1.0×10^{-3}

B 8.0×10^{-4}

✓ **C** 5.0×10^{-4}

D 4.0×10^{-4}

Solution

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
initial / mol dm^{-3}	0.0200/2.0 = 0.0100		0		0
change / mol dm^{-3}	–0.00200		+0.00200		+0.00200
equilibrium / mol dm^{-3}	0.00800		0.00200		0.00400/2.0 = 0.00200

$K_c = \frac{0.00200^2}{0.0080} = 5.0 \times 10^{-4}$

Students would have chosen A if they had taken $\frac{0.00400^2}{0.0160} = 1.0 \times 10^{-3}$

Students would have chosen B if they had taken $\frac{0.00400^2}{0.0200} = 8.0 \times 10^{-4}$

Students would have chosen D if they had taken $\frac{0.00200^2}{0.0100} = 4.0 \times 10^{-4}$

Comment: Most students could get this question correct with the most common error being A.

11 The value of pK_w at 40 °C is 13.54.

What is the pH of an aqueous solution of 0.05 mol dm^{-3} $Ba(OH)_2$ at 40 °C?

A 12.23

✓ **B** 12.54

C 12.70

D 13.00

Solution

$[OH^-]$ = 0.10 mol dm^{-3}

pOH = 1

pH = pK_w – pOH = 13.54 – 1 = 12.54

12 In which of the following solutions will solid calcium phosphate, $Ca_3(PO_4)_2$, be the least soluble at 25 °C? The numerical value of K_{sp} of $Ca_3(PO_4)_2$ is 2.07×10^{-33}.

✓ **A** 0.3 mol dm^{-3} $Ca(NO_3)_2$ (aq)

B 0.3 mol dm^{-3} Na_3PO_4 (aq)

C 0.6 mol dm^{-3} HNO_3 (aq)

D water

Solution

Notice that common ion effect is involved in options A and B – the common ion being Ca^{2+} and PO_4^{3-} respectively. Option D should be ruled out straightaway once it is realized that the question is asking for the least solubility and that common ion effects are involved in options A and B.

Notice that the concentrations of Ca^{2+} and PO_4^{3-} are equal in options A and B. Hence we can look at the power of the ion's concentration in the K_{sp} expression – the larger the power the more the solubility of the salt will be decreased.

Option C actually enhances the solubility.

13 A cell diagram is written as follows:

$$Ti(s) \mid Ti^{2+}(aq) \parallel H_2SO_4(aq) \mid SO_2(g) \mid Pt(s)$$

Use relevant data from the *Data Booklet*, and the following electrode potential

$$Ti^{2+}(aq) + 2e^- \rightleftharpoons Ti(s) \qquad E^\ominus = -1.63V$$

to calculate the standard Gibbs free energy change of the cell in kJ mol^{-1}.

A −37 **B** −157 **C** −282 **D** −347 ✓

Solution

From Data Booklet, $SO_4^{2-} + 4H^+ + 2e \rightleftharpoons SO_2 + 2H_2O$ **+0.17 Volt**

$E^\ominus_{cell} = (+0.17) - (-1.63) = +1.80$ **Volt**

$\Delta G = -nF E^\ominus_{cell} = -(2)(96500)(+1.80) = -347$ **kJ** mol^{-1}

14 *Use of the Data Booklet is relevant to this question.*

The standard reduction potentials of some vanadium species are tabulated below.

half-reaction	$E^\ominus$ / V
$V^{2+}(aq) + 2e^- \rightleftharpoons V(s)$	–1.20
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34

Which of the following metals, when added in excess, will reduce VO^{2+} to V^{3+}?

1 Sn

2 Zn

3 Pb

✓ **A** 1 and 3

B 2 and 3

C 1 only

D 2 only

Solution

E_{cell} between Sn and VO^{2+} is positive, +0.48 V. But E_{cell} between Sn and V^{3+} is negative, -0.12 V. Hence V^{3+} will be the final vanadium species.

E_{cell} between Zn and VO^{2+} is positive, +1.10 V. E_{cell} between Zn and V^{3+} is also positive, +0.50 V. Hence V^{3+} will NOT be the final vanadium species.

E_{cell} between Pb and VO^{2+} is positive, +0.47 V. But E_{cell} between Pb and V^{3+} is negative, -0.13 V. Hence V^{3+} will be the final vanadium species.

15 *Use of the Data Booklet is relevant to this question.*

Impure copper containing traces of cobalt, iron and silver was purified via electrolysis.

Which cations of the trace metals can be found in solution?

A Ag^+ only

B Ag^+ and Fe^{2+}

✓ **C** Co^{2+} and Fe^{2+}

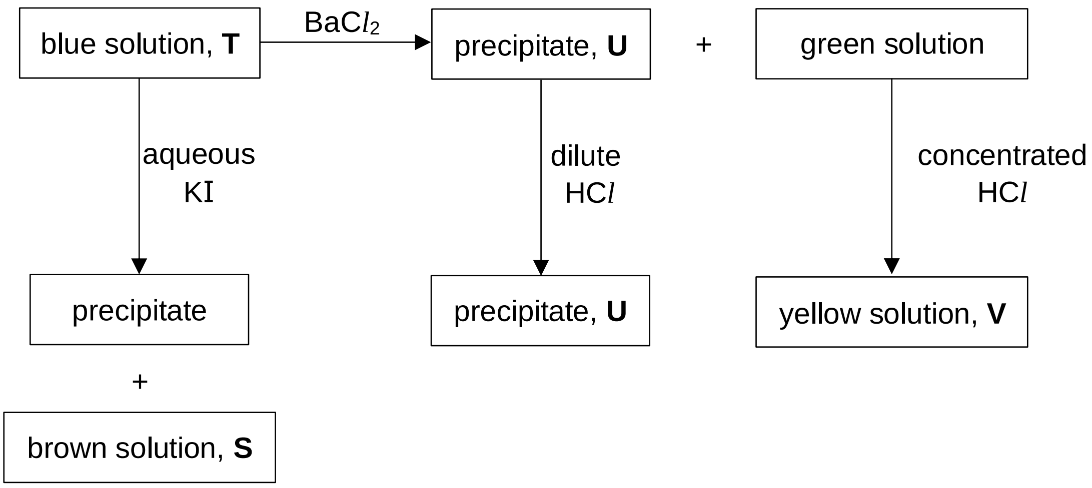
D Co^{3+} and Fe^{3+}

Solution

$Ag^+ + e^- \rightleftharpoons Ag$	+0.80 V
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28 V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.89 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44 V
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77 V

During the electrolysis of impure copper, Cu is oxidised to Cu^{2+} in solution. As such, Co and Fe will oxidise to Co^{2+}, Fe^{2+} and Fe^{3+}. It's unlikely we'd get any significant oxidation of Ag due to its electrode potential being more positive than Cu. Further oxidation of Co^{2+} to Co^{3+} is unlikely to occur too.

16 An aqueous transition metal compound, **T**, was subjected to a series of reactions.



Which statements are correct?

1 The anion in **S** is I^-.

2 The anion in **U** is SO_3^{2-}.

3 The anion in **V** is $CuCl_4^{2-}$

A 1 and 2

B 2 and 3

C 1, 2 and 3

✓ **D** 3 only

Solution

T is $CuSO_4$.

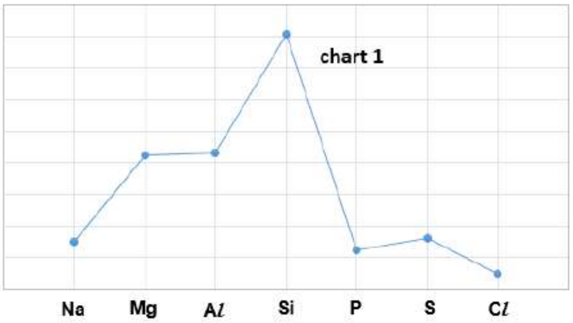
Ppt formed on reaction with KI is CuI and anion in brown solution, S, is I_3^-.
$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$
$I_2 + I^- \rightleftharpoons I_3^-$

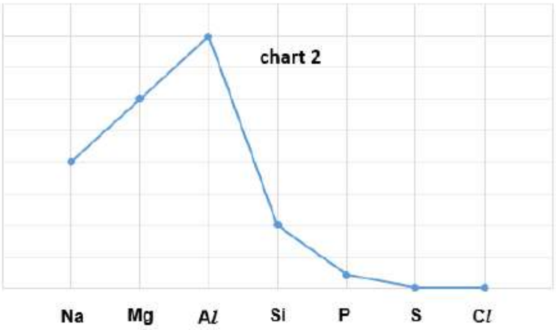
Ppt U is $BaSO_4$ which does not react with HCl.
$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

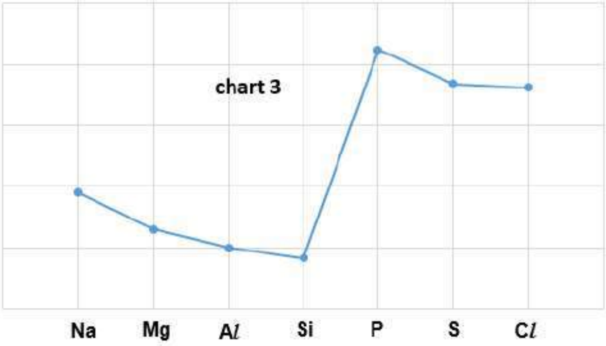
Green solution formed is $CuCl_2$ which reacts further with more Cl^- ligands to form $CuCl_4^-$ anion complex in V.

Comment: Approximately 40% of students chose C and 40% chose the correct option D.

17 Three charts below show the variation of three physical properties for the Period 3 elements.







Which of the following is correct?

	chart 1	chart 2	chart 3
A	ionic radius	electrical conductivity	melting point
B	electrical conductivity	melting point	ionic radius
C	melting point	ionic radius	electrical conductivity
✓ **D**	melting point	electrical conductivity	ionic radius

Solution

Chart 1 (Melting Point):
Silicon has highest mp.
Na, Mg, Al as a group has the second highest mp.
P_4, S_8 and Cl_2 as a group has the lowest mp.

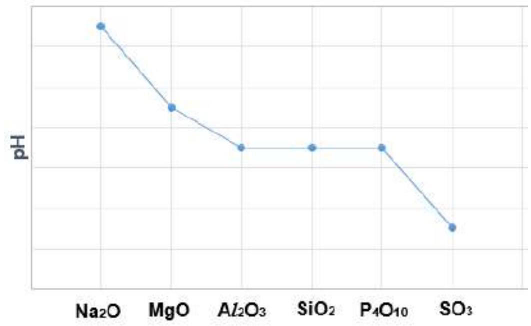
Chart 2 (Electrical Conductivity):
Na, Mg, Al as a group has the highest electrical conductivity.
Silicon is a semi-conductor.
P_4, S_8 and Cl_2 as a group has the lowest electrical conductivity.

Chart 3 (Ionic Radius):
Na^+, Mg^{2+}, Al^{3+} and Si^{4+} as a group has the smallest ionic radii.
P^{3-}, $S^{2}-$ and Cl^- as a group has the lowest electrical conductivity.

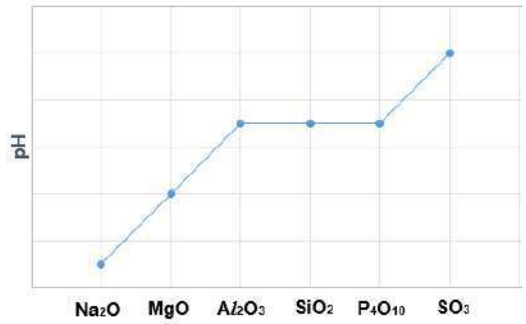
18 The highest oxides of the elements sodium to sulfur are added separately to water.

Which of the following diagrams best represents the pH of the solutions produced?

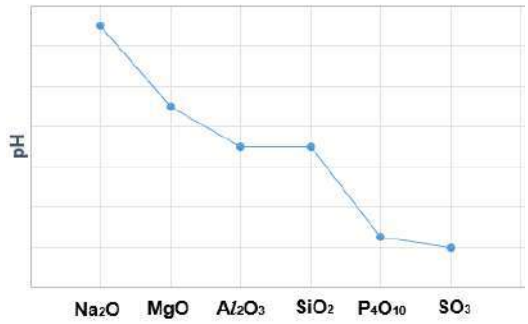
A



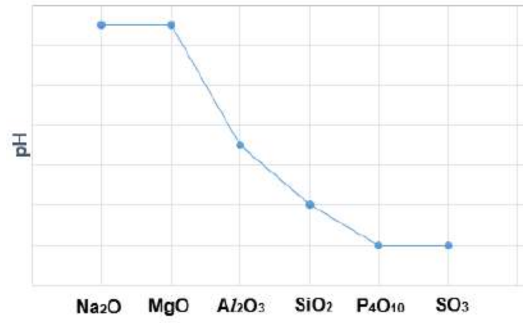
B



✓ **C**



D



Solution

Al_2O_3 and SiO_2 are insoluble in water. Hence water remains at pH = 7.

Na_2O dissolves in water to give alkaline solution of about pH = 13

MgO dissolves slightly in water to give alkaline solution of about pH = 9.

P_4O_{10} and SO_3 dissolve in water to give acidic solution of about pH = 2.

19 Stability constants and colours are given in the following table for this reaction.

$$Fe(H_2O)_6^{3+} + L^- \rightleftharpoons Fe(L)(H_2O)_5^{2+} + H_2O$$

ligand	lg K_{stab}	colour of $Fe(L)(H_2O)_5^{2+}$
SCN^-	2.1	blood red
F^-	5.4	colourless

What would be observed when the following reagents are added to a solution of iron(III) nitrate?

- potassium fluoride
- followed by potassium thiocyanate

A Solution turns from green to colourless, and then blood red.

B Solution turns from green to colourless, and then remains colourless.

C Solution turns from yellow to colourless, and then to blood red.

✓ **D** Solution turns from yellow to colourless, and then remains colourless.

Solution

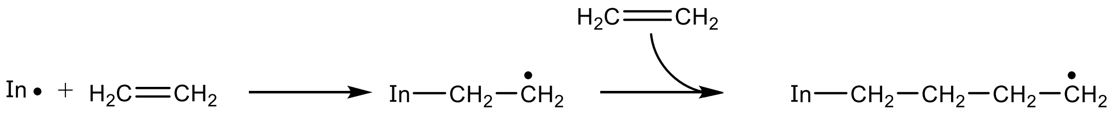
$Fe(H_2O)_6^{3+}$ is yellow; $FeF(H_2O)_5^{2+}$ is colourless.

Since lg K_{stab} = 5.4, F^- is a stronger ligand than H_2O and F^- will replace H_2O ligand to form $FeF(H_2O)_5^{2+}$. Hence yellow solution turns colourless.

$Fe(SCN)(H_2O)_5^{2+}$ is blood red.

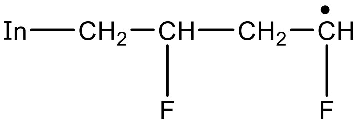
Since Since lg K_{stab} = 2.1 is smaller than lg K_{stab} = 5.4, SCN^- is a weaker ligand than F^-. Hence SCN^- will not replace F^-. Solution remains colourless.

20 Free radical addition is a mechanism used in the synthesis of some addition polymers. Alkene monomers will polymerise in the presence of a radical initiator (In•). For instance, the synthesis of polyethene begins as such.



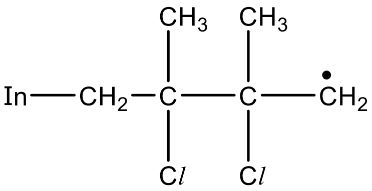
Which of the following chains could **not** have arisen from free radical addition?

A



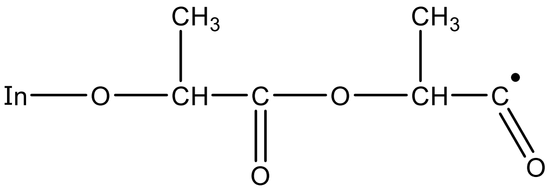
$$\mathrm{In{-}CH_2{-}CH(F){-}CH_2{-}\dot{C}H(F)}$$

B



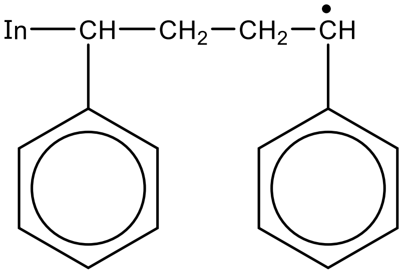
$$\mathrm{In{-}CH_2{-}C(CH_3)(Cl){-}C(CH_3)(Cl){-}\dot{C}H_2}$$

✓ **C**



$$\mathrm{In{-}O{-}CH(CH_3){-}C({=}O){-}O{-}CH(CH_3){-}\dot{C}{=}O}$$

D



Solution

For free radical addition to occur, students must recognise that an alkene is needed as the monomer.

A uses fluoroethene, $H_2C{=}CHF$

B uses 2-chloropropene, $H_2C{=}C(CH_3)Cl$

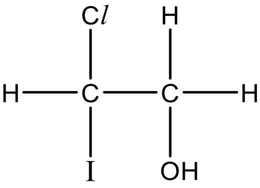
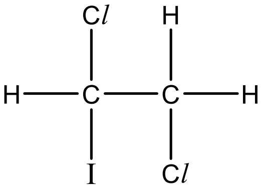
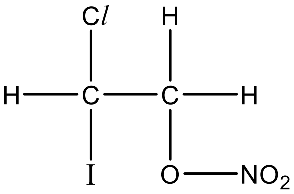
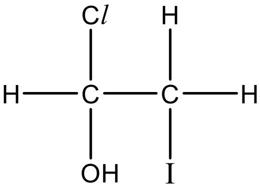
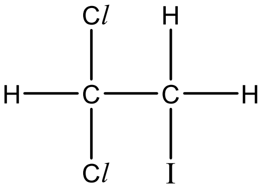
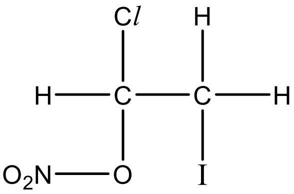
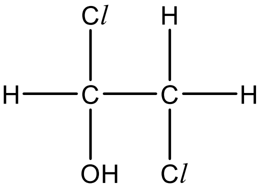
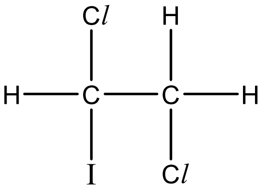
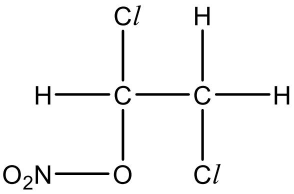
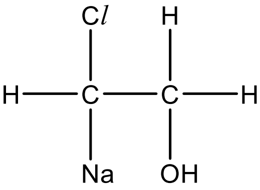
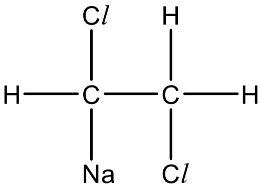
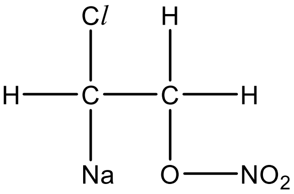
D uses phenylethene, $(C_6H_5)CH{=}CH_2$

There is no known monomer that can reasonably give rise to the structure in C. More accurately, it should be formed as a condensation polymer of lactic acid, 2-hydroxypropanoic acid.

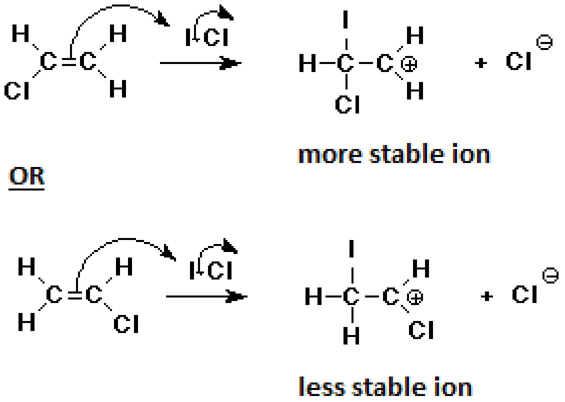
Comment: Fairly well done with approximately 70% of students getting it right.

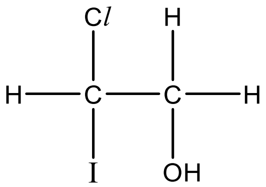
21 Chloroethene is reacted with iodine monochloride in the presence of aqueous sodium nitrate.

Which are the major and minor products?

	major product	minor products	
✓ **A**			
B			
C			
D			

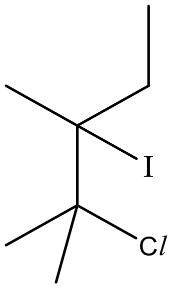
Step 1





In Step 2, H_2O being the solvent, is present in large amount. H_2O has the highest chance of attacking the more stable ion to give rise to the major product.

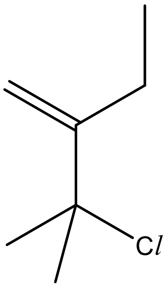
22 The following compound **Y** is reacted with ethanolic sodium hydroxide.



Compound **Y**

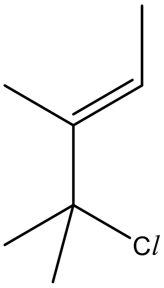
Which of the following is the **major** product?

A

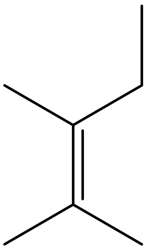


B

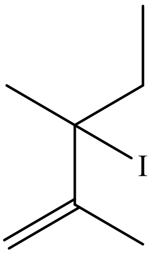
✓



C



D



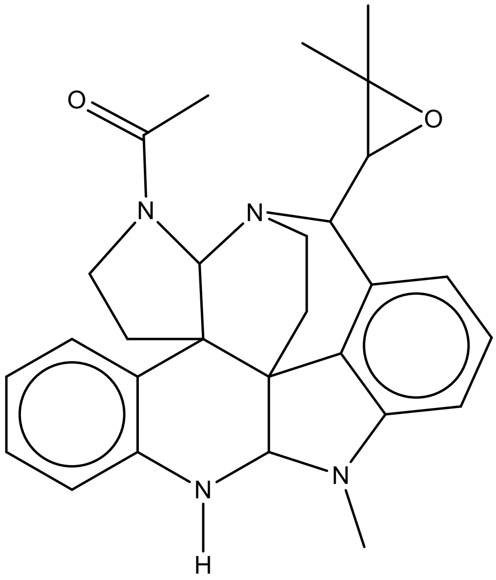
Solution

Elimination takes place when RX is heated with NaOH (in ethanol).

C−I being weaker than C−Cl, will break, forming an alkene.

Zaitsev's Rule says that "more substituted alkene will be the major product". Hence tri-substituted alkene will be the major product, not the di-substituted alkene.

23



Which of the following statements about communesin A is correct?

A Communesin A gives a yellow precipitate when warmed with alkaline iodine solution.

B There are three tertiary amines in communesin A.

C It is a planar molecule.

✓ **D** One of the oxygen atoms is sp^3 hybridised; the other is sp^2 hybridised.

Solution

Option A is deceptive because students will mistake the tertiary amide at the top left hand corner of the molecule as a methyl ketone.

Option B is deceptive because while communesin A indeed contains three amines, only two of them are actually tertiary.

Option C is out because there are many sp^3 hydridised carbon atoms present in the structure of communesin A.

Option D: Do take note that it is possible to talk about the hybridization of terminal (non-central) atoms. The ketone O is sp_2 hybridised and the O involved in the ring is sp^3 hybridised.

24 Compound **B**, $C_6H_{12}O_6$, is an important biomolecule abundant in the brain as it mediates cell signal transduction in response to a variety of hormones and neurotransmitters.

All the atoms (besides the hydrogen atoms) in **B** are sp^3 hybridised.

On adding excess sodium to **B**, hydrogen gas is liberated.

Which of the following statements about compound **B** is true?

A Compound **B** forms a purple colouration with neutral iron(III) chloride solution.

✓ **B** Compound **B** forms a yellow precipitate with warmed alkaline iodine solution.

C Compound **B** forms a bright orange precipitate with 2,4-dinitrophenylhydrazine.

D Compound **B** forms a brick-red precipitate with Fehling's solution.

Solution

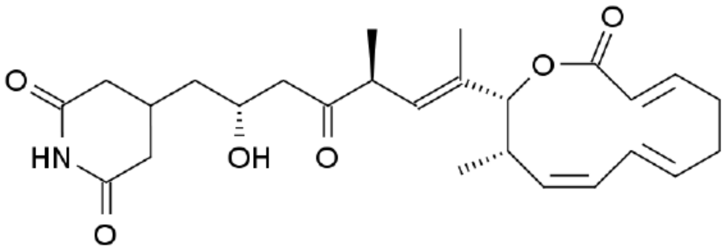
Option A requires a phenol. But no phenol is present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

Option B requires a methyl ketone or a –CH(CH_3)OH group. It is still possible for B to possess the latter.

Option C requires an aldehyde or ketone. But no such functional groups are present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

Option D requires an aldehyde. But no aldehyde is present in B because "all the atoms (besides the hydrogen atoms) in B are sp^3 hybridised."

25



Which statements about lactimidomycin are correct?

1 One mole of lactimidomycin reacts completely with four moles of 2,4-dinitrophenylhydrazine.

2 On reacting lactimidomycin with hot acidified $KMnO_4$, there is no gas evolved.

3 On heating lactimidomycin with KOH(aq), there is ammonia gas evolved.

A 1 and 2

B 2 and 3

C 1 only

✓ **D** 3 only

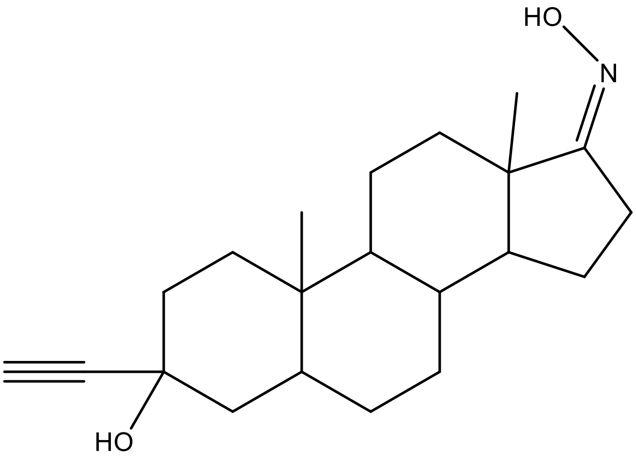
Solution

Statement 1 is deceptive because only one out of the four C=O groups will undergo condensation with 2,4-dinitrophenylhydrazine. Three of these groups are actually ester and amides.

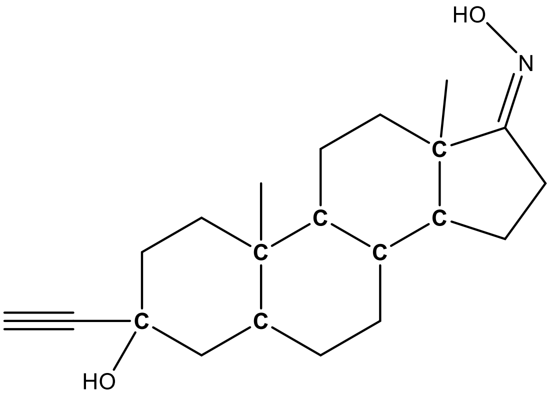
Statement 2 is wrong because carbon dioxide gas will be released; in fact four moles of it per mole of lactimidomycin.

Statement 3 involves alkaline hydrolysis. Indeed ammonia will be released from the "di-amide" (actually it is called imide) on the LHS of the molecule.

26 Golexanolone is a drug currently being studied for the treatment of hypersomnia.



What is the total number of stereoisomers exhibited by golexanolone?

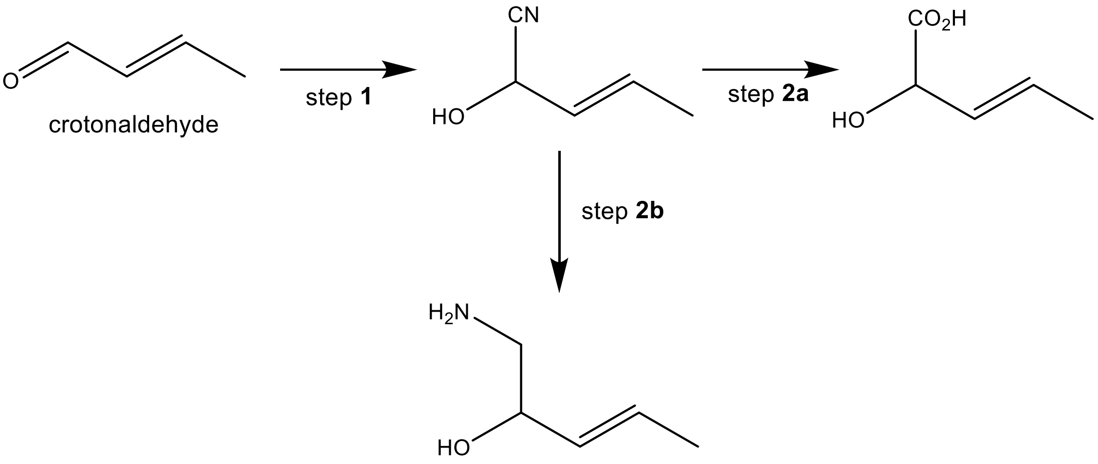


A 512 **B** 256✓ **C** 128 **D** 64

Solution

There are seven chiral carbons – bolded in the above structure. The C=N at the top right hand corner can show cis-trans isomerism. Hence the total number of stereoisomers is 2 raised to the power of 8, which is 256.

27 Crotonaldehyde is an important biomolecule.



Which of the following statements is true about the above synthetic scheme?

✓ **A** The reaction of crotonaldehyde with hot acidified $KMnO_4$ produces only one organic product.

B Step **1** involves heating crotonaldehyde with NaCN in ethanol.

C Step **2a** involves the oxidation of crotonaldehyde because it gained oxygen atoms.

D $NaBH_4$ is the reagent used in step **2b**.

Solution

Option A: Two products are formed – CO_2 (which is NOT organic) and ethanoic acid.

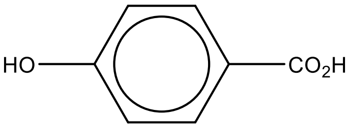
Option B: Step 1 is nucleophilic addition. The reagents and conditions mentioned in this option is for nucleophilic substitution.

Option C: Step 2a is a hydrolysis reaction, not an oxidation reaction.

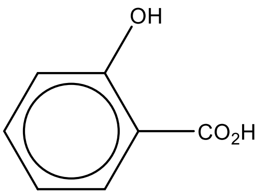
Option D: $LiAlH_4$ can reduce nitriles but $NaBH_4$ is not reducing enough for this purpose.

28 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde share the same molecular formula.

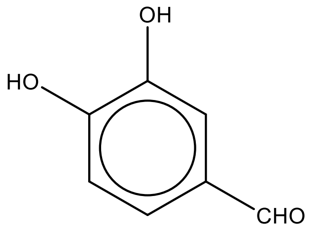
The standard enthalpy changes of formation for 4-hydroxybenzoic acid, 2-hydroxybenzoic acid and 3,4-dihydroxybenzaldehyde are –481 kJ mol^{-1}, –493 kJ mol^{-1} and –392 kJ mol^{-1} respectively.



4-hydroxybenzoic acid



2-hydroxybenzoic acid



3,4-dihydroxybenzaldehyde

Which of the following statements is correct?

1 The thermodynamic stability of these three compounds decrease in the order:
2-hydroxybenzoic acid > 4-hydroxybenzoic acid > 3,4-dihydroxybenzaldehyde

2 3,4-dihydroxybenzaldehyde and 4-hydroxybenzoic acid are positional isomers.

3 The magnitude of the standard enthalpy change of combustion of these three compounds increase in the order:
3,4-dihydroxybenzaldehyde < 4-hydroxybenzoic acid < 2-hydroxybenzoic acid

✓ **A** 1 only

B 2 only

C 1 and 3

D 2 and 3

Solution

Statement 2: They are functional group isomers.

To verify statements 1 and 3, it is best to represent both the enthalpy changes of formation and combustion in the same energy level diagram. With this combined energy level diagram, it is clear that statement 1 is true while statement 3 is false.

29 Chloroethane can be used to make sodium propanoate.

$$\text{chloroethane} \longrightarrow \textbf{Z} \longrightarrow \text{sodium propanoate}$$

The intermediate, **Z**, is treated with boiling aqueous sodium hydroxide to give sodium propanoate.

Which reagent would produce the intermediate, **Z**, from chloroethane?

✓ **A** potassium cyanide in ethanol

B hydrogen cyanide

C sodium hydroxide in ethanol

D alkaline $KMnO_4$

Solution

Recognise that the number of carbon atoms increased by 1 from chloroethane to sodium propanoate – there is a step-up reaction involving cyanide somewhere in the two steps. We seem to need to perform nucleophilic substitution on chloroethane as the first step.

Option B is the reagent for nucleophilic addition on aldehydes and ketones.

Option C is the reagent for elimination; but is there a point in converting chloroethane to ethene in this context?

Option D is the reagent for mild oxidation; but how does chloroethane actually react with it?

30 A polypeptide is subjected to hydrolysis by cyanogen bromide and two digestive enzymes.

- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide.
- The enzyme chemotrypsin hydrolyses a peptide bond at the carboxylic end of tryptophan (trp) to give two dipeptides and a tripeptide.
- The enzyme trypsin, which hydrolyses a peptide bond at the carboxylic end of lysine (lys) to give 2 tripeptides and gly.

What is the sequence of the amino acids in this polypeptide?

A ser-trp-lys-trp-met-lys-gly

✓ **B** ser-trp-lys-met-trp-lys-gly

C gly-lys-met-trp-lys-trp-ser

D gly-lys-trp-met-lys-trp-ser

Solution

"At the carboxylic end of [some amino acid]" – the RHS end of the mentioned amino acid.

Option A is out because cyanogen bromide cleaves it into a pentapeptide and a dipeptide instead. It is possible that the student think that this is the correct option if he cleaves at the LHS end of methionine.

Option C is out because trypsin does not cleave it to give glycine. In fact, instead of obtaining 2 tripeptides and glycine, we obtain two dipeptides and a tripeptide. Neither does it fit the description under chemotrypsin – there would be a tetrapeptide formed.

Option D is out because chemotrypsin cleaves it into two tripeptides and serine instead. It is possible that the student think that this is the correct option if he cleaves at the LHS end of tryptophan.

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

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY 9729/02
Higher 2

Paper 2 Structured Questions **26 August 2019**
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 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	**/ 7**
2	**/ 21**
3	**/ 15**
4	**/ 7**
5	**/ 11**
6	**/ 14**
TOTAL	**/ 75**

This document consists of **21** printed pages and **1** blank page.

1	**(a)**	The element aluminium and its compounds have some properties characteristic of metals, and some of non-metals. Aluminium hydroxide, for example, is known to be *amphoteric*.	
		(i)	Explain the meaning of the word “amphoteric”. [1]
			The ability to react with both acids and bases.
		Aluminium sulfate and calcium oxide are sometimes added to water supplies to co-precipitate suspended solids and bacteria. A small amount of aluminium-containing ions remains in solution and its presence in drinking water may contribute to the mental illness known as Alzheimer’s disease.	
		(ii)	Write a balanced equation for the reaction that occurs when aluminium sulfate and calcium oxide are added to water, given that aluminium hydroxide is one of the products formed. [1]
			$Al_2(SO_4)_3 + 3CaO + 3H_2O \rightarrow 2Al(OH)_3 + 3CaSO_4$
		(iii)	By considering the nature of calcium oxide, explain why adding too much of it would increase the risk of contracting Alzheimer’s disease. Write an equation to illustrate how “aluminium-containing ions remains in (drinking water)” as a result of adding too much calcium oxide. [2]
			CaO dissolves slightly to form an alkaline solution. OH^- thus formed reacts with $Al(OH)_3$ to form a soluble complex. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
1	**(b)**	Beryllium oxide (BeO) is amphoteric, just like $Al(OH)_3$.	
		(i)	Beryllium oxide reacts with sodium hydroxide according to the equation, $2NaOH + BeO \longrightarrow Na_2BeO_2 + H_2O$ Given the position of beryllium in the Periodic Table, explain how this reaction illustrates the amphoteric nature of beryllium oxide. [2] BeO: Gp 2 (**metallic**) oxide, expected to form basic oxide and to react with acid. but here it is reacting with an alkali, illustrating its acidic nature.

(ii) To further illustrate its amphoteric nature, at 500 °C, BeO reacts with Na_2O to form compound **F** as the **sole product**. The molar masses of all three compounds are tabulated below.

compound	molar mass / g mol^{-1}
BeO	25
Na_2O	62
F	149

Write a balanced equation of the above reaction. [1]

$BeO + 2Na_2O \rightarrow Na_4BeO_3$

[Total: 7]

2 **(a)** In the laboratory, there are three bottles labelled **X**, **Y** and **Z**. Each bottle contains one of the following reagents:

KI(aq), Cl_2(aq), and NaBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

test	procedure	observations
1	mix reagent in bottle **X** with reagent in bottle **Z**	no change in colour
2	mix reagent in bottle **Y** with reagent in bottle **Z**	mixture turns brown
3	mix reagent in bottle **Y** with reagent in bottle **X**	mixture turns reddish-brown

(i) By comparing relevant standard reduction potential values from the Data Booklet, explain how it can be deduced that **Y** is aqueous chlorine. There is **no** need for calculations. [1]

Chlorine has the most positive standard reduction potential (compared to that of bromine and iodine) hence it is able to oxidise both iodide and bromide.

(ii) Tests 2 and 3 were executed to determine the reagents in bottles **X** and **Z**.

Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand.

State the observations that will indicate whether the bottles contained KI(aq) or NaBr(aq) initially. [2]

The bottle with orange-red organic layer contains NaBr (aq) initially.
The bottle with violet / purple organic layer contains KI (aq) initially.

2 **(b)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure.

SCl_2 is formed from S_8 and Cl_2.

(i) Explain why S_8 exists as a solid while Cl_2 exists as a gas at room temperature. [2]

Both exist as non-polar simple covalent molecules.

The size of the electron cloud of sulfur is so much larger hence the idid interactions amongst sulfur molecules are stronger than the idid amongst chlorine molecules.

Therefore the melting point of sulfur is significantly higher than that of chlorine.

(ii) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps.

The first step involves disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write the equation of the second step. [1]

$$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$$

Some chemists speculate that the intermediate is not disulfur dichloride but **K**.
K shares the same elemental mass percentages as sulfur dichloride and has a molar mass of 206.2 g mol^{-1}.

(iii) State the molecular formula of **K**. [1]

S_2Cl_4

(iv) All the chlorine atoms in **K** are terminal.
There are only two central atoms in **K**.
The bond angles about each central atom are different.

State the shape around each central atom and the respective bond angles. [2]

See-saw (90^0 and/or 120^o). (88^0 and/or 118^0)

and

bent (105^0 or 104.5^0)

2	**(c)**	Sulfuryl chloride, SO_2Cl_2, is commonly confused with thionyl chloride, $SOCl_2$. The properties of these two sulfur oxychlorides are quite different. SO_2Cl_2 is a source of chlorine while $SOCl_2$ is a source of chloride ions for various organic reactions. When heated, sulfuryl chloride decomposes endothermically as follows: $SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$ In an experiment, 1.00 mol of SO_2Cl_2 vapour was heated in a closed 4.00 dm^3 flask at 500 K until equilibrium was established. The flask was then rapidly cooled to liquefy SO_2Cl_2. After removing gaseous SO_2 and Cl_2, excess water was then carefully added to the liquid SO_2Cl_2, causing the following reaction to occur. $SO_2Cl_2\,(l) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + 2HCl\,(aq)$ The resulting solution was made up to 250 cm^3 in a standard graduated flask. 20.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH. 40.00 cm^3 of NaOH was required for complete neutralisation.	
		(i)	Write an expression for K_c for the equilibrium above and state its units. [2] $K_c = [SO_2][Cl_2] / [SO_2Cl_2]$ mol dm^{-3}
		(ii)	Calculate the equilibrium amount of SO_2Cl_2, SO_2, and Cl_2 in the original equilibrium at 500 K. Hence calculate a value for the K_c for the equilibrium. [4] $n(H_2SO_4) = ¼\,(40.00/1000)(250/20.0) = 0.125$ $n(SO_2Cl_2)$ at eqm = 0.125 $n(SO_2)$ and $n(Cl_2)$ at eqm are 1.00 – 0.125 = 0.875 each $K_c = (0.875)^2 / (0.125 \times 4) = 1.53$ mol dm^{-3}
2	**(c)**	**(iii)**	A student suggested to carry out the decomposition process at a higher temperature and high pressure to decrease the time required for the process. Discuss the effects of the proposed changes on the rate and the yield. [2] At a higher temperature, both rate and yield would increase. However, at high pressures, the rate (but not the yield) would increase as the position of equilibrium will be shifted to the LHS

2 **(d)** SO_2Cl_2 is widely used as a reagent in chlorination of the hydrocarbons. Such reactions occur under free radical conditions using H_2O_2 as an initiator.

For example, methylbenzene undergoes free radical substitution with SO_2Cl_2 to give benzyl chloride, $C_6H_5CH_2Cl$.

The mechanism of this reaction involves three stages:

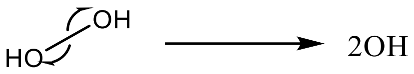
I. Initiation
II. Propagation
III. Termination

- The **initiation** stage is unique as it involves two successive steps.

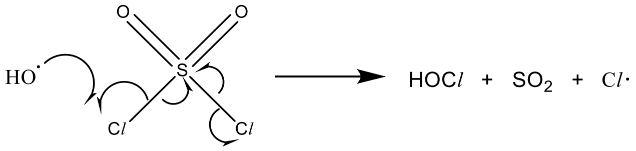
(i) In the first step, there is an initial homolytic breaking of the peroxide bond in hydrogen peroxide forming two hydroxyl radicals.

Using curly arrows, show the mechanism for this step.

[1]



The second initiation step involves the reaction between the hydroxyl radical and SO_2Cl_2 to give SO_2, $HOCl$ and a chlorine radical. It has been drawn for you below.



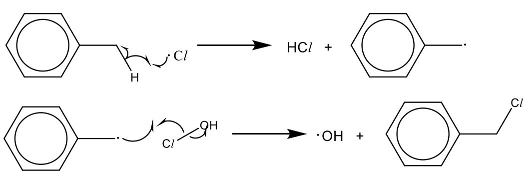
After these two initiation steps,

- The chlorine radical then reacts with methylbenzene in two **propagation** steps to form benzyl chloride and regenerating the hydroxyl radicals.
- The chain reaction **terminates** when two radicals combine to give stable compounds.

(ii) Complete the mechanism by writing the steps for the **propagation** and **termination** stages.

[3]

Propagation

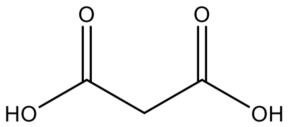


Termination

2OH → H_2O_2
HO + Cl → HOCl

[Total: 21]

3 Malonic acid is an important precursor to some polyesters.



(a) Malonic acid can be synthesised in more than one way.

(i) Suggest a three-step synthetic route from ethene to malonic acid. [5]

1) aqueous bromine
2) KCN (ethanolic) heat
3) acidified $KMnO_4$ (or $K_2Cr_2O_7$), heat with reflux

Intermediates: 2-bromoethanol; 3-hydroxypropanenitrile.

(ii) Malonic acid can be made by reacting two moles of **L** with a mole of carbon suboxide. [1]

$$O{=}C{=}C{=}C{=}O$$

carbon suboxide

Identify **L**.

H_2O

(b) Malonic acid behaves as a diprotic acid. The values of its K_{a1} and K_{a2} are 1.51×10^{-3} mol dm^{-3} and 2.00×10^{-6} mol dm^{-3} respectively.

In an experiment, 15.0 cm^3 of a 0.100 mol dm^{-3} solution of malonic acid was titrated against 0.100 mol dm^{-3} NaOH.

(i) Calculate the initial pH. [1]

pH = - log (1.51×10^{-2}) = 1.91

(ii) Calculate the volume of NaOH required for the first equivalence point. [1]

15.0 times 0.100 / 0.100 = 15.00 cm^3

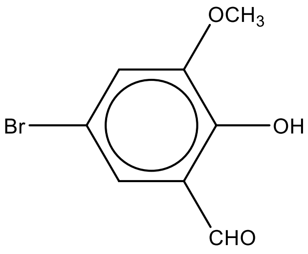
(iii) Write an equation to explain why the second equivalence point is above 7. [1]

$$^-O_2CCH_2CO_2^- + H_2O \rightleftharpoons HO_2CCH_2CO_2^- + HO^-$$

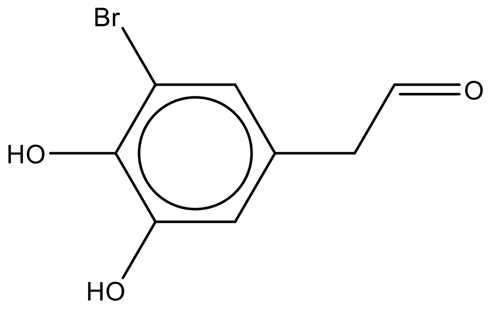
(iv) Calculate the second equivalence pH. [2]

2nd equivalence volume = 30.0 cm^3
[$^-OOCCH_2COO^-$] at 2nd equivalence point = 15/(30+15) X 0.100
= 0.0333 mol dm^{-3}

$K_b = 10^{-14} / K_{a2} = 5.00 \times 10^{-9}$ mol dm^{-3}
pOH = - ½ log ($5.00 \times 10^{-9} \times 0.0333$) = 4.89
pH = 14 – pOH = 9.11

3	**(b)**	A buffer is obtained after the addition of 12.00 cm^3 of NaOH solution.	
		(v)	Write an equation for the reaction that occurs when a drop of HNO_3 is added to this buffer. [1] $HO_2CCH_2CO_2^- + H^+ \rightarrow HO_2CCH_2CO_2H$
		(vi)	Calculate the pH of this buffer. [2] n(malonic acid) remaining = [(15.0)(0.100)-(12.00)(0.100)] / 1000 $= 3.00 \text{ X } 10^{-4}$ n($HO_2CCH_2CO_2^-$) = (12.00)(0.100) / 1000 $= 1.20 \text{ X } 10^{-3}$ pH = – log (1.51 × 10^{-3}) + log (12.0/3.00) = 3 + log (4/1.51) = 3.42
		(vii)	Another buffer is obtained after the addition of 22.50 cm^3 of NaOH solution. Calculate its pH. [1] pH = pK_{a2} = - log (2.00 × 10^{-6}) = 6 – lg 2.00 = 5.70
			[Total: 15]
4	**V** is a mono-brominated derivative of *ortho*-vanillin. *Ortho*-vanillins are used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals.  **V**		
	(a)	Define the term "constitutional isomerism". [1] Compounds having the same molecular formula but different structural formulae/different structures.	

(b) **U** is a constitutional isomer of **V**.



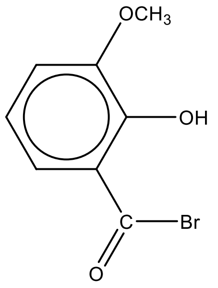
U

State a simple chemical test to distinguish between **U** and **V**. State the observations. [2]

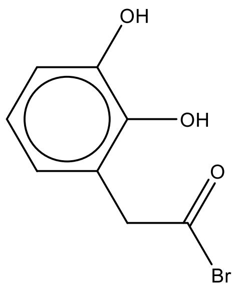
Fehling's test.
No ppt for V. brick-red/brown/reddish-brown ppt for U.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

(c) Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by cold $AgNO_3$ solution. State the observations. [2]



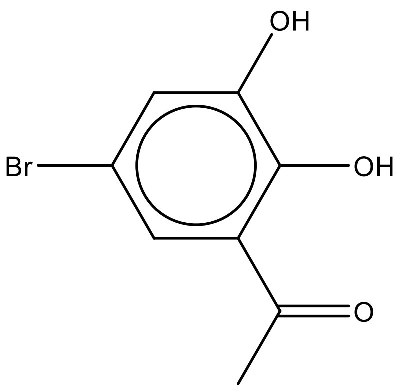
or



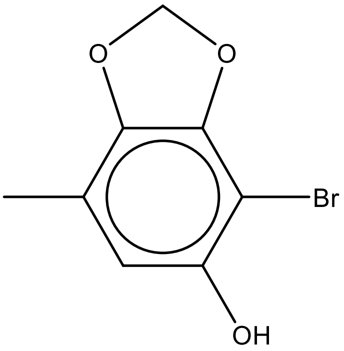
No ppt for X.
Cream/off-white ppt for this constitutional isomer.

The structures you draw from 4(c) to 4(e) must contain one benzene ring.

4 **(d)** Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself by warm alkaline iodine. [1]



	(e)	Draw the structural formula of a constitutional isomer of **V** which can be distinguished from **V** itself via 2,4-dinitrophenylhydrazine but not neutral iron(III) chloride solution not sodium metal. [1]



[Total: 7]

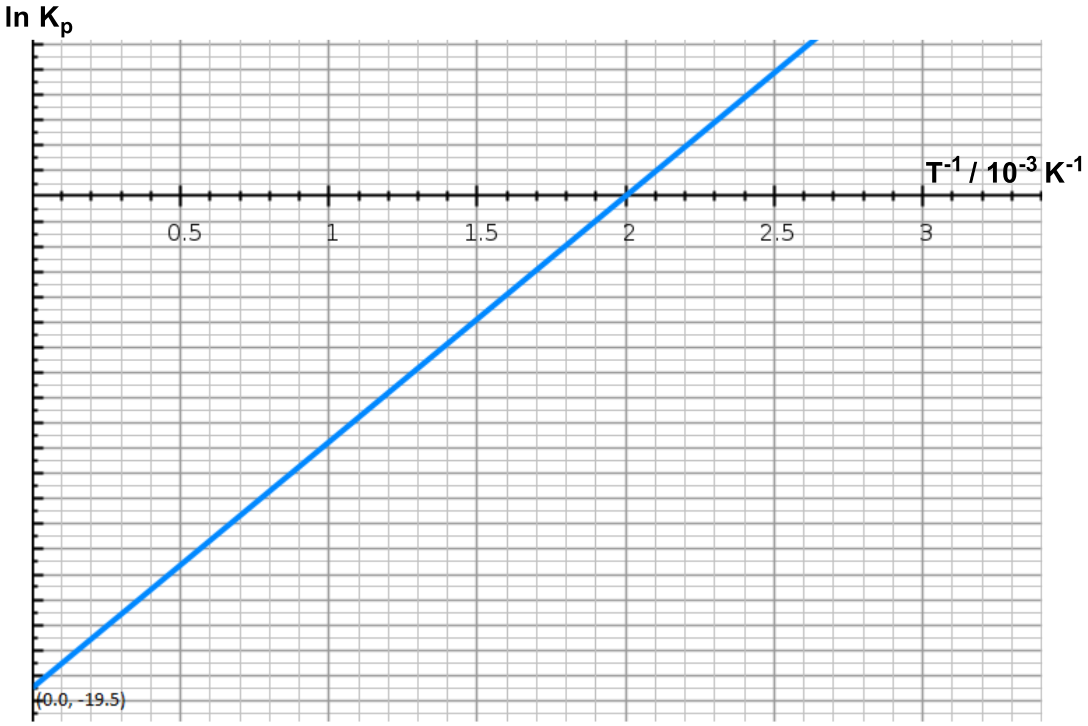
5 Space-suits need to be designed in such a way to supply oxygen to astronauts and to remove the carbon dioxide exhaled by them.

(a) Metal oxides like silver oxide, Ag_2O, are used to get rid of the carbon dioxide.

Ag_2O reacts reversibly with carbon dioxide, as described in the equilibrium equation,

$$Ag_2O\ (s) + CO_2\ (g) \rightleftharpoons Ag_2CO_3\ (s)$$

The van't Hoff plot shows how the equilibrium constant, K_p, of this reaction varies with temperature.



(i) From the above graph, deduce the relationship between K_p and T. [1]

When one increases, the other decreases/inversely related/inverse relationship.

(ii) Hence, explain whether the reaction between silver oxide and carbon dioxide is exothermic or endothermic. [2]

The reaction is exothermic.
Explanation:
as the T increases/decreases, K_p decreases/increases,
implying that PoE shifted left/right,
which further implies that the backward reaction is endothermic/forward reaction is exothermic.

5 **(a)** **(iii)** Given that the straight line graph for ln K_p versus T^{-1} is described by the equation

$$\ln K_p = \left(\frac{-\Delta H^0}{R}\right)\frac{1}{T} + \frac{\Delta S^0}{R}$$

Calculate the standard entropy change of this reaction and explain the significance of its sign with respect to the reaction. [2]

y-intercept = -19.5

$\Delta S = (-19.5) \times 8.31 = -162$ J mol^{-1} K^{-1}

The sign is negative because there is a decrease in the amount of gas. [

After absorbing carbon dioxide for some time, most if not all of the silver oxide would have been depleted. To **recharge** the system, heat is applied into the system to form Ag_2O again.

(iv) ΔG^0 and K_p are mathematically related by the equation

$$\Delta G^0 = -RT \ln K_p$$

Using the graph, estimate the minimum temperature at which the **recharging** of this system becomes spontaneous. [1]

x-intercept = 2×10^{-3} K^{-1}

minimum temperature = $1 / (2 \times 10^{-3}$ K$^{-1}) = 500$ K

5 **(b)** Silver carbonate (relative formula mass = 275.8) is a sparingly soluble salt. At 25 °C, its solubility is 0.032 g dm^{-3} of water.

(i) Show that the value of the K_{sp} of silver carbonate at 25 °C is 6.25×10^{-12}. [1]

$4(0.032 / 275.8)^3 = 6.25 \times 10^{-12}$ mol^3 dm^{-9}

(ii) Calculate the solubility of silver carbonate in 0.100 mol dm^{-3} silver nitrate at 25 °C. [1]

$6.25 \times 10^{-12} = (0.100 + 2x)^2 x$

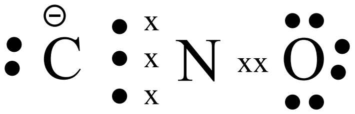
$x = 6.25 \times 10^{-10}$ mol dm^{-3}

(iii) 1.00 cm^3 of a 1.20×10^{-5} mol dm^{-3} silver nitrate solution was mixed with 3.00 cm^3 of a 7.45×10^{-5} mol dm^{-3} sodium carbonate solution.

Determine whether there would be precipitation of silver carbonate. [2]

Ionic Product = $(0.25 \times 1.20 \times 10^{-5})^2(0.75 \times 7.45 \times 10^{-5})$
$= 5.03 \times 10^{-16}$ mol^3 dm^{-9}

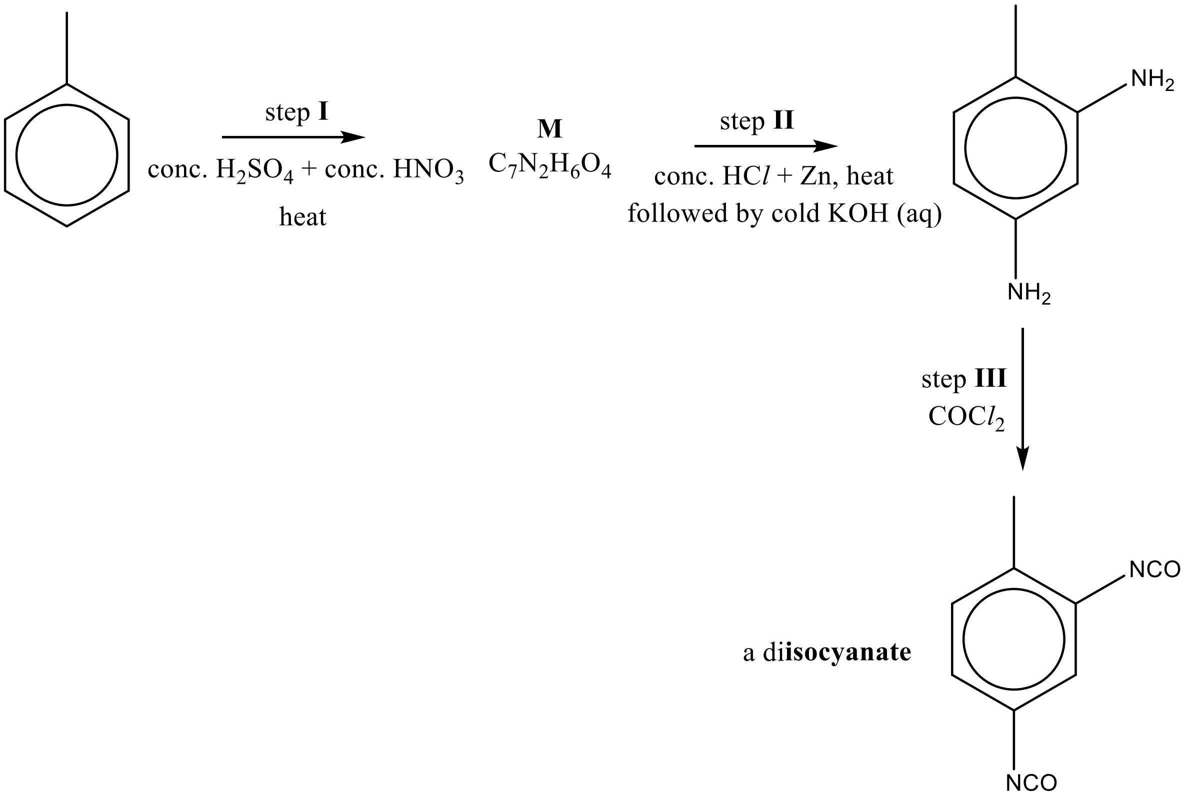
As IP < K_{sp}, there will not be precipitate of silver carbonate.

5	**(c)**	Silver carbonate can be reacted with ammonia to form silver fulminate, AgCNO, a powerful primary explosive. $4\ \mathrm{Ag_2CO_3} + 4\ \mathrm{NH_3} \rightarrow 4\ \mathrm{AgCNO} + 6\ \mathrm{H_2O} + 4\ \mathrm{Ag} + \mathrm{O_2}$	
		Draw the dot-and-cross diagram of the fulminate ion given that the N is the central atom and the negative charge is on the carbon. [1] 	
			[Total: 11]

6 The isocyanate functional group is a constitutional isomer of the fulminate, which was mentioned in question **5(c)**. The isocyanate has the carbon atom instead of nitrogen atom as the central atom.

Isocyanates are important industrial chemicals; they react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

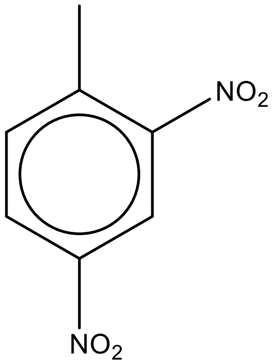
(a) This part is about the synthesis of a diisocyanate from methylbenzene.

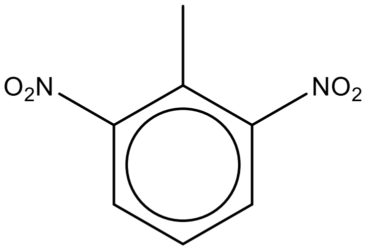
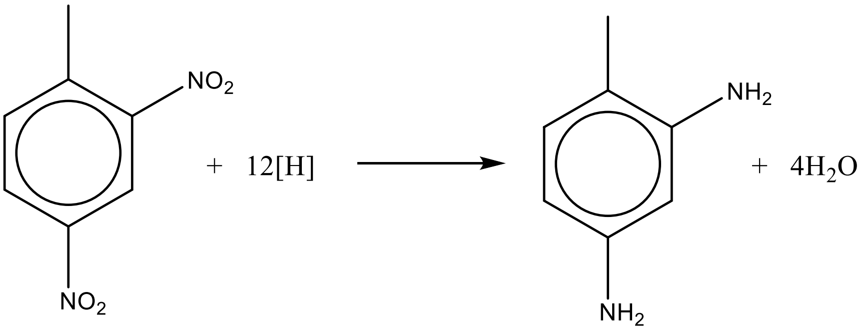


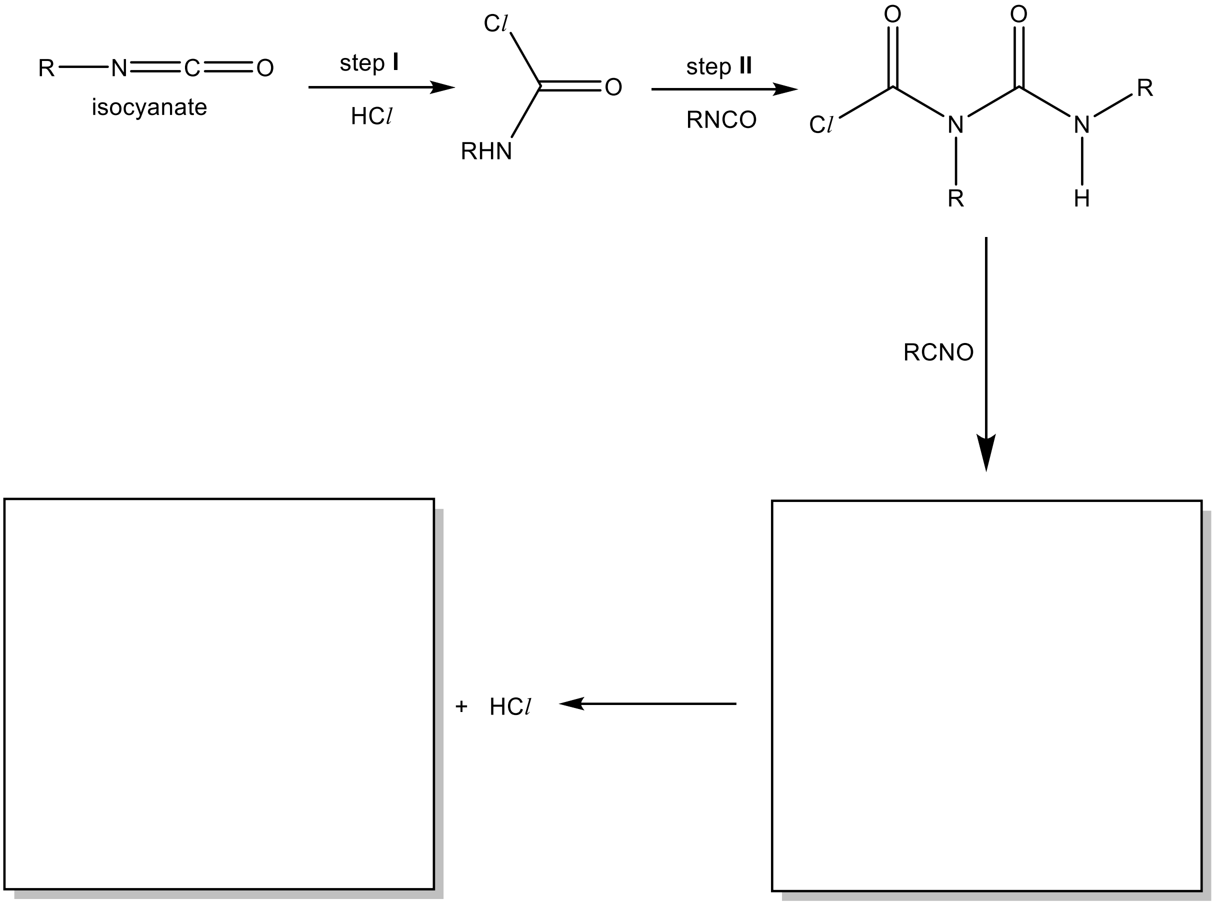
(i) State the type of reaction in step **I**. [1]

Electrophilic substitution.

(ii) Draw the structure of **M**. [1]



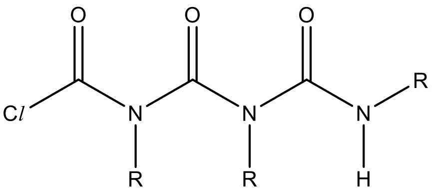
6	**(a)**	**(iii)**	Draw the structure of the isomer of **M** which is formed as a side-product in step **I**. [1] 
		(iv)	Explain the purpose of KOH in step **II**. [1] It is to liberate the amine from its protonated form. It is to form the amine from its protonated form.
		(v)	Write a balanced equation for the overall reaction in step **II**. You are to use [H] to balance the equation. [1] 
		(vi)	State the type of reaction in step **III**. [1] Condensation / addition-elimination
6	**(b)**	Examine the synthetic route below.	

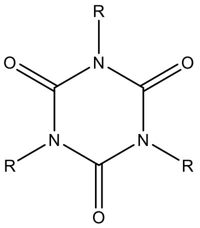


cyclic trimer **T**
$R_3C_3N_3O_3$

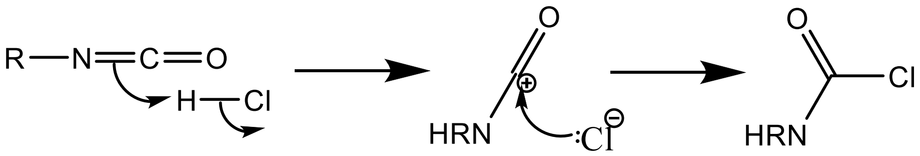
Q
$R_3C_3N_3O_3HCl$

(i) Draw the skeletal formulae of **Q** and the cyclic trimer **T** in the boxes provided. [2]





(ii) Step **I** is an electrophilic addition reaction. Draw the mechanism of step **I**. [3]



6 **(c)** When heated with $\text{HC}l\,(aq)$, organic isocyanates (RNCO) are hydrolysed to the amine salt ($\text{RNH}_3^+\text{C}l^-$) and carbon dioxide.

$$\text{RNCO} + \text{HC}l + \text{H}_2\text{O} \rightarrow \text{RNH}_3^+\text{C}l^- + \text{CO}_2$$

A 1.13 g sample of an organic isocyanate was treated in this way, and the carbon dioxide produced was absorbed in an excess of aqueous Ba(OH)_2, according to the equation shown.

$$\text{Ba(OH)}_2\,(aq) + \text{CO}_2\,(g) \longrightarrow \text{H}_2\text{O}\,(l) + \text{BaCO}_3\,(s)$$

The mixture was filtered and the residue BaCO_3 washed and dried thoroughly. The mass of the residue was 1.97 g.

(i) Show that the molecular mass of the organic isocyanate is 113 g mol^{-1}. [1]

n(org. isocyanate) = 1.97 / 197.3 = 1.00×10^{-2}

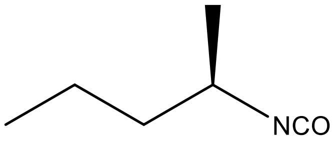
molecular mass of org. isocyanate = 1.13 / (1.00×10^{-2}) = 113.2 g mol^{-1}

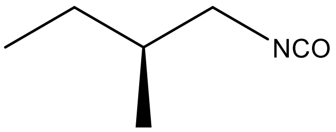
(ii) The R group in RNCO and $\text{RNH}_3^+\text{C}l^-$ contains only carbon and hydrogen.

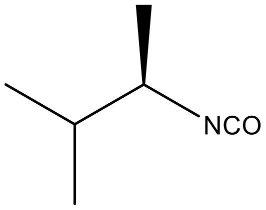
Use the molecular mass mentioned in **(i)** to suggest the molecular formula of the organic isocyanate. [1]

$\text{C}_6\text{H}_{11}\text{NO}$

(iii) Given that a pure sample of this organic isocyanate rotates plane-polarised light, draw a possible stereochemical formula of it. [1]







[Total: 14]

~ End of Paper ~

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 9729/03

Paper 3 Free Response

2 September 2019
2 hours

Candidates answer on separate paper.

Additional Materials: Cover Page
Answer Paper
Insert

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 page of writing paper.
Fasten the insert in front of all writing paper at the end of the examination.

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.

This document consists of **21** printed pages and **1** blank page.

Section A

Answer **all** the questions from this section.

1 **(a)** *Use of the insert is necessary for this question.*
Fasten the insert in front of all writing paper at the end of the examination.

An iodoalkane, RI, is hydrolysed by aqueous sodium hydroxide. The results obtained from two experiments are plotted on the insert. In each experiment, the overall [NaOH(aq)] remained virtually constant at the value given beside each graph.

(i) Use the graphs on the insert to determine the following. Show all workings clearly.

I Use the half-life method to deduce the order of reaction with respect to the iodoalkane.

II Use the initial rates method to deduce the order of reaction with respect to sodium hydroxide.

III Construct a rate equation for the reaction and use it to calculate a value for the rate constant. Include its units. [7]

From working on graph, when [OH^-] = 0.10 M, half-life = 58 min OR
From working on graph, when [OH^-] = 0.15 M, half-life = 39 min [1]
∴ reaction is first order w.r.t. RI. [1]

From working on graph, when [OH^-] = 0.10 M,
initial rate = 0.0100/96 = 0.000104 mol dm^{-3} min^{-1} &
From working on graph, when [OH^-] = 0.15 M,
initial rate = 0.0100/64 = 0.000156 mol dm^{-3} min^{-1} [1]
When [OH^-] x1.5, rate x1.5, ∴ reaction is first order w.r.t. OH^-. [1]

rate = k[RI][OH^-] [1] (if S_N1, do not award this mark)

$k = \frac{0.000104}{[0.010][0.10]} = 0.104\ mol^{-1}\ dm^3\ min^{-1}$ OR

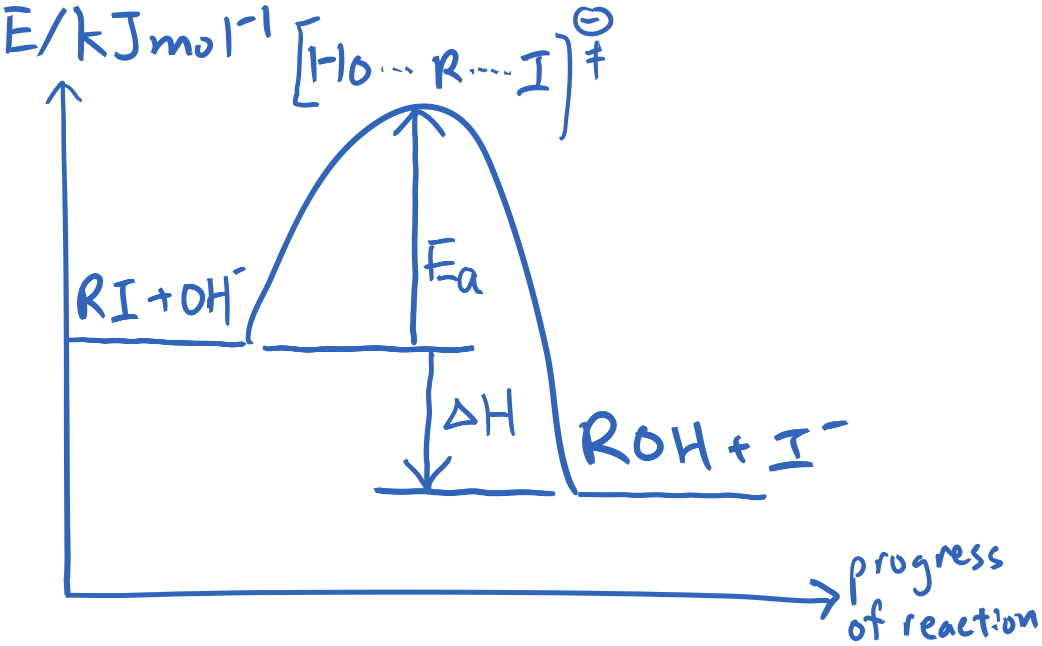
$k = \frac{0.000156}{[0.010][0.15]} = 0.104\ mol^{-1}\ dm^3\ min^{-1}$ [1+1]

Allow ecf if rate equation is rate = k[RI], then

$k = \frac{0.000104}{[0.010]} = 0.0104\ mol^{-1}\ dm^3\ min^{-1}$ OR

$k = \frac{0.000156}{[0.010]} = 0.0156\ mol^{-1}\ dm^3\ min^{-1}$ [1+1] (D.N.A. if rate = k[OH^-])

(ii) Hence draw a fully labelled energy profile diagram of the reaction. [3]



Shape and axes [1]
Reactants, Products [1] (if S_N1, mark for intermediate)
Ea and ΔH [1]
Allow ecf if deduced S_N1 in part (i)

(b) Silver(I) iodide and iodine are two solids which have low solubility in water. However when both are mixed together with water and left to stand, they dissolve completely to give a coloured solution of silver(I) triiodide.

(i) State the expected colour of the silver(I) triiodide solution. [1]

Yellow or Brown (answer is concentration dependent)

(ii) Write three relevant equilibria equations and use them to explain how the two solids can completely dissolve when mixed with water. [3]

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$--------- (1) [√]
$I_2(s) + aq \rightleftharpoons I_2(aq)$------------------ (2) [√]
$I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$----------- (3) [√]

Equilibria (1) and (2) exist for each of the poorly soluble compounds. However, equilibrium (3) is set up in the presence of $I^-(aq)$ and $I_2(aq)$ in solution and the position of equilibrium lies strongly to the right hand side[√]. With [I^-] and [I_2] constantly falling in (1) and (2), their positions of equilibria will constantly shift to the right[√][√] as well, causing AgI(s) and $I_2(s)$ to dissolve. OWTTE

[√] for each eqn and [√] for accompanying POE shift.
6[√]-3m, 4[√]-2m, 2[√]-1m

(c) Another triiodide compound, nitrogen triiodide, NI_3 is a simple covalent molecule that is very sensitive to shock and will decompose rapidly. A touch of a feather or even alpha particles from radioactive decay can trigger an explosion.

$$2NI_3(s) \longrightarrow N_2(g) + 3I_2(g) \qquad \Delta H = -290\ \text{kJ mol}^{-1}$$

76.5 kJ mol^{-1} of energy is needed to convert solid NI_3 to gaseous NI_3.

Use the above information and relevant information from the *Data Booklet* to calculate the N–I bond energy. [2]

$$\begin{tikzcd}
2NI_3(s) \arrow[r, "-290"] \arrow[d, "2(+76.5)"'] & N_2(g) & + \ 3I_2(g) \\
2NI_3(g) \arrow[r, "6BDE(N\text{–}I)"'] & 2N(g) \arrow[u, "2(-944)"] & + \ 6I(g) \arrow[u, "3(-151)"']
\end{tikzcd}$$

$-290 = 2(+76.5) + 6\text{BDE}(N\text{–}I) + (-944) + 3(-151)$
$\text{BDE}(N\text{–}I) = 159\ \text{kJ mol}^{-1}$

[1] using –290, +76.5, –944 & –151, no need coefficients and sign.
[1] answer 159, no ECF

(d) Alpha particles, ${}^{4}_{2}He^{2+}$ are produced from the radioactive decay of certain isotopes. An example of one is from the decay of Americium-241.

$${}^{241}_{95}Am \rightarrow {}^{4}_{2}He^{2+} + \mathbf{M}$$

(i) Use the *Data Booklet* to identify species **M** that is formed. [1]

${}^{237}_{93}Np^{2-}$, ${}^{237}Np^{2-}$ minimally, no need for $_{93}$.

(ii) Calculate the angle of deflection for **M** in a uniform electric field if the angle of deflection for ${}^{4}_{2}He^{2+}$ is +7.11°. [1]

Angle of deflection, AOD = $k\frac{Q}{m}$

$$\frac{AOD_1 m_1}{Q_1} = \frac{AOD_2 m_2}{Q_2}$$

$AOD_{Np^{2-}} = \frac{+7.11 \times 4 \times (-2)}{(+2)237} = -0.12^{o}$ (2 or 3 sf)

Americium is often used in smoke detectors as the compound AmO_2 and is made from the thermal decomposition of americium(III) ethanedioate, $Am_2(C_2O_4)_3$.

$$Am_2(C_2O_4)_3 \longrightarrow 2AmO_2 + 4CO + 2CO_2$$

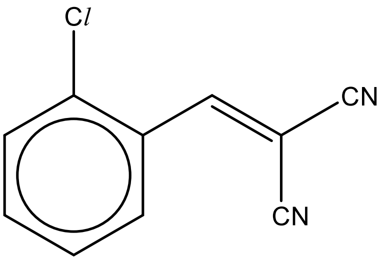
(iii) Explain why the thermal decomposition is a redox reaction in terms of oxidation state changes. [2]

Am in $Am_2(C_2O_4)_3$ is oxidised from +3 oxidation state to +4 in AmO_2. [1]
C in $Am_2(C_2O_4)_3$ is reduced from +3 oxidation state to +2 in CO and oxidised +4 in CO_2. [1]

[Total: 20]

2 **(a)** On 12 June 2019, Hong Kong police fired tear gas into the crowds as many took to the streets to protest against a proposed extradition Bill.

The active compound in tear gas is 2-chlorobenzalmalononitrile.



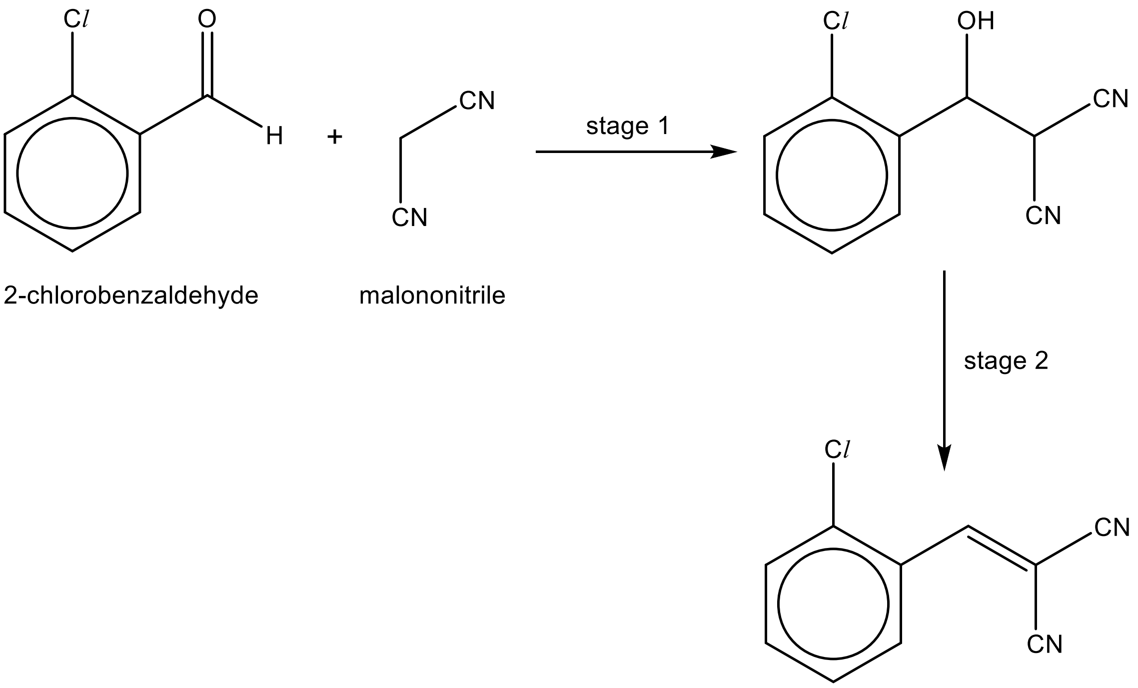
2-chlorobenzalmalononitrile

2-chlorobenzalmalononitrile is a solid at room temperature and is dispersed as an aerosol dissolved in a suitable organic solvent, typically dichloromethane, CH_2Cl_2. Its effects are felt when the solvent evaporates in air and the dry powder touches the eyes, nose and mouth.

(i) Suggest, with reasoning, two physical properties that make dichloromethane a suitable solvent. [2]

1. Polar to favour pd-pd interactions.
2. High volatility/low BP to dry/evaporate in the air.

2-chlorobenzalmalononitrile can be synthesised via the 2-stage Knoevenagel condensation.



2-chlorobenzalmalononitrile

(ii) State the type of the reaction in stage 2. [1]

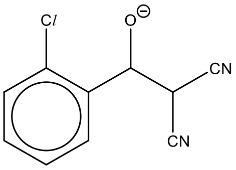
Elimination

(iii) Instead of purchasing malononitrile as a starting reagent, it can be made from dichloromethane.

Suggest the reagent and conditions needed to convert dichloromethane to malononitrile. [1]

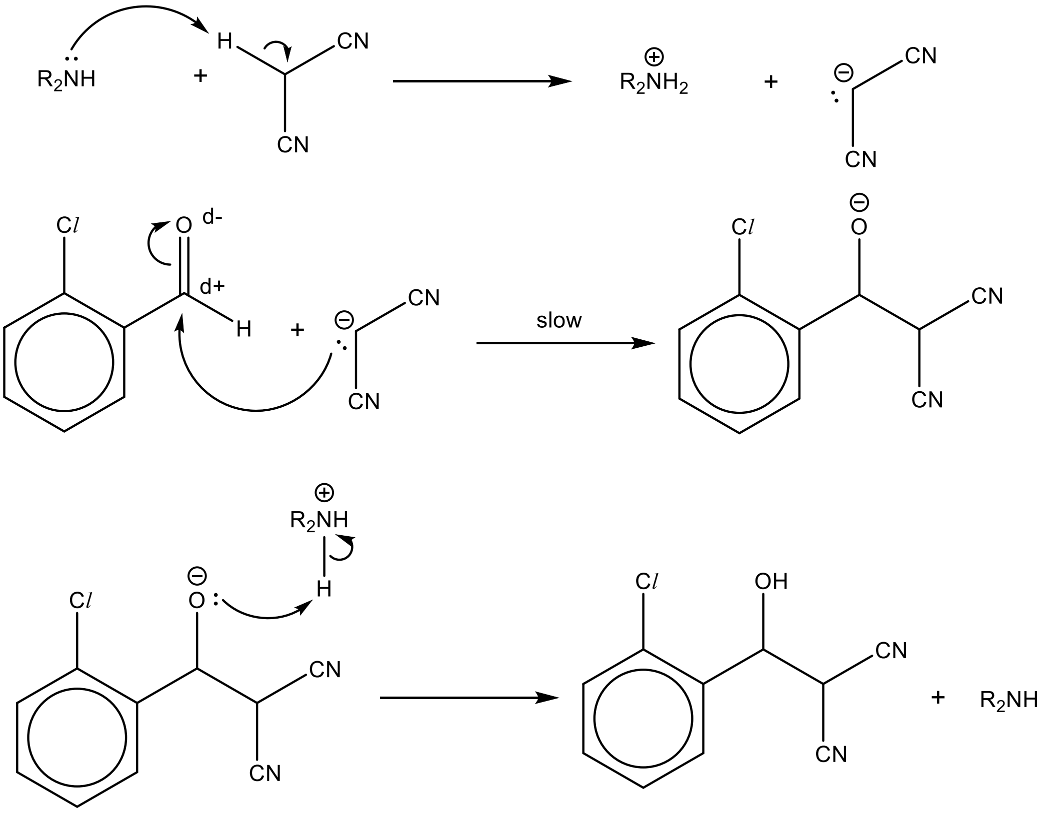
KCN (alc), heat under reflux

The following 3-step mechanism illustrates stage 1.

- Malononitrile is deprotonated by a weak base, R_2NH to form its conjugate base, $(NC)_2CH^-$.
- The conjugate base of malononitrile undergoes nucleophilic addition with 2-chlorobenzaldehyde to give  as an intermediate.
- The conjugate acid of R_2NH is deprotonated by the intermediate.

(iv) Describe the 3-step mechanism illustrated above.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]



Step 1:
2 correct arrows – [√]
$R_2NH_2^+$ & $(NC)_2CH^-$ – [√]

Step 2:
2 correct arrows – [√]
δ+ & δ– – [√]
slow – [√]

Step 3:
2 correct arrows – [√]

6[√] – 3m
4[√] – 2m
2[√] – 1m

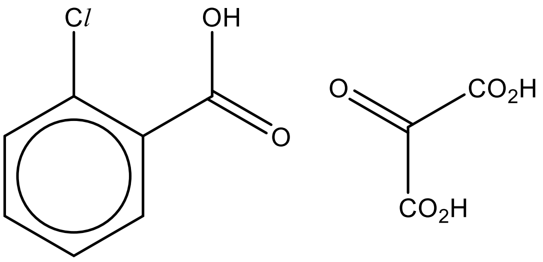
(v) Suggest another role of the weak base, R_2NH. [1]

Catalyst

(vi) Compare, and explain, the relative acidities of dichloromethane and malononitrile. [2]

Malononitrile is more acidic than dichloromethane. The two nitrile groups are more electron withdrawing than the two chloro groups and they stabilise the negative charge on the conjugate base of malononitrile better than dichloromethane.

(vii) Draw the **only two** organic products formed when 2-chlorobenzalmalononitrile is heated with acidified potassium manganate(VII). [2]

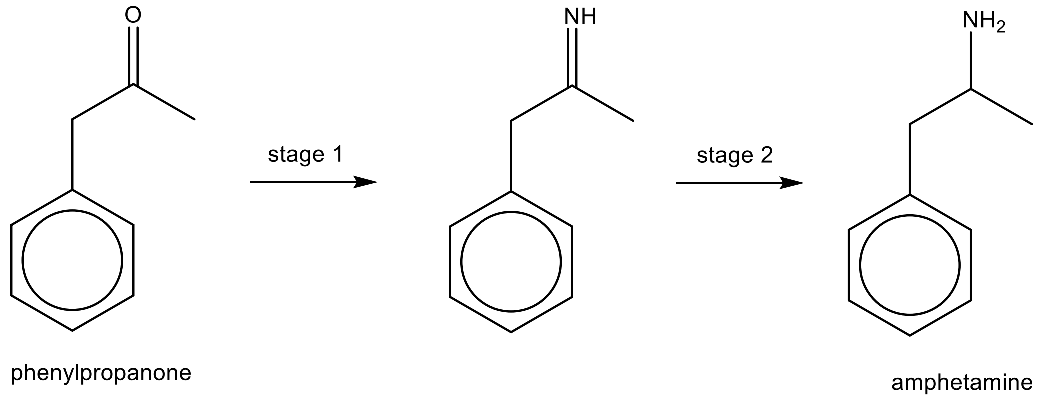


Note: Mesoxalic acid product is thermally stable and will not give 3 CO_2. More appropriately, it will be further hydrated in aqueous medium to form dihydroxymalonic acid, $(HO)_2C(CO_2H)_2$, but we can accept mesoxalic acid as the answer.

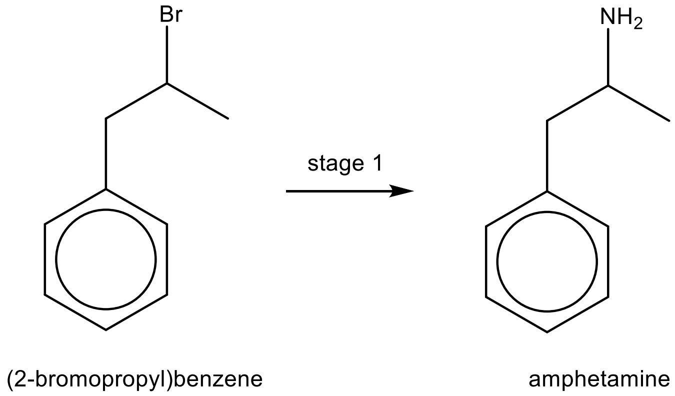
(b) During World War II, amphetamine pills were issued to the German army as they promoted alertness and self-confidence while reducing pain, hunger and the need for sleep.

Study the two methods of synthesis and answer the questions below.

Method 1



Method 2



(i) State the reagent used in stage 1 for both methods of synthesis. [1]

NH_3

(ii) One would think that Method 2 would give better yield of amphetamine during synthesis since it only involves one stage as compared to two stages in Method 1, but this is not true.

Suggests why the yield of amphetamine via Method 2 would be poor. [1]

Amphetamine synthesised via Method 2 can react further with more (2-bromopropyl)benzene to undergo polysubstitution/polyalkylation. OWTTE

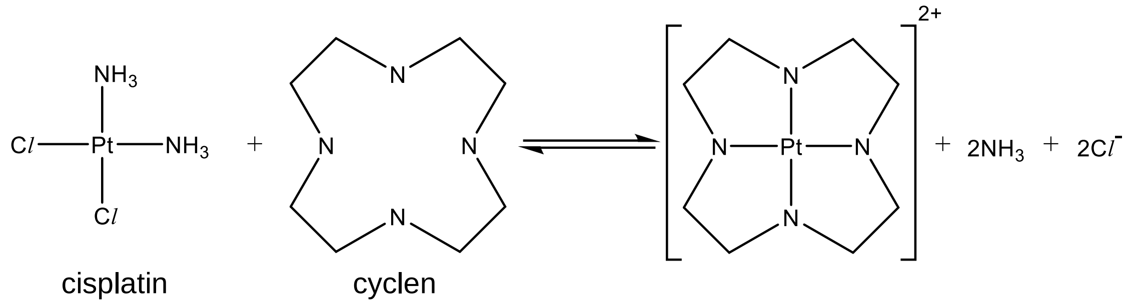
(iii) Only half of the product formed via Method 1 was biologically active in the body.

Account for this observation. [2]

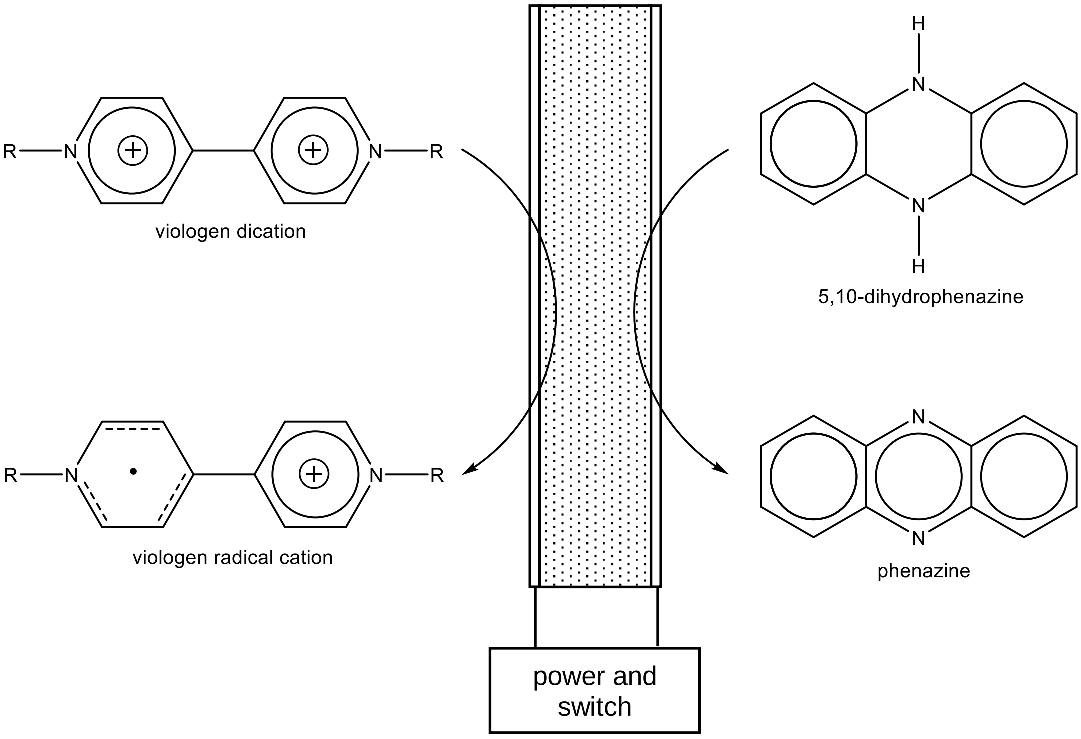
Amphetamine produced exists as a racemic mixture (idea of 50:50) and only one of the enantiomers possesses the correct configuration to be biologically active. OWTTE

(iv) Stage 2 of Method 1 employs the use of platinum metal as a catalyst.

State the type of catalysis involved and briefly outline the stages involved in the reaction. [3]

			Heterogeneous catalyst. [1] Diffusion – adsorption – reaction (bond breaking and forming) – desorption – diffusion. [2] OWTTE
		(v)	Explain why transition metals are useful as catalysts. [1] Variable oxidation state OR ability for substances to adsorb on to/form dative bonds on their surface for reaction. OWTTE.
	(c)	Cisplatin is an anti-cancer drug containing a platinum centre and appears as a light yellow powder. When cisplatin is dissolved in water and allowed to react with the cyclen *ligand*, the position of equilibrium lies strongly to the right hand side.  	
		(i)	Define the term *ligand*. [1] A ligand is a neutral molecule or anion with at least one lone pair of electrons capable of dative bonding to the central metal atom or ion.
		(ii)	Suggest signs for the enthalpy change of reaction and entropy change of reaction for the forward reaction, and comment on the spontaneity of the reaction across different temperatures. [2] Sign for ΔH is negative and sign for ΔS is positive. [1] Thus the reaction is spontaneous for all temperatures. [1]
		(iii)	Explain why transition metal compounds are coloured. [2] In presence of ligands, degenerate d-orbitals split into two energy levels with difference of ΔE. [√] When white/visible light falls on the complex ion, a particular wavelength of light with energy equal to ΔE is absorbed [√] by the transition metal ion and the electron is promoted from a lower-energy d-orbital to a higher-energy d-orbital. [√] The colour observed is complementary in colour to the light that is absorbed. [√] [√] ligands cause degenerate levels to split [√] energy gap absorbs visible wavelength / promote e^- lower to higher level [√] colour seen is complementary 3[√] – 2m, 2[√] – 1m
			[Total: 25]

3 **(a)** Boeing 787-9 Dreamliners are equipped with electronically dimmable windows. When a constant current is applied, electrochemical reactions happen within a panel and the conversion of colourless viologen dication to viologen radical cation forms an intense dark purple that shields out sunlight. A simplified diagram together with the chemical changes is shown.



The viologen dication and phenazine are aromatic species. Hückel's rule states that planar cyclic species with 4n+2 pi electrons, where n = 0, 1, 2 ..., are considered aromatic.

(i) State the hybridisation of the nitrogen atoms in the viologen dication. [1]

sp^2

(ii) State the number of pi electrons in phenazine. [1]

14

(iii) State the electrode at which the conversion of 5,10-dihydrophenazine to phenazine occurs. [1]

Anode

(iv) Write the half-equation for the reaction of 5,10-dihydrophenazine to phenazine in alkaline medium. You may write the names of both compounds respectively. [1]

5,10-dihydrophenazine + $2OH^-$ ⟶ phenazine + $2H_2O$ + $2e^-$

(v) 0.0300 g of 5,10-dihydrophenazine is finely coated on to one side of the panel.

Calculate the time needed to react all of the coated 5,10-dihydrophenazine to completely darken a window panel, given that a constant current of 0.150 A is supplied. [4]

M_r of 5,10-dihydrophenazine = 182.0 [1]

$n_{5,10\text{-dihydrophenazine}} = \frac{0.0300}{182.0} = 0.000165$ mol
$n_e = 0.000165 \times 2 = 0.000330$ mol [1] (allow ecf from (iv))

$Q = n_eF = 0.000330 \times 96500 = 31.8$ C [1]

$Q = It$
$t = Q/I = 31.8/0.150 = 212$ s [1]

(b) It is mandatory for all aircrafts to provide an inflatable life vest for every passenger. One particular model of life vests uses a rapid inflation system of compressed CO_2 in a canister.

A student read that the canisters typically pack 11.0 g of CO_2 and commented that the amount of CO_2 present will inflate a life vest fully to 6.00 dm^3 in capacity.

(i) Show how the student obtained 6.00 dm^3 as the capacity of the life vest and state the assumption made in the calculation. [2]

Vol. $CO_2 = \frac{11.0}{44.0}$ mol x 24.0 dm^3 mol^{-1} = 6.00 dm^3 [1]

Assumption is that the life vest was inflated at r.t.p. conditions (1 atm, 293 K). [1]

Don’t penalise 3sf.

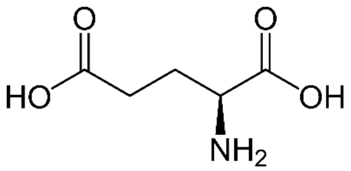
(ii) State two assumptions of the ideal gas law which allowed the student to make the calculations. [2]

1. Volume occupied by particles is negligible compared to the volume of space around them.
2. Negligible intermolecular forces exist between the particles.
3. Collisions are elastic and of negligible duration. (3 choose 2)

(c) Passengers on planes often find that they are more drawn to *umami*-rich flavours as the sweet and salty tastes are dulled due to changes in altitude.

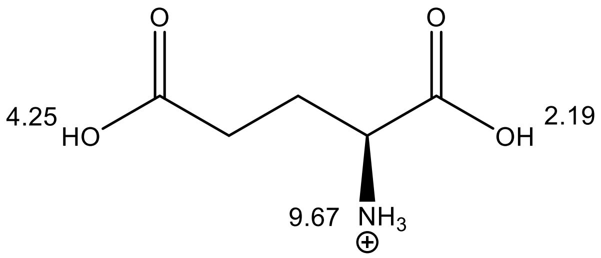
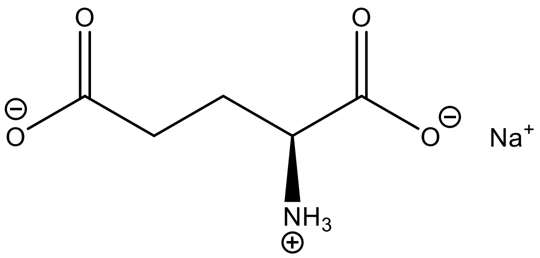
Monosodium glutamate (MSG) is one compound responsible for providing *umami* flavouring and it is the monosodium salt of glutamic acid.

The pK_a values associated with glutamic acid are 2.19, 4.25 and 9.67.



glutamic acid

(i) Draw the structure of glutamic acid at pH 1 and assign the three pK_a values. [2]

			 Structure [1]. 3 correct [1].
		(ii)	Draw the structure of monosodium glutamate. [1]  Na^+ can be anywhere. Allow molecular form and 1 COO^- group. ECF pk_{a1} from previous structure.
			[Total: 15]

Section B

Answer **one** question from this section.

4 (a) The thermal decomposition reactions for calcium ethanoate and calcium methanoate are given as follows:

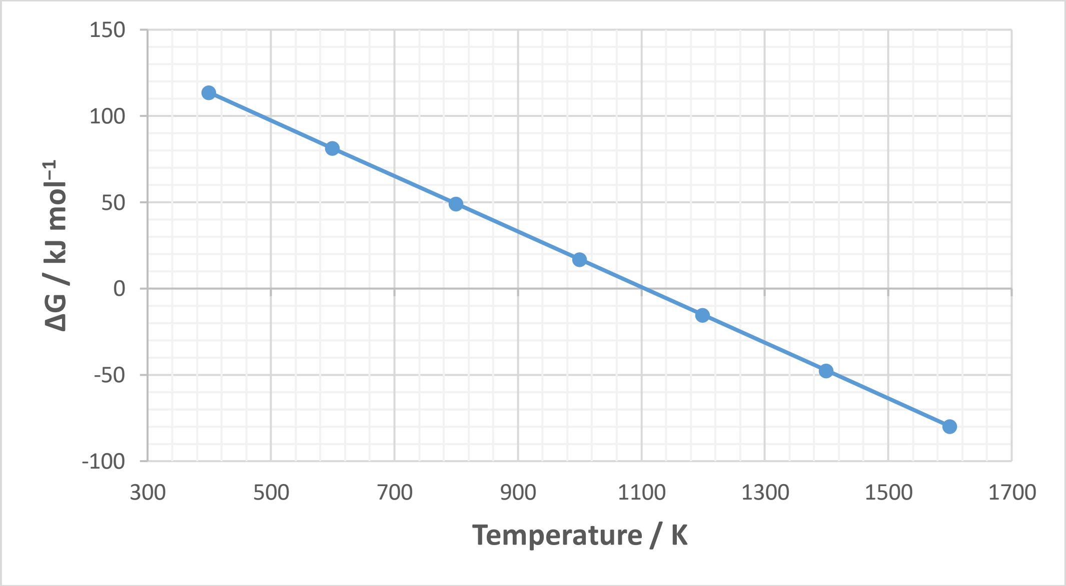
$Ca(HCOO)_2 \rightarrow CaCO_3 + HCHO$

$Ca(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

Predict the organic product, other than propanone and methanal, when a mixture of calcium methanoate and calcium ethanoate undergoes thermal decomposition. [1]

CH_3CHO **[1]**

(b) The following Ellingham diagram shows the variation of Gibbs free energy change with temperature for the thermal decomposition of calcium carbonate.



(i) State the range of temperatures where solid calcium carbonate would decompose upon heating. [1]

$T > 1100$ Kelvin or $T \geq 1000$ K (where $\Delta G < 0$ kJ mol^{-1}), cancel upper bound.

(ii) Calculate the entropy change of the reaction. [1]

Gradient of Line = $-\Delta S$

$[115 - (-80)] \div (400 - 1600) = -\Delta S$

$\Delta S = +0.1625 \text{ kJ mol}^{-1} \text{ K}^{-1} = +163 \text{ J mol}^{-1} \text{ K}^{-1}$ (3sf)

(iii) Hence, calculate the enthalpy change of the reaction. [1]

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - (1100)(+163)$ [Choose any data point.]

$\Delta H = +179{,}300 \text{ J mol}^{-1} = +179 \text{ kJ mol}^{-1}$ (3sf)

(c) Dolomite consists of $CaCO_3$ and $MgCO_3$ with the formula $CaMg(CO_3)_2$. It can be added to soil or marine aquarium as a pH buffer.

(i) Write a balanced equation for the action of heat on dolomite. [1]

$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$

(ii) Each carbonate is heated separately.

Predict and explain the difference in the thermal decomposition temperatures of the two carbonates. [3]

$MgCO_3$ has lower thermal decomposition temperature than $CaCO_3$. **[1]**

Mg^{2+} is smaller than Ca^{2+}. Mg^{2+} has greater charge density (and hence greater polarising power) than Ca^{2+}. **[1]**

Mg^{2+} polarised the CO_3^{2-} ion to a greater extent compared to Ca^{2+}. The C−O bond is weakened more. Less energy is needed to break it. **[1]**

Hence $MgCO_3$ has lower thermal decomposition temperature.

(iii) Explain why Li_2CO_3 decomposes in a similar way compared to these two carbonates. [1]

Li^+ is smaller than Mg^{2+}, though Li^+ has smaller charge than Mg^{2+}.
Li^+ has the similar charge density (and hence similar polarising power) as Mg^{2+}. **[1]**

(d) **(i)** Predict and explain the difference in melting points of calcium oxide and magnesium oxide. [2]

$$Lattice\ Energy \propto \left|\frac{Q_+Q_-}{r_+ + r_-}\right|$$

Mg^{2+} is smaller **[√]** than Ca^{2+}. The electrostatic attraction between Mg^{2+} and O^{2-} is stronger **[√]** than that between Ca^{2+} and O^{2-}. More energy is required to separate the Mg^{2+} and O^{2-} ions. **Two [√]: [1]**

Hence MgO has higher melting point and boiling point than CaO. **[1]**

(ii) In power plant or trash incineration plant, large quantities of sulfur dioxide gas are produced. Calcium oxide can be used to remove sulfur dioxide from these exhaust gases in a process called flue-gas desulfurisation.

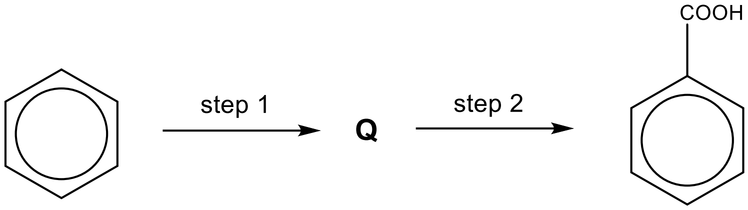
$$CaO + SO_2 \rightarrow CaSO_3$$

State the type of reaction for the above reaction. [1]

Acid-Base **[1]**

(e) Benzoic acid is an important precursor for the industrial synthesis of many other organic substances. Its salts are also used as food preservatives.

(i) Benzoic acid can be made from benzene by a two-step synthesis.



For steps 1 and 2, state the

- reagents and conditions, and
- type of reaction.

[4]

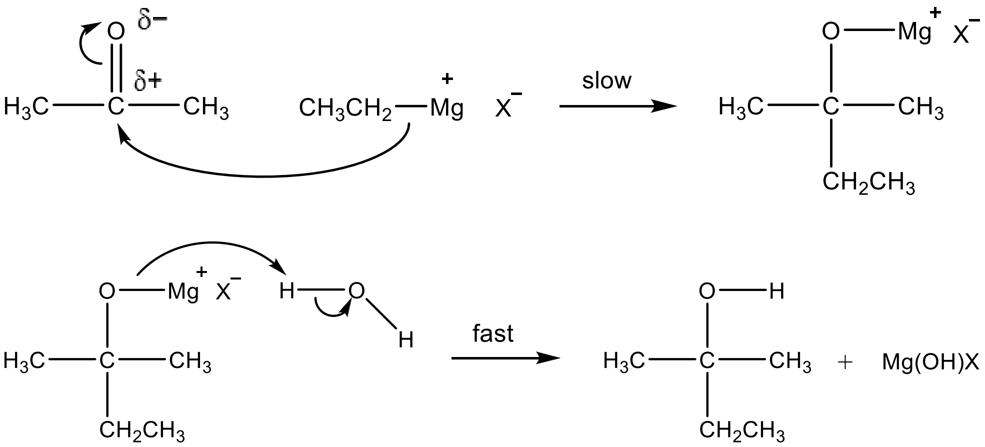
	Step 1	Step 2
Reagents and Conditions	CH_3Br and $FeBr_3$ **[1]** Room Temperature	$KMnO_4$(aq) **[1]** Dilute H_2SO_4(aq) Heat under reflux
Type of Reaction	Electrophilic Substitution **[1]**	Strong Oxidation **[1]**

(ii) Group 2 elements are known to form organometallic compounds. One example is the Grignard reagent with general formula RMgX. It is produced by reacting an alkyl halide or aryl halide with magnesium.

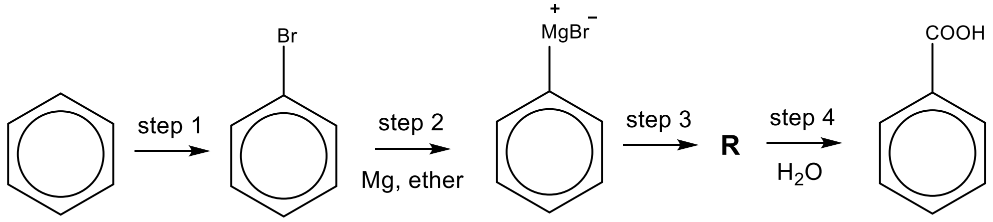
$RX + Mg \rightarrow R\text{–}Mg^+ X^-$ where X can be C*l* or Br.

The carbon-magnesium covalent bond is polarised as such; $\overset{\delta-}{C}-\overset{\delta+}{Mg}$.

Grignard reaction is important in making a new C–C bond. The mechanism for the reaction of ethylmagnesium bromide with propanone is shown as follows.

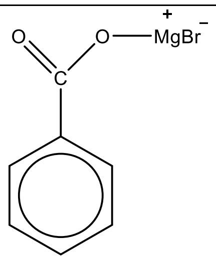


Benzoic acid can also be made from benzene by a four-step synthesis, using the Grignard reagent.



For step 3, state the reagent and intermediate **R**.

For steps 3 and 4, state the type of reaction. [4]

	Step 3	Step 4
Reagent	CO_2 **[1]**	
Intermediate **R**	 **[1]**	
Type of Reaction	Nucleophilic Addition **[1]**	Hydrolysis **[1]**

[Total: 20]

5 (a) (i) A compound **X** consists only of carbon, hydrogen and oxygen. During the complete combustion of 4 g of the compound, 8 g of carbon dioxide and 3.273 g of water were produced.

Determine the empirical formula of the compound **X**. [2]

	C	H	O
Mass / gram	(8)(12.0/44.0) = 2.182	(3.273)(2/18.0) = 0.3637	4 – 2.182 – 0.3637 = 1.454
Amount / mole	0.1818	0.3637	0.09088
Simplest Ratio	2	4	1

Empirical Formula: C_2H_4O **[1]** **Table [1]**

(ii) Another 4 g sample of compound **X** was vaporised at 160 °C and 101 kPa, and found to occupy a volume of 1620 cm^3.

Determine the relative molecular mass of this compound. [1]

$PV = nRT$
$(101,000)(1620 \div 10^{-6}) = (8.31)(160+273)(4 \div Mr)$
$Mr = 88.0$

(iii) Hence determine the molecular formula of compound **X**. Show your working clearly. [1]

(M_r of C_2H_4O) x n = 88.0
n = 2
Molecular Formula of X is $C_4H_8O_2$.

(b) Butanoic acid is used in the preparation of various esters. These esters have pleasant aromas or tastes. As a consequence, they are used as food and perfume additives.

(i) Biological methods have been developed to produce methane from waste organic matter using bacteria.

Based on the changes in oxidation numbers of carbon, construct a balanced equation for the disproportionation of **aqueous** butanoic acid to produce methane and carbon dioxide only. [1]

$2CH_3CH_2CH_2COOH + 2H_2O \rightarrow 5CH_4 + 3CO_2$

(ii) Given the following data,

- Enthalpy change of combustion of butanoic acid is −2184 kJ mol^{-1}.
- Enthalpy change of combustion of methane is −890 kJ mol^{-1}.

Calculate the enthalpy change for the reaction in **(b)(i)** for **liquid** butanoic acid instead of aqueous butanoic acid. [1]

$2CH_3CH_2CH_2COOH(l) + 2H_2O(l) \rightarrow 5CH_4(g) + 3CO_2(g)$
$\Delta H^{e}_{r} = (2)(-2184) - (5)(-890) = +82 \text{ kJ mol}^{-1}$

(iii) Given that

$CH_3CH_2CH_2COOH(l) \rightarrow CH_3CH_2CH_2COOH(aq)$ $\Delta H^\ominus_{soln} = -16.7$ kJ mol^{-1}

Use you answer in **(b)(ii)** to calculate the enthalpy change of reaction in **(b)(i)**. [2]

$$\begin{tikzcd}
2CH_3CH_2CH_2COOH(aq) + 2H_2O(l) \arrow[r, "\Delta H^\ominus_r"] & 5CH_4(g) + 3CO_2(g) \\
2CH_3CH_2CH_2COOH(l) + 2H_2O(l) \arrow[u, "(-16.7)(2)"'] \arrow[ur, "+82"'] &
\end{tikzcd}$$

[1] cycle

By Hess's Law,

$\Delta H^\ominus_r = -(-16.7)(2) + (+82) = +115$ kJ mol^{-1} (3sf) **[1]**

(iv) Butanoic acid boils at 117.7 °C. During boiling, the liquid phase is at equilibrium with the gas phase.

Calculate the entropy change of vaporisation of butanoic acid, given that the enthalpy change of vaporisation of butanoic acid is +52.0 kJ mol^{-1}. [1]

At boiling, $\Delta G_{vap} = 0$

$\Delta H_{vap} - T\Delta S_{vap} = 0$

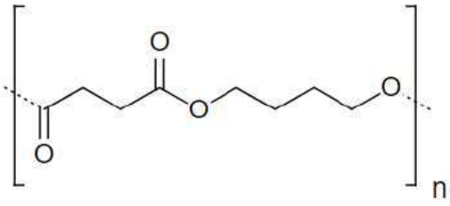
$\Delta S_{vap} = \Delta H_{vap} \div T = +52{,}000 \div (117.7 + 273) = +133$ J mol^{-1} K^{-1}

(v) Trouton's Rule states that the entropy change of vaporisation of many liquids, such as benzene and propanone, is about +88 J mol^{-1} K^{-1}.

Compare and explain the calculated result in **(b)(iv)** in relation to Trouton's Rule. [1]

$\Delta S^\ominus_{vap}$(butanoic acid) is more positive than +85 J mol^{-1} K^{-1}, as hydrogen bonds between butanoic acid molecules reduces its entropy in the liquid state.

(c) Polybutylene succinate (PBS) is a polyester used in packaging. It is receiving renewed interest due to increased demand for biodegradable polymers.



Polybutylene succinate

Hydrolysis of PBS produces two monomers **E** and **F**.

E can be reduced to **F**.

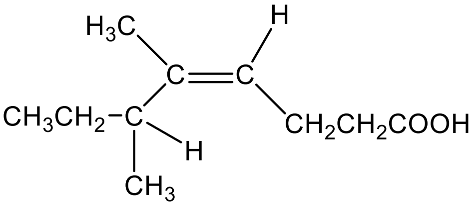
When an organic compound **D**, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.

G produces a yellow precipitate on warming with iodine in aqueous sodium hydroxide, and rotates the plane of polarised light.

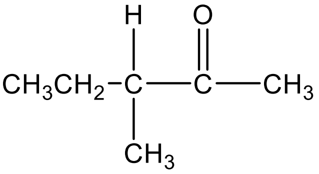
Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** to **H**, and explain the observations described above. [7]

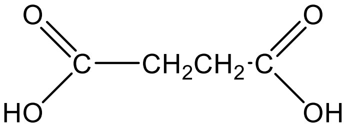
D :



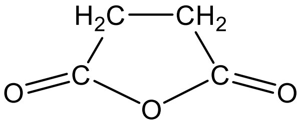
G :



E :

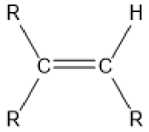
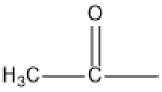


H :



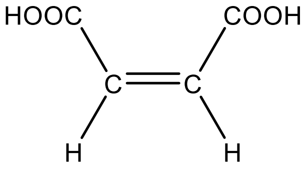
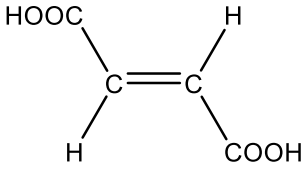
F : $HO{-}CH_2CH_2CH_2CH_2{-}OH$

Structures: [1] each. Total = [5]

Information	Type of Reaction	Deduction
D, $C_{10}H_{18}O_2$ is heated with acidified potassium manganate (VII), two products, **E**, $C_4H_6O_4$ and **G**, $C_6H_{12}O$ are formed.	Strong Oxidation	**D** has trisubstituted alkene:  √
G produces a yellow precipitate on heating with iodine in aqueous sodium hydroxide.	Mild Oxidation	**G** has this:  √
G rotates the plane of polarised light.		**G** has chiral carbon. √
Upon gentle heating, **E** produces a neutral compound **H**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4-dinitrophenylhydrazine.	Dehydration	**H** is not carboxylic acid, alcohol, ketone, or aldehyde. OR **H** is anhydride. √

Deduction: 4 ticks: [2] ; 2 or 3 ticks: [1] ; 1 tick : [0]

(d) Maleic acid and fumaric acid are two isomers with the same molecular and structural formulae, but with very different physical properties.

	 maleic acid	 fumaric acid
melting point / ºC	130	287
pK_{a1}	1.9	3.0
pK_{a2}	6.5	4.5

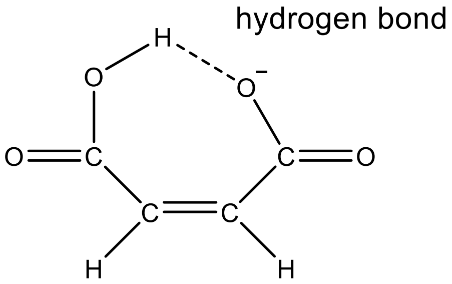
(i) Give two reasons to explain why maleic acid has a lower melting point than fumaric acid. [2]

Maleic acid has intra-molecular hydrogen bonds due to close proximity of its two –COOH groups. It has less inter-molecular hydrogen bonds. **[1]**

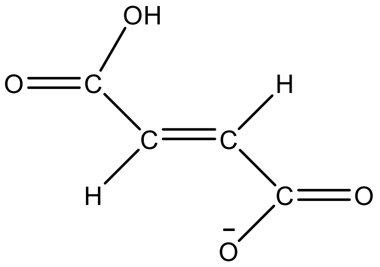
Maleic acid has lower packing efficiency of molecules in the solid state. **[1]** The molecules are further apart. There will be weaker forces of attraction between molecules.

Hence less energy needed to separate the molecules. Maleic acid has lower melting point.

(ii) Explain why maleic acid has a lower pK_{a1} value than fumaric acid. [1]



Carboxylate ion of Maleic acid



Carboxylate ion of Fumaric acid

Due to close proximity of the two –COOH groups, intra-molecular hydrogen bond can be formed in the carboxylate ion of maleic acid **[√]**. But such intra-molecular hydrogen bond is not possible in the carboxylate ion of fumaric acid.

This ion of maleic acid is more stable **[√]** and more readily formed than that of fumaric acid. Hence pK_{a1} value of maleic acid is lower than that of fumaric acid.

Two [√] : 1 mark

[Total: 20]

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 **9729/03**

Paper 3 Free Response **2 September 2019**
2 hours

Insert

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.

The insert is for use in **Question 1(a)**.
Fasten the insert in front of all writing paper at the end of the examination.

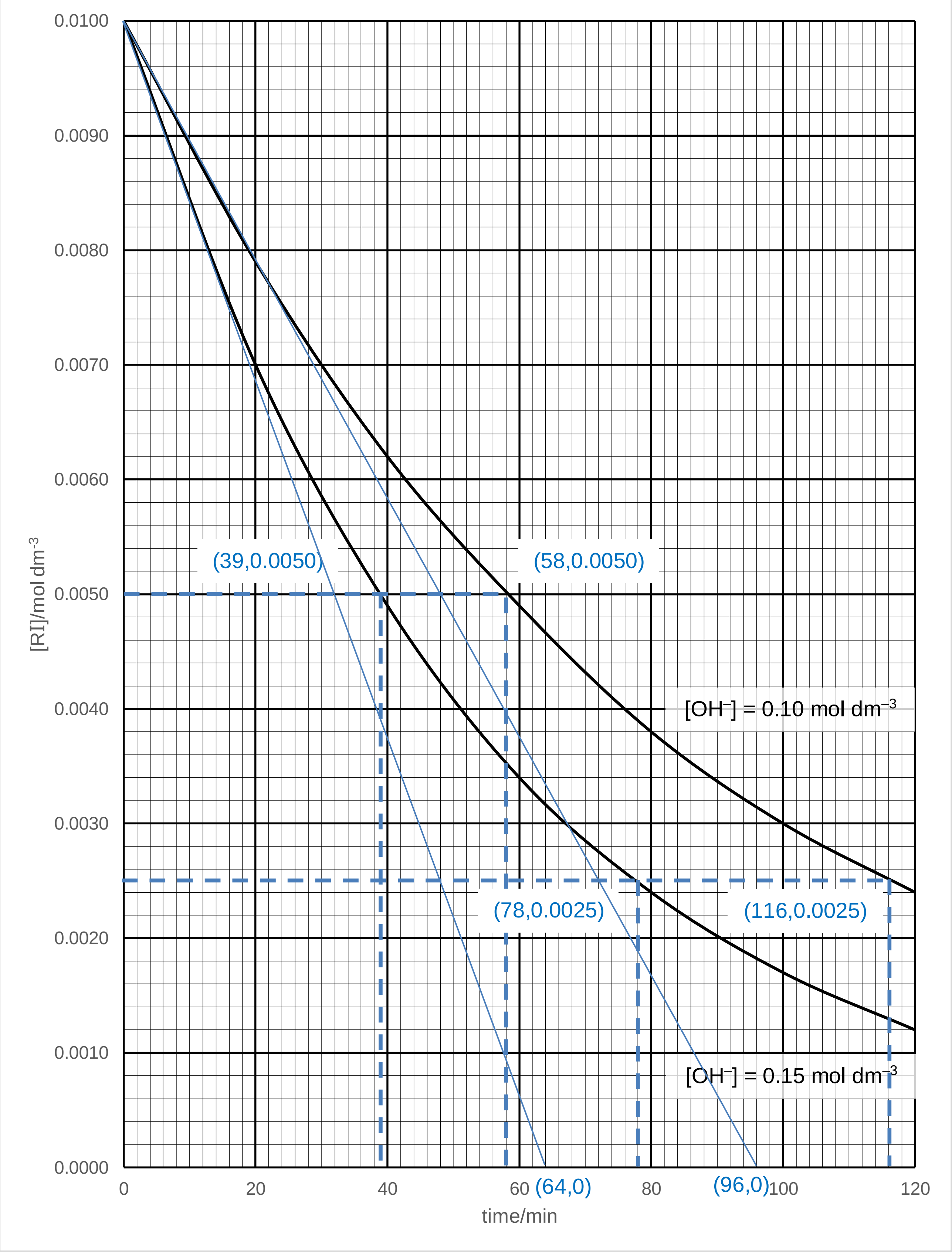
This document consists of **2** printed pages.

[Turn over

○

Index No.	Name	Form Class	Tutorial Class	Subject Tutor
			2CH________	

For use in Question 1(a)



1 Determination of solubility product, K_{sp}, of magnesium carbonate

Magnesium carbonate is basic and sparingly soluble in water, resulting in its use as drying agents in sports and antacids.

You are to carry out a titrimetric analysis to determine the solubility product of magnesium carbonate.

A saturated solution of magnesium carbonate can be prepared by dissolving excess solid magnesium carbonate into a measured volume of water. The mixture will be left to stand for some time before filtering. The filtrate can then be analysed through titration with a standard solution of hydrochloric acid.

The saturated solution of magnesium carbonate, FA 1, has been prepared for you, according to the procedure in **(a)**.

(a) Preparation of FA 1

1. Use a measuring cylinder to transfer 50 cm^3 of deionised water into a 100 cm^3 beaker.
2. Use a spatula to add solid magnesium carbonate into the same beaker, a little at a time with stirring until no more can dissolve.
3. Leave to stand for five minutes.
4. Filter the mixture to obtain the filtrate in a 250 cm^3 conical flask. Ensure that the filtrate is clear. Do not wash the residue.
5. The filtrate is **FA 1**.

You are provided with:
FA 1 saturated solution of magnesium carbonate
FA 2 0.0300 mol dm^{-3} hydrochloric acid solution
Methyl orange indicator

(b) (i) Dilution of FA 2

The concentration of **FA 2** is too high to be used in the titration. You will dilute **FA 2** before using it in **(c)**.

1. Pipette 25.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Top up to the mark with deionised water.
3. Stopper and shake thoroughly.

(b) **(ii)** Calculate the concentration of hydrochloric acid in **diluted FA 2**.

Conc = 0.025 x 0.03 / 0.25 = 0.00300 mol dm^{-3}

[HC*l*] in **diluted FA 2** = ………………………………… [1]

(c) **(i)** **Titration of FA 1 against diluted FA 2**

1. Fill the burette with **diluted FA 2** from **(b)**.
2. Use a pipette to transfer 10.0 cm^3 of **FA 1** into a 100 cm^3 conical flask.
3. Add 1 – 2 drops of methyl orange indicator into the conical flask.
4. Run **diluted FA 2** from the burette into this flask until the appropriate colour change is observed.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 1 to 5 until consistent results are obtained.

Results

Final burette reading / cm^3	**17.00**	**34.00**	
Initial burette reading / cm^3	**0.00**	**17.00**	
Vol of diluted FA 2 used / cm^3	**17.00**	**17.00**	

[3]

(c) **(ii)** From your titrations, obtain a suitable volume of **diluted FA 2**, to be used in your calculations. Show clearly how you obtained this volume.

(17.00 + 17.00) / 2 = 17.00 cm^3

Volume of **diluted FA 2** = ... [3]

(d) **(i)** Calculate the concentration of carbonate ions in **FA 1**, using your answers in **(b)(ii)** and **(c)(ii).**

Amount of H$^+$ = ans in (b)(ii) x ans in (c)(ii)/1000

Amount of CO$_3^{2-}$ = amount of H$^+$ / 2

Concentration of CO$_3^{2-}$ = Amount of CO$_3^{2-}$ / 0.0100
= 0.5 [ans in (b)(ii) x ans in (c)(ii)/1000] / 0.0100

[CO$_3^{2-}$] in **FA 1** = ... [2]

(ii) Hence, calculate the solubility product of magnesium carbonate. State its units.

K$_{sp}$ = [Mg^{2+}][CO$_3^{2-}$] = [ans from (d)(i)]^2

Units = mol^2 dm^{-6}

K_{sp} of magnesium carbonate = ...

units .... [1]

(e) In **(a)**, it was instructed that the filtrate had to be clear and that the residue should not be washed.

(i) State and explain the effect on titre volume if the filtrate was **not** clear.

effect on titre volume **Titre volume will be larger**

explanation **The residual carbonate will react with the HC*l* added**

[1]

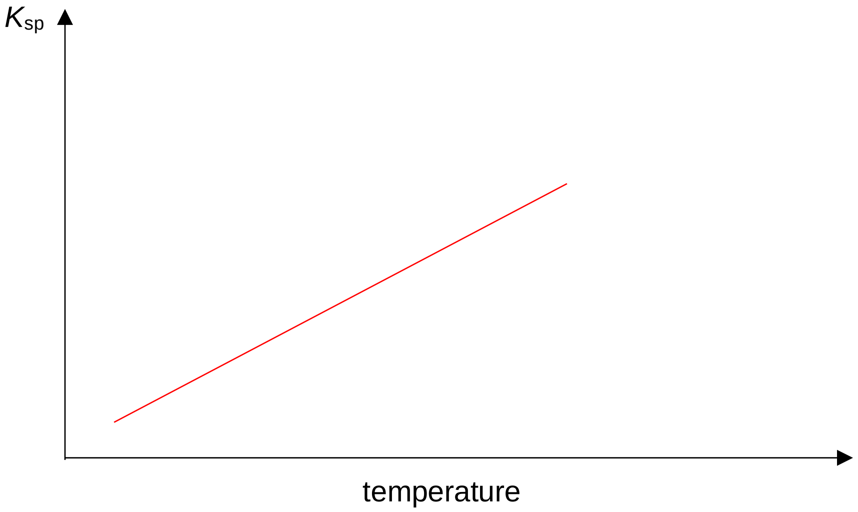
(ii) Explain why the residue should not be washed.

Washing the residue will disturb the equilibrium and cause the solution to be below saturation point (and the titration results will be lower than actual, leading to lower than expected K_{sp}).

[1]

(f) The dissociation of magnesium carbonate in water is endothermic.

Sketch a graph to show how the solubility product of magnesium carbonate varies with temperature. Explain your answer.



explanation

As dissociation is endothermic, increase in temperature cause POE of $MgCO_3(s) \leftrightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$ to shift right to favour reaction that absorbs heat, increasing concentration of ions, increasing K_{sp}

OR

When temperature increases, there is greater kinetic energy for the ions to break away from the ionic lattice, hence increasing concentration of ions, increasing K_{sp}

OR

Since reaction is endothermic, and entropy change is positive, when temperature is higher, reaction is more spontaneous, hence more $MgCO_3$ dissolves.

[2]

(g) **Planning**

The technique of gravimetry includes all analytical methods in which the analytical property is a measurement of mass or a change in mass. This technique can also be used in determining the solubility product of magnesium carbonate.

One of the possible approaches is to determine the mass of precipitate formed after mixing two solutions of known concentration. After preparing a mixture of saturated solution containing the precipitate, it can be passed through a pre-weighed filter paper that retains the precipitate. Residual moisture can be removed by drying the filter paper and the precipitate. The amount of precipitate can be determined, from which the concentration of ions in the saturated solution and hence solubility product can be determined.

(i) Plan an investigation to determine the solubility product of magnesium carbonate using the approach outlined above.

You are provided with the following:

- 0.400 mol dm^{-3} sodium carbonate solution
- 0.400 mol dm^{-3} magnesium nitrate solution
- apparatus and equipment normally found in a school laboratory

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use,
- the procedure you would follow,
- the measurements you would make to allow for gravimetric analysis.

- **Measure 50.00 cm^3 of sodium carbonate solution and 50.00 cm^3 magnesium nitrate solution using two separate 50.00 cm^3 burettes into a 250 cm^3 beaker (and place the beaker in a temperature controlled water bath)**
- **Stir the mixture and leave to stand for some time.**
- **Filter the mixture using a pre-weighed filter paper (M1 g)**
- **Dry precipitated $MgCO_3$ together with filter paper**
- **Weigh the dried precipitated $MgCO_3$ together with the filter paper (M2 g).**

[4]

(ii) Show how the measurements recorded in **(g)(i)** can be used to calculate the concentration of Mg^{2+} and CO_3^{2-}, in mol dm^{-3}, in the saturated solution.

Amount of ppt = (M2-M1)/ Mr of $MgCO_3$ = amount of Mg^{2+} not dissolved = amount of CO_3^{2-} not dissolved

Therefore, amount of Mg^{2+} dissolved = 0.4 x 50/1000 - (M2-M1)/Mr of $MgCO_3$
amount of CO_3^{2-} dissolved = 0.4 x 50/1000 - (M2-M1)/Mr of $MgCO_3$

concentration of Mg^{2+} = [0.4 x 50/1000 - (M2-M1)/ Mr of $MgCO_3$]/100/1000
concentration of CO_3^{2-} = [0.4 x 50/1000 - (M2-M1)/ Mr of $MgCO_3$]/100/1000

***depends on mass and volume used in g(i)**

[2]

[Total: 20]

2 Determination of the concentration of $NaHCO_3$ and the value for the enthalpy change of reaction of $NaHCO_3$ and NaOH

FA 3 is a solution of sodium hydrogencarbonate, $NaHCO_3$, of unknown concentration.
FA 4 is 1.50 mol dm^{-3} sodium hydroxide, NaOH.

In this experiment, you will perform a thermometric titration to determine the equivalence point for the reaction of **FA 3** and **FA 4**, where maximum heat is evolved, without the use of an indicator.

You will follow the reaction by measuring the temperature as volumes of **FA 4** are added in regular portions from a burette to a fixed volume of **FA 3** placed in a Styrofoam cup.

The data obtained will allow you to determine the temperature change and then analyse your results graphically in order to determine the equivalence point of the reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 4**:

- Total volume of **FA 4** added from the burette, starting from 0.00 cm^3, up to the point in time
- Total volume of solution in the cup, V_{total}
- Temperature measured, T

In the same table, you also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 3**
- ($V_{total} \times \Delta T$) to 3 significant figures

State clearly the units of each parameter on the header of the column.

Procedure

1. Fill the burette to the 0.00 cm^3 mark with **FA 4**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup.
3. Use a measuring cylinder to transfer 40.0 cm^3 of **FA 3** into the cup.
4. Measure and record the initial temperature of **FA 3**, T_0.
5. Run 3.00 cm^3 of **FA 4** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
6. Immediately run a further 3.00 cm^3 of **FA 4** from the burette into the cup, stir and record the maximum temperature as before.
7. Continue the addition of **FA 4** in 3.00 cm^3 and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Results

Total volume of FA 4 added, V_{FA4} / cm^3	Total volume of solution in the cup, V_{total} / cm^3	Temperature measured, T / °C	$\Delta T = T - T_0$ / °C	$(V_{total} \times \Delta T)$ / cm^3 °C
0.00	40.0			
3.00	43.0			
6.00	46.0			
9.00	49.0			
12.00	52.0			
15.00	55.0			
18.00	58.0			
21.00	61.0			
24.00	64.0			
27.00	67.0			
30.00	70.0			
33.00	73.0			
36.00	76.0			
39.00	79.0			
42.00	82.0			
45.00	85.0			

Precision:

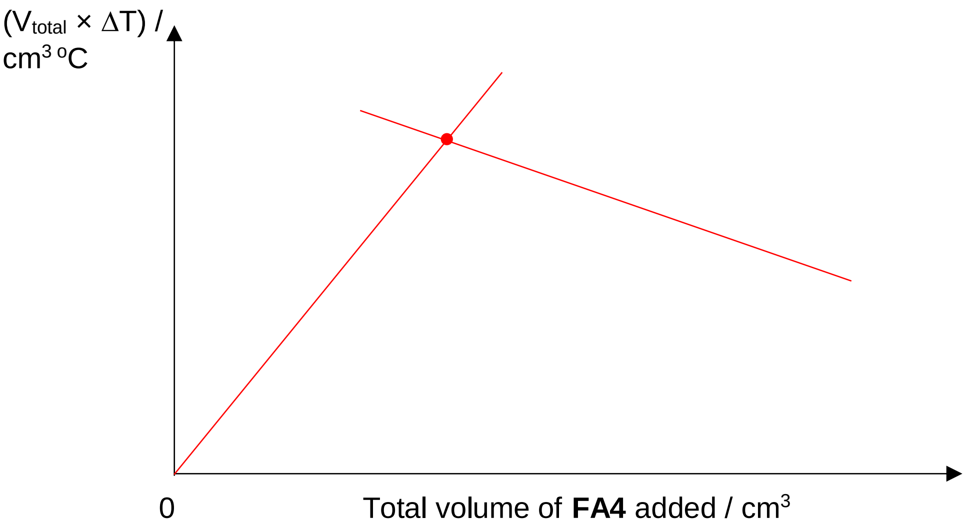
- **2 d.p. for V_{FA4}**
- **1 d.p. for T and ΔT**
- **3 s.f. for $(V_{total} \times \Delta T)$**

[3]

(a) **(ii)** Plot a graph of (V_{total} × ΔT) against total volume of **FA 4** added.

Draw two best-fit straight lines for the ascending and descending points respectively. Extrapolate both lines until they intersect to determine the:

- equivalence point of the reaction, V_{eq}
- maximum value of (V_{total} × ΔT)



V_{eq} = ……………………………………

Value of (V_{total} × ΔT) = ……………………………… [5]

(b) **(i)** Write down the chemical equation, with state symbols, for the reaction of $NaHCO_3$ and NaOH.

$NaHCO_3$ (aq) + NaOH (aq) → Na_2CO_3 (aq) + H_2O (*l*)

[1]

(ii) Calculate the concentration of $NaHCO_3$ in **FA 3**.

n_{NaOH} = (V_{eq}/1000 x 1.50) mol
n_{NaHCO3} = n_{NaOH}
[$NaHCO_3$] = (n_{NaHCO3} ÷ 40.0/1000) mol dm^{-3}

***obtained from the intersection point in (a)(ii)**

[$NaHCO_3$] in **FA 3** = ………………………………… [2]

(iii) Given that the heat capacity of solution is 4.2 J K^{-1} cm^{-3}, calculate the enthalpy change of the reaction of $NaHCO_3$ and NaOH, ΔH_r.

Heat released, q = mcΔT = 4.2(V_{total} × ΔT) J
ΔH_r = (-q/n_{NaHCO3}) J mol^{-1}

***obtained from the intersection point in (a)(ii)**

ΔH_r = …………………………………… [2]

(c) You plotted a graph of (V_{total} × ΔT) against total volume of **FA 4** added in **(a)(ii)**. Suggest, with explanation, whether plotting a graph of ΔT against total volume of **FA 4** instead is likely to yield a more accurate result for the equivalence point.

Doing so is unlikely to yield a more accurate result. As V_{total} is not constant (or increasing) throughout the experiment,

- **ΔT will vary less linearly with (or not be directly proportional to) the total volume of FA4 added**
  OR
- **curves may be obtained instead since the same amount of heat energy released is distributed over a larger volume**

[2]

(d) Performing the same experiment using a burette instead of a measuring cylinder to transfer **FA 3** into the Styrofoam cup is **not** expected to improve the accuracy of the results obtained. Suggest a reason why is this so.

Heat loss to the surroundings throughout the experiment outweighs the improved accuracy of using a burette to transfer FA3.

[1]

(e) You are provided with methyl orange indicator in **Question 1**.

Explain whether methyl orange indicator can be used to determine the end-point of the titration of $NaHCO_3$ against NaOH instead of performing thermometric titration.

$NaHCO_3$ acts as a weak acid in the presence of a strong alkali of NaOH, as such the equivalence point (at a relatively high pH) lies outside of the (relatively low) working pH range of methyl orange indicator.

[2]

[Total: 18]

3 Qualitative Analysis and Planning

You are provided with four different compounds labelled **FA 5**, **FA 6**, **FA 7** and **FA 8**. Each of these four bottles contains one of the following:

primary alcohol aldehyde monocarboxylic acid metal halide

You will identify **FA 5**, **FA 6**, **FA 7** and **FA 8** by carrying out the prescribed experiments, as well as planning and conducting your own experiments.

For the prescribed experiments, record your observations in Table 3.1 below carefully. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You are advised to carry out the experiments in test (a) and (b) on each unknown compound one at a time. You are not required to carry out experiments in test (c) as the results are provided.

Table 3.1

Test		*Observations*			
		FA 5	**FA 6**	**FA 7**	**FA 8**
(a)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of sodium nitrite. **Test and determine if any gas is evolved.**	**effervescence** **pungent brown/ yellow gas evolved** **blue litmus paper turned red**	**effervescence** **pungent brown/ yellow gas evolved** **blue litmus paper turned red**	**no gas evolved**	**no gas evolved**
(b)	To 1 cm depth of the unknown in a test-tube, add 1 cm depth of dilute sulfuric acid, followed by 5 drops of potassium manganate(VII) solution. Place the test-tube in the hot water bath.	**purple $KMnO_4$ decolourised/ discharged upon standing in hot water bath**	**purple $KMnO_4$ turned brown/ yellow/ formed brown ppt/ decolourised/ discharged upon standing in hot water bath**	**purple $KMnO_4$ decolourised/ discharged / turned brown / turned colourless upon standing in the hot water bath**	**purple $KMnO_4$ decolourised/ discharged / turned colourless upon standing in the hot water bath**

	Test and determine if any gas is evolved.	**colourless odourless gas evolved** **blue litmus turned paper red** **gas produced white ppt with aqueous $Ca(OH)_2$**	**pungent gas evolved** **blue litmus turned red and bleached**	**no gas evolved**	**no gas evolved**
(c)	To 1 cm depth of aqueous iodine, add aqueous sodium hydroxide dropwise until a permanent yellow colour is obtained. Then add 3 drops of the unknown into the same test-tube. Place the test-tube in the hot water bath.	No yellow precipitate	No yellow precipitate	Yellow precipitate obtained	Yellow precipitate obtained

[4]

(d) **Identifying unknown metal halide**

(i) From your observations in Table 3.1, suggest which one of the unknown compounds is the metal halide. [1]

FA …**6**…

explanation… **It decolourised purple $KMnO_4$ with the production of a pungent gas which turns blue litmus paper red and then bleaches.** …

(ii) Suggest the reagent and carry out the test to confirm the identity of the halide in the metal halide. [2]

reagent … **silver nitrate** …

observations … **white ppt formed …**

FA …**6**……… contains …**chloride/ Cl^-** …anion.

(d) **(iii)** In Table 3.2 below, describe two tests that will allow you to identify the cation in the metal halide. Perform the tests and record the observations in the same table. Use only bench reagents provided. [3]

Table 3.2

Test	*Observations*
	FA … 6 …
Add NaOH(aq) dropwise until no further change is observed/ until in excess.	**White ppt formed soluble in excess NaOH.**
Add NH_3(aq) dropwise until no further change is observed/ until in excess.	**White ppt formed insoluble in excess NH_3(aq).**

The cation in metal halide is … **Al^{3+}** …

(iv) The nature of the cation of the metal halide in aqueous solution accounts for its observations in test **(a)**. Describe and explain the nature of the cation by means of an equation. [2]

equation … **$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$**

explanation … **Since Al^{3+} is small and highly charged/ has high charge density, it undergoes hydrolysis with water to produce an acidic solution.**

(e) **Identifying organic liquids**

(i) The three unknown organic compounds are primary alcohol, aldehyde and monocarboxylic acid.

Based on your observations in tests **(a)** and **(b)**, identify which is the monocarboxylic acid. Suggest the identity of the monocarboxylic acid and support your answer by giving the evidence. [3]

FA …**5** …

The identity of monobasic carboxylic acid is …**methanoic acid/ HCOOH** …

evidence … **In test (b), oxidation of methanoic acid by $KMnO_4$ produced CO_2 which turned blue litmus paper red/ white ppt with limewater.**

(ii) Describe how you would conduct a chemical test, using only the bench reagents provided, to distinguish between the remaining two unknown organic compounds.

Carry out the chemical test.

With aid of your observations and results provided in test **(c)**, identify which is the primary alcohol and the aldehyde. [3]

chemical test … **Tollens' reagent (To 1 cm depth of $AgNO_3$, add NaOH(aq) dropwise till a ppt is formed. Then add NH_3(aq) dropwise till ppt dissolves completely.)**

observations … **silver mirror formed with FA8 but not FA7**

The primary alcohol is **FA** …**7**…

The identity of the primary alcohol is …**ethanol/ CH_3CH_2OH**…

The aldehyde is **FA** …**8**…

The identity of the aldehyde is …**ethanal/ CH_3CHO** …

[Total: 17]

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 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

Catholic Junior College

JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/01

Paper 1 Multiple Choice

Tuesday 3 September 2019
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 **15** printed pages and **1** blank page.

1 In a titration experiment, 15 cm^3 of 0.10 mol dm^{-3} phosphorous acid, H_3PO_3 was found to react with 10 cm^3 of 0.30 mol dm^{-3} sodium hydroxide, NaOH. Using this information, deduce the formula of the salt formed in this neutralisation process.

A NaH_2PO_3

B Na_2HPO_3

C Na_3PO_3

D Na_3PO_4

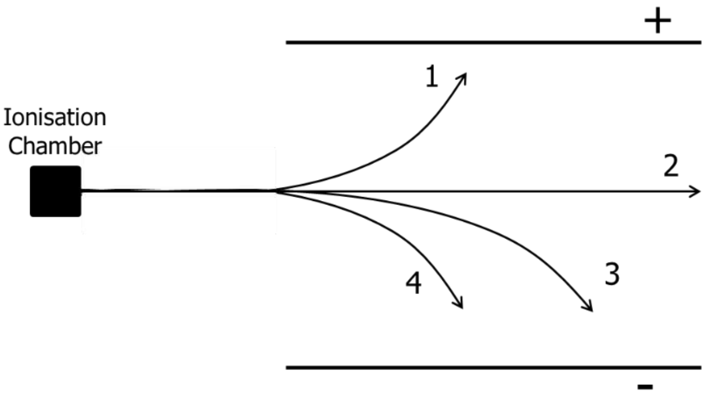
2 50 cm^3 of a mixture of ethene and propane gas were exploded in excess oxygen. The volume of the residual gases was found to be 200 cm^3. On being shaken with potassium hydroxide, the final volume was found to be 90 cm^3. What is the composition of the mixture? *(All volumes are measured at r.t.p)*

	volume of ethene	volume of propane
A	10	40
B	20	30
C	30	20
D	40	10

3 Plutonium-239 is a radioactive substance that emits a constant stream of α–particles which are similar to the nucleus of ^{4}He.

Rubidium-87 is another radioactive substance that emits β–particles which can be considered as electrons.

A small amount of Plutonium-239 and Rubidium-87 are separately placed in an ionisation chamber to emit a constant stream of radiation and the emitted particles are passed through an electric field.



What would be the path of the emitted particles in the electric field?

	Plutonium-239 (α–particles)	Rubidium-87 (β–particles)
A	1	2
B	1	3
C	4	1
D	3	1

4 Diazene has a molecular formula of N_2H_2. Given that the nitrogen and hydrogen show their usual valencies, which of the following correctly describes the shape and bond angle around each central atom?

	shape	bond angle
A	bent	110º
B	linear	180º
C	tetrahedral	109º
D	trigonal planar	120º

5 Which of the following contains delocalised electrons?

1 Graphite
2 Sodium
3 Ethanoate ion
4 Cyclohexene

A 1 and 2 only
B 2 and 3 only
C 1, 2 and 3 only
D 3 and 4 only

6 Which equation corresponds to the enthalpy change stated?

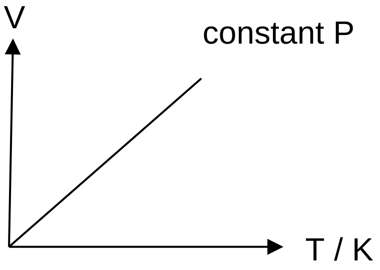
A	$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$	$\Delta H^{\ominus}_{neutralisation}$
B	$Na_2SO_4(s) + aq \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$	$\Delta H^{\ominus}_{solution}$
C	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$	$\Delta H^{\ominus}_{formation}$
D	$Br_2(l) \rightarrow 2Br(g)$	$\Delta H^{\ominus}_{atomisation}$

7 In which of the following processes will ΔS be negative?

A photosynthesis
B electrolysis of water
C boiling of water
D dissolving solid $MgSO_4$ in water

8 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas?
(P = pressure, ρ = density, V = volume, T = temperature).

1



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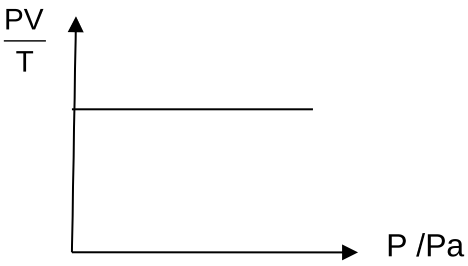

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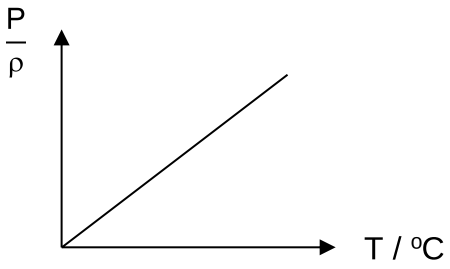


A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

9 A sample of HBr gas was decomposed in a sealed container at temperature T. The decomposition equation is given below.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g) \qquad \Delta H \text{ is positive}$$

Which of the following statements is **false**?

A Equal amounts of H_2 and Br_2 are formed at equilibrium.

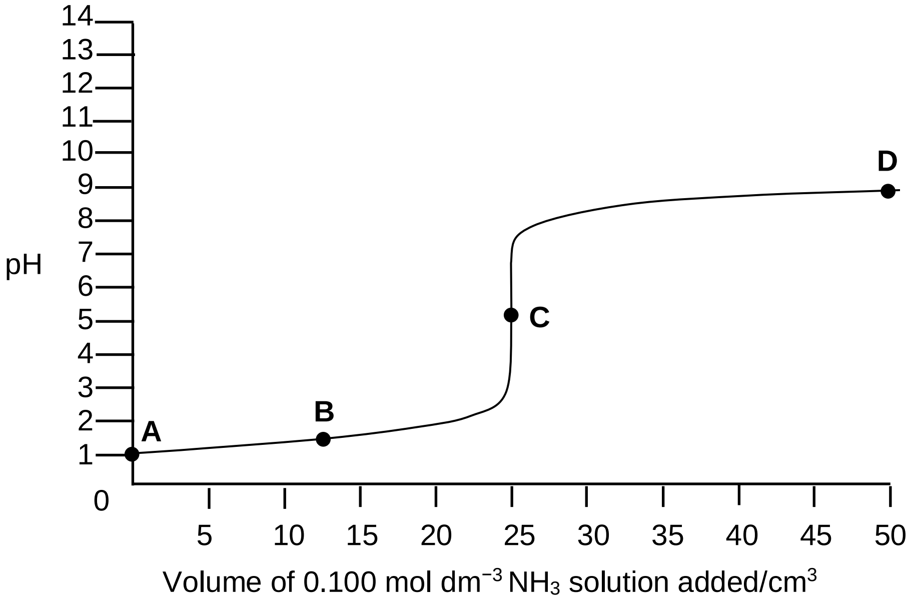
B When a catalyst is added, the rates of the forward and reverse reactions are increased by the same extent.

C The K_c will decrease if the reaction is carried out at higher temperature.

D The equilibrium position is unaffected when the volume of the container is decreased.

10 The pH changes when 0.100 mol dm^{-3} NH_3(aq) is added dropwise to 25.0 cm^3 of 0.100 mol dm^{-3} HC*l* as shown below.

At which point on the graph does pOH = pK_b, where K_b is the base dissociation constant of the weak base?



11 Ammonia usually reacts as a base. In which reaction does it behave as an acid?

1 $Hg_2Cl_2 + 2NH_3 \rightarrow Hg + HgCl(NH_2) + NH_4^+ + Cl^-$
2 $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
3 $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

12 The table shows experimental results obtained for the reaction of hydrogen peroxide with acidified iodide ions to liberate iodine.

initial concentrations of reactants / mol dm^{-3}			*initial rate of formation of iodine*
[H_2O_2]	[I^-]	[H^+]	/ mol dm^{-3} s^{-1}
0.010	0.010	0.010	2.0×10^{-6}
0.030	0.010	0.010	6.0×10^{-6}
0.030	0.020	0.010	1.2×10^{-5}
0.030	0.020	0.020	1.2×10^{-5}

What can be deduced from these results?

1 The rate equation for the reaction can be written: rate = $k\,[H_2O_2][I^-]$.
2 The reaction is zero order with respect to acid.
3 The units of rate constant is mol^{-2} dm^{6} s^{-1}.
4 Both hydrogen peroxide and iodide ions are involved in the rate-determining step.

A 1 and 2 only
B 3 and 4 only
C 1, 2 and 4
D 2, 3 and 4

13 The mechanism for a certain reaction is given below:

$$2P \longrightarrow R \text{ (fast)}$$

$$R + Q \rightleftharpoons S \text{ (slow)}$$

$$S + Q \longrightarrow P_2Q_2 \text{ (fast)}$$

What conclusion can be drawn from the above mechanism?

A The rate equation is rate = $k[P]^2[Q]$.

B The overall order of reaction is 2.

C The units of the rate constant, k, is mol^{-1} dm^{3} s^{-1}.

D The half-life of Q is halved when [Q] is doubled,

14 Four elements with atomic numbers from 11 to 17 inclusive have the following properties.

- Chloride of **E** dissolves in water and turns moist blue litmus red.
- Oxide of **F** is amphoteric.
- **G** has the lowest electronegativity among these four elements.
- **H** has the smallest atomic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

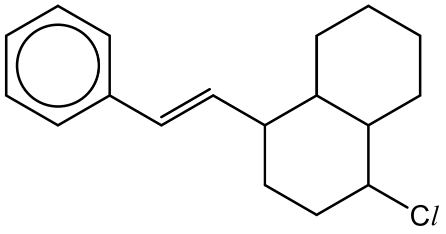
A **F**, **G**, **H**, **E**
B **F**, **G**, **E**, **H**
C **G**, **F**, **E**, **H**
D **G**, **F**, **H**, **E**

15 *Use of Data Booklet is relevant to this question.*
Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power increases from chlorine to iodine.
2 The strength of the covalent bonds in the molecules decreases from chlorine to iodine.
3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 only
B 2 only
C 2 and 3 only
D 1, 2 and 3

16 How many stereoisomers does compound **Q** exhibit?



Compound **Q**

A 2 **B** 5 **C** 16 **D** 32

17 Which of the following is a **propagation** step in the formation of 1,1-dibromopropane from the reaction between propane and bromine in the presence of ultraviolet light?

A $CH_3CH_2CH_2Br + Br\bullet \rightarrow CH_3CH_2CH_2\bullet + Br_2$
B $CH_3CH_2CH_2\bullet + Br\bullet \rightarrow CH_3CH_2CH_2Br$
C $CH_3CH_2CH_2\bullet + Br_2 \rightarrow CH_3CH_2CHBr\bullet + HBr$
D $CH_3CH_2CHBr\bullet + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br\bullet$

18 Methane is a greenhouse gas but is destroyed in the troposphere by the action of hydroxyl radicals.

$$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$$

Which statement about this reaction is correct?

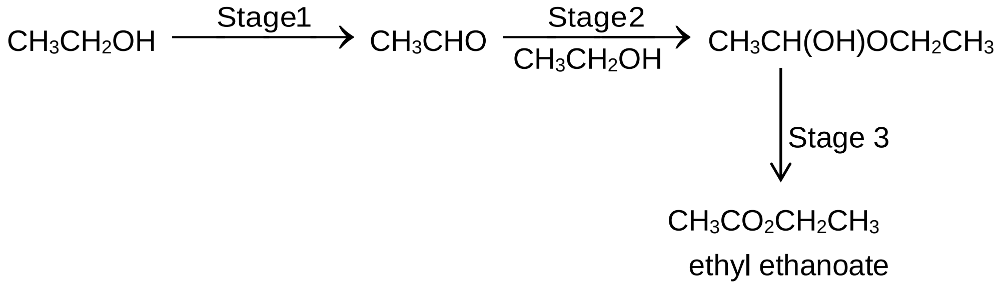
A The reaction involves homolytic fission and σ bond formation.

B The reaction involves heterolytic fission and σ bond formation.

C The reaction involves heterolytic fission and π bond formation.

D The total number of electrons in the two reacting species is 20.

19 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.



$$\begin{tikzcd} CH_3CH_2OH \arrow[r, "\text{Stage1}"] & CH_3CHO \arrow[r, "\text{Stage2}", "CH_3CH_2OH"'] & CH_3CH(OH)OCH_2CH_3 \arrow[d, "\text{Stage 3}"] \\ & & CH_3CO_2CH_2CH_3 \end{tikzcd}$$

ethyl ethanoate

Which process is involved at some stage in this reaction sequence?

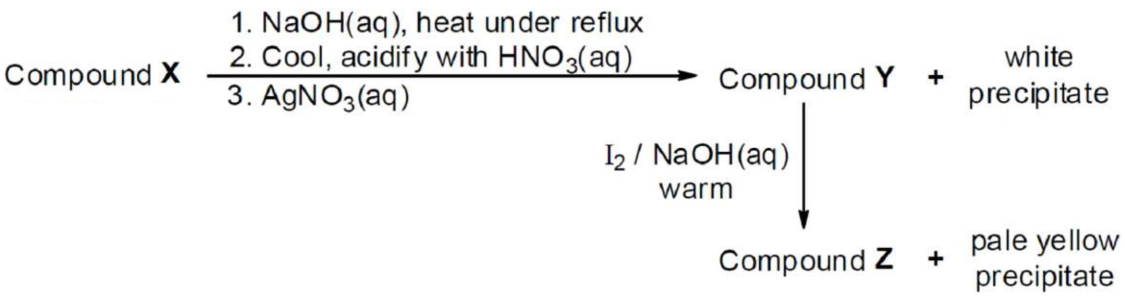
A electrophilic addition

B nucleophilic substitution

C nucleophilic addition

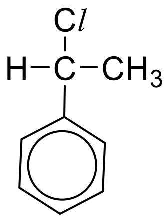
D condensation

20 Compound **X** was subjected to the following sequence of reactions.

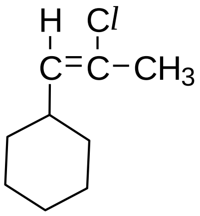


Which of the following could be the structure of **X** ?

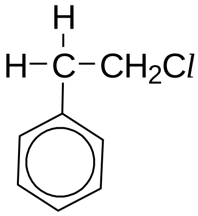
A



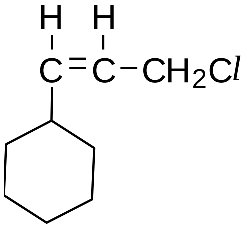
C



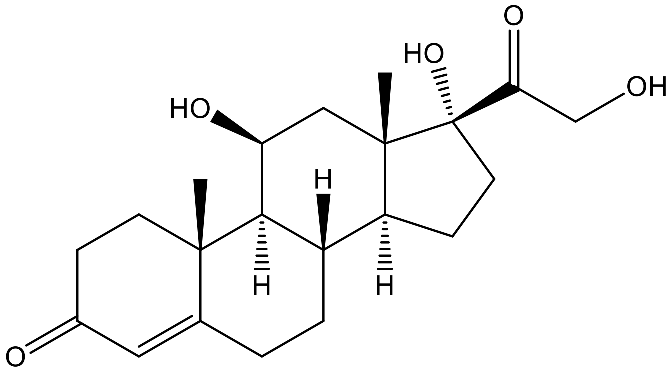
B



D



21 Hydrocortisone is commonly used as an active ingredient in anti-inflammatory creams and has the following structure.



hydrocortisone

Which of the following statements about hydrocortisone is correct?

A When treated with an excess of hot acidified $KMnO_4$, it forms a compound containing six carbonyl 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 two additional hydroxy groups.

D When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing seven hydroxy groups.

22 Compound **P**, $C_4H_8O_2$, has an unbranched carbon chain. An aqueous solution of **P** has an approximate pH of 3. Compound **Q**, C_3H_8O, is a secondary alcohol.

P and **Q** are reacted together in the presence of a small amount of concentrated sulfuric acid to form **R** as the major organic product.

What is the structural formula of **R**?

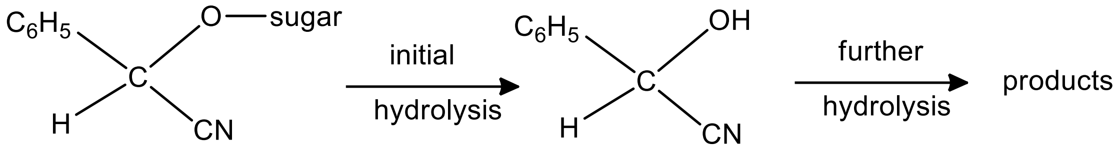
A $(CH_3)_2CHCO_2CH_2CH_2CH_3$

B $CH_3(CH_2)_2CO_2CH(CH_3)_2$

C $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$

D $(CH_3)_2CHCO_2CH(CH_3)_2$

23 *Amygdalin* is partly responsible for the flavour of almonds. On hydrolysis, it first gives compound **X**, which is then further hydrolysed to give other products.



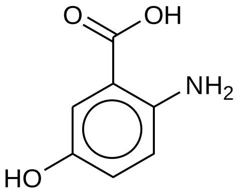
amygdalin

X

What are the other products formed after further hydrolysis?

A $C_6H_5CH(OH)CO_2H$ and NH_3
B $C_6H_5CH_2OH$ and CO_2 and NH_3
C $C_6H_5CO_2H$ and HCHO and NH_3
D C_6H_5OH and CH_3CN

24 5-hydroxyanthranillic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.

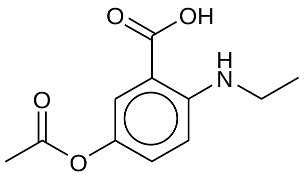


5-HAA

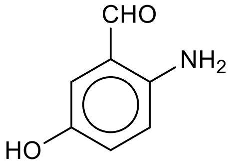
When 5-HAA was reacted with ethanoyl chloride followed by lithium aluminium hydride, $LiAlH_4$, in dry ether, the product was found to give a purple colouration with neutral $FeCl_3$(aq).

Which is a likely product?

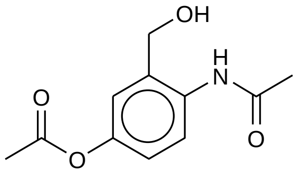
A



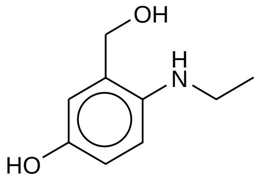
B



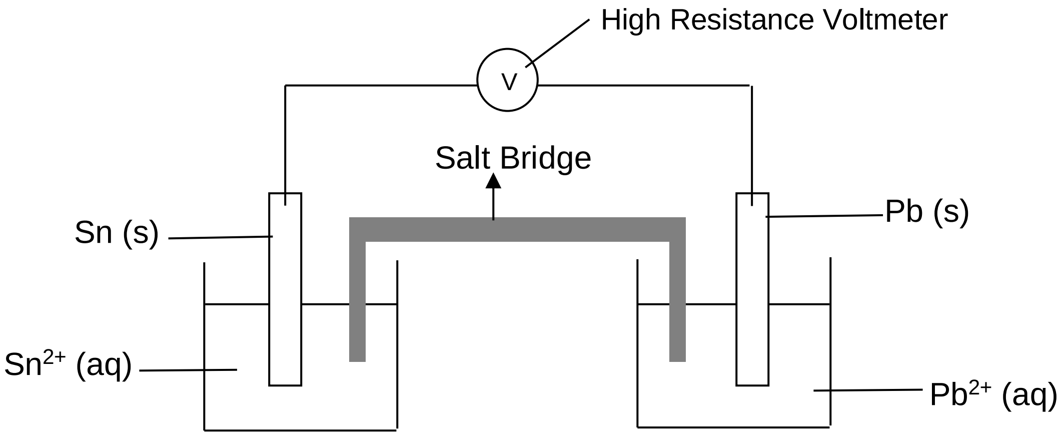
C



D



25 Use of the *Data Booklet* is relevant to this question.



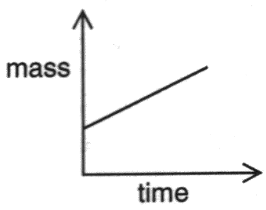
A student set up an electrochemical cell as above and made the conclusion listed below. Which of the statements are correct?

1 The reaction is feasible and Pb electrode grows larger with time.
2 Electrons flow from the Sn electrode to the Pb electrode.
3 Sn is the positive electrode while Pb is the negative electrode.
4 Concentrated KC*l* is suitable to be used as salt bridge.

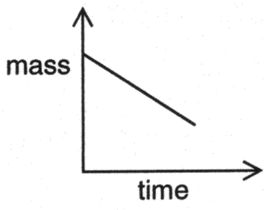
A 1 and 2 only **B** 2 and 3 only **C** 1, 2 and 3 only **D** 1, 2, 3 and 4

26 Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?

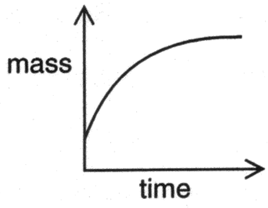
A



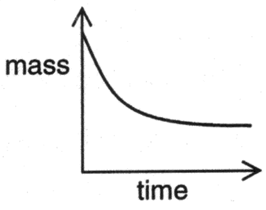
B



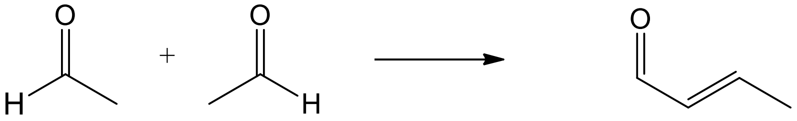
C



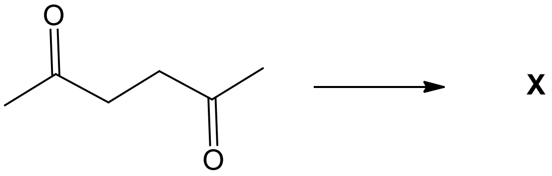
D



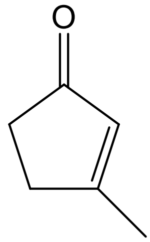
27 Aldol condensation is used in the manufacture of pharmaceuticals. One example of such a reaction is as shown below in the presence of a base.



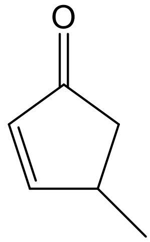
Under similar conditions, what would be the product **X**?



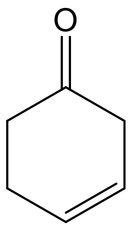
A



B



C



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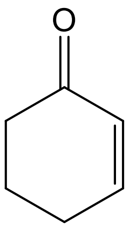
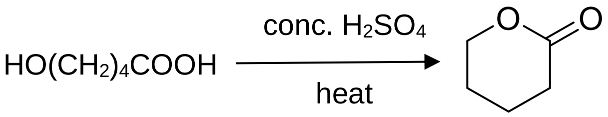
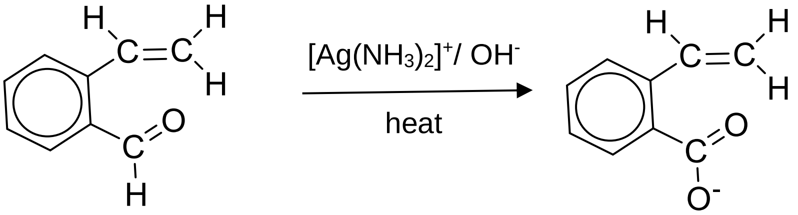


28 Which of the following reactions would yield the product shown?

1



2



3 $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{\text{NaBr(aq)}} CH_3CH_2CH_2Br$

A 1 only

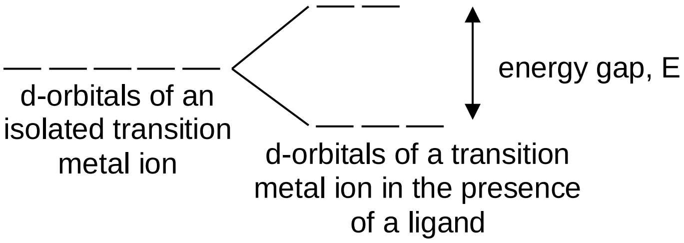
B 2 only

C 1 and 2 only

D 1, 2 and 3 only

29 *Use of Data Booklet is relevant to this question.*

The following diagram shows how the d–orbitals are split in an octahedral environment.



Some transition metal ions exhibit the ability to change their 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 first, before starting to pair up in the lower energy d–orbitals.

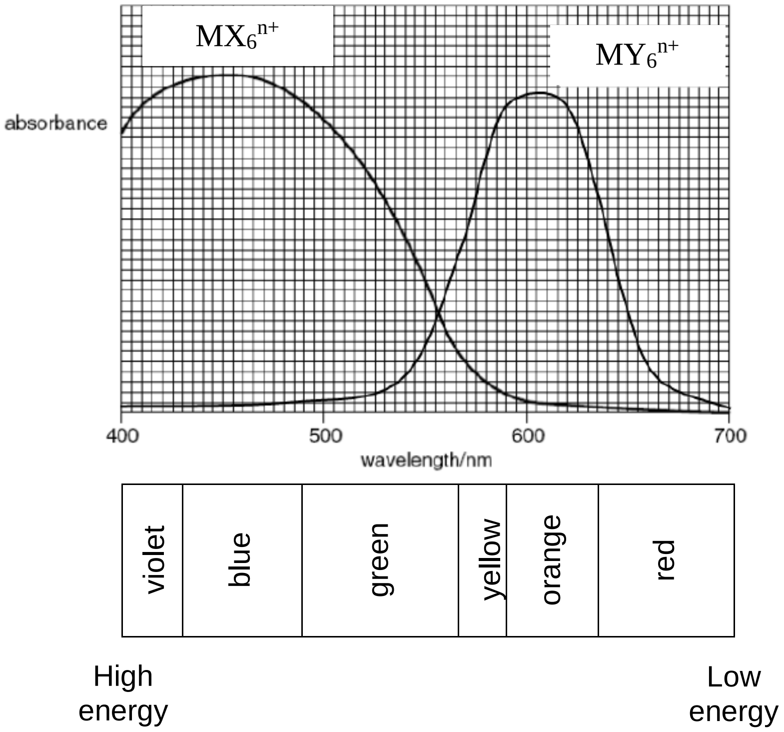
In a 'low spin' state, the lower energy d–orbitals are first filled, by pairing up if necessary, before the higher energy d–orbitals are used.

Which one of the following transition metal ions is likely to be able to exhibit both spin states?

1 Fe^{3+}
2 Cu^{2+}
3 Cr^{3+}
4 Co^{3+}

A 1 only **B** 1 and 4 only **C** 1, 2 and 4 only **D** 2 and 3 only

30 The absorbance graph below shows the visible spectra of two complexes of transition metal M, MX_6^{n+} and MY_6^{n+}.



What is the colour of each complex and which ligand causes a larger d-orbital splitting?

	Colour of MX_6^{n+}	**Colour of MY_6^{n+}**	**ligand which causes a larger d-orbital splitting**
A	Violet	Orange-red	X
B	Red	Green-blue	X
C	Violet	Orange-red	Y
D	Red	Green-blue	Y

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Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/02

Paper 2 Structured Questions

Friday 23 August 2019

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
Paper 2	**Q 1**	/11	
	Q 2	/18	
	Q 3	/18	
	Q 4	/10	
	Q 5	/10	
	Q6	/8	/75
Paper 3	**Q 1**	/22	
	Q 2	/19	
	Q 3	/19	
	Q 4 / 5	/20	/80
Paper 4			/55
Total			/240
Total % and Grade			

This document consists of **19** printed pages and **1** blank page.

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

1 The Taj Mahal is an ivory-white marble monument in the Indian city of Agra. The famous building is becoming brown and green from environmental pollution. Acid rain accelerates the erosion of marble monuments. Marble consists primarily of calcium carbonate.

(a) You should refer to the following solubility product data to help answer the following questions.

Substance	$CaCO_3$	$CaSO_4$	$BaCO_3$	$BaSO_4$
Solubility product / $mol^2\,dm^{-6}$	1.69×10^{-8}	2.03×10^{-3}	8.28×10^{-9}	8.84×10^{-11}

The pollutant SO_2 dissolves in rainwater to form sulfuric acid. The sulfuric acid slowly converts calcium carbonate into solid calcium sulfate.

(i) Write an equation for the reaction between calcium carbonate and sulfuric acid.

.... [1]

(ii) By calculating the solubilities of calcium carbonate and calcium sulfate, deduce why acid rain accelerates the erosion of marble.

[3]

The lifespan of Taj Mahal can be extended by treatment with an aqueous mixture of barium hydroxide, $Ba(OH)_2$ and urea, $CO(NH_2)_2$. As this solution soaks into the porous marble, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide in the mixture forming barium carbonate.

(iii) Write an equation for the reaction between barium hydroxide and carbon dioxide.

.... [1]

(iv) By considering the reaction between surface barium carbonate and acid rain, explain how the erosion process can be slowed down.

....

....

.... [1]

(b) Group 2 carbonates undergo decomposition in the same way at different temperatures.

(i) Predict and explain the order of decomposition temperatures for the three carbonates, $MgCO_3$, $CaCO_3$ and $BaCO_3$.

....

....

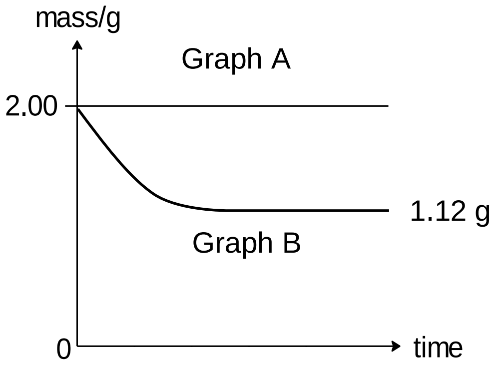
....

....

....

.... [3]

The graph given below shows the change in mass when 2.00 g of each $CaCO_3$ and $BaCO_3$ were heated separately at a temperature, T °C.



(ii) From the shapes of the graphs, identify $CaCO_3$ and $BaCO_3$ in the spaces provided below.

Graph A: ....

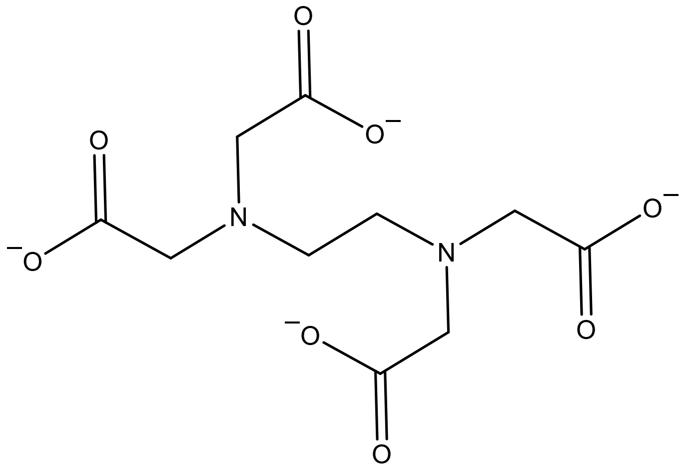
Graph B: ....

[1]

(iii) Sketch on the same axes, a graph that would be obtained by heating 2.00 g of magnesium carbonate, $MgCO_3$, at the same temperature, T °C. [1]

[Total: 11]

2 Hydrogen peroxide is a common bleaching agent used to whiten wood pulp during the manufacture of paper. Transition metal ions such as Fe^{3+}(aq), that are naturally present in wood pulp, would catalyse the decomposition of hydrogen peroxide, and hence reduce the bleaching efficiency. The wood pulp is therefore washed with a chelating agent such as EDTA to remove the transition metal ions before hydrogen peroxide is added.
[EDTA = $(^{-}O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^{-})_2$]



EDTA

(a) **(i)** Any Fe^{3+}(aq) in the wood pulp would form a polydentate complex with EDTA. Give the formula of the complex formed. You may use the abbreviation 'EDTA' in your answer.

.... [1]

(ii) State the coordination number of the complex in **(a)(i)**.

.... [1]

(b) **(i)** H_2O and NH_3 are simple molecules. Explain why, at room temperature, H_2O is a liquid while NH_3 is a gas.

....

....

....

....

....

.... [2]

(ii) While EDTA is a polydentate *ligand*, H_2O and NH_3 are examples of monodentate *ligands* in transition metal complexes. Explain what is meant by the term *ligand*.

....

....

.... [1]

(c) Consider the ion $[Cu(H_2O)_6]^{2+}$ present in an aqueous solution of copper(II) sulfate. When a central metal is surrounded by water ligands, it is known as an aqua complex. Addition of NH_3 to the copper(II) sulfate solution brings about a stepwise replacement of the water ligands by ammonia ligands such that the overall equation is shown below.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The stability constant, K_{stab}, for the above equilibrium is given as:

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2\,]^{2+}}{[Cu(H_2O)_6{}^{2+}][NH_3]^4} = 1 \times 10^{13}\ \text{mol}^{-4}\ \text{dm}^{12}$$

In the above expression, the square brackets imply concentrations in mol dm^{-3}. Similar to the example shown above for $[Cu(H_2O)_6]^{2+}$, complexes of iron have values of K_{stab} which are measured against the relative stability of the aqua complex of iron.

The following table lists some iron complexes together with their colours and their stability constants.

aqueous complex	**colour**	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}$	deep red	1×10^2
$[FeF_6]^{3-}$	colourless	2×10^{15}
Fe^{3+}(aq) complex with EDTA	yellow	x
$[Fe(CN)_6]^{3-}$	pale yellow	1×10^{31}

(i) Including equations where appropriate, use the data to explain

- why an addition of KSCN(aq) to a solution of Fe^{3+}(aq) produces a deep red solution.

....

....

....

.... [2]

- what is observed when KF(aq) is added to the deep red solution mentioned above.

....

....

....

.... [2]

(ii) Deduce if the value of ***x*****,** the K_{stab} of the Fe^{3+}(aq) complex with EDTA, is expected to be higher or lower than the K_{stab} value of $[FeF_6]^{3-}$.

....

.... [1]

(iii) Give the electronic configuration of Fe in $[Fe(CN)_6]^{3-}$(aq).

.... [1]

(iv) $[Fe(CN)_6]^{3-}$(aq) is a weaker oxidising agent than Fe^{3+}(aq). Explain this statement by quoting appropriate $E^{\ominus}$ values from the *Data Booklet*.

....

....

....

....

.... [2]

(d) **(i)** Carbon monoxide, CO, is a toxic gas. Draw the dot-and-cross structure of CO.

[1]

CO is also a ligand in iron pentacarbonyl, $Fe(CO)_5$. CO binds to the central metal via the carbon atom.

(ii) What is the oxidation state of iron in $Fe(CO)_5$?

.... [1]

(iii) Draw and name the shape of the complex, $Fe(CO)_5$.

[2]

(iv) When iron pentacarbonyl reacts with iodine in hexane solution, iron is oxidised and an octahedral complex, $Fe(CO)_4I_2$, is formed.

Isomerism can occur in $Fe(CO)_4I_2$ due to different positions of the ligands with respect to the central metal ion. Draw the two isomers of $Fe(CO)_4I_2$.

[1]

[Total: 18]

3 **(a)** Converting harmful greenhouse gases such as CO_2 into useful chemical commodities, such as methanol, CH_3OH, is gaining traction in green chemistry as it is economically viable and environment–friendly.

A mixture containing 1.0 mol of CO_2 and 3.0 mol of H_2 is allowed to reach *dynamic equilibrium* at 200°C and 55 bar. Under these conditions, 32% CO_2 is converted to methanol, CH_3OH.

$$CO_2\,(g) \;+\; 3H_2\,(g) \rightleftharpoons CH_3OH\,(g) \;+\; H_2O\,(g)$$

Calculate the equilibrium pressure of each gas and hence calculate the K_p value, with the units for this reaction at 200°C.

[4]

(b) Methanol reacts with carbon monoxide with the help of catalyst to produce ethanoic acid.

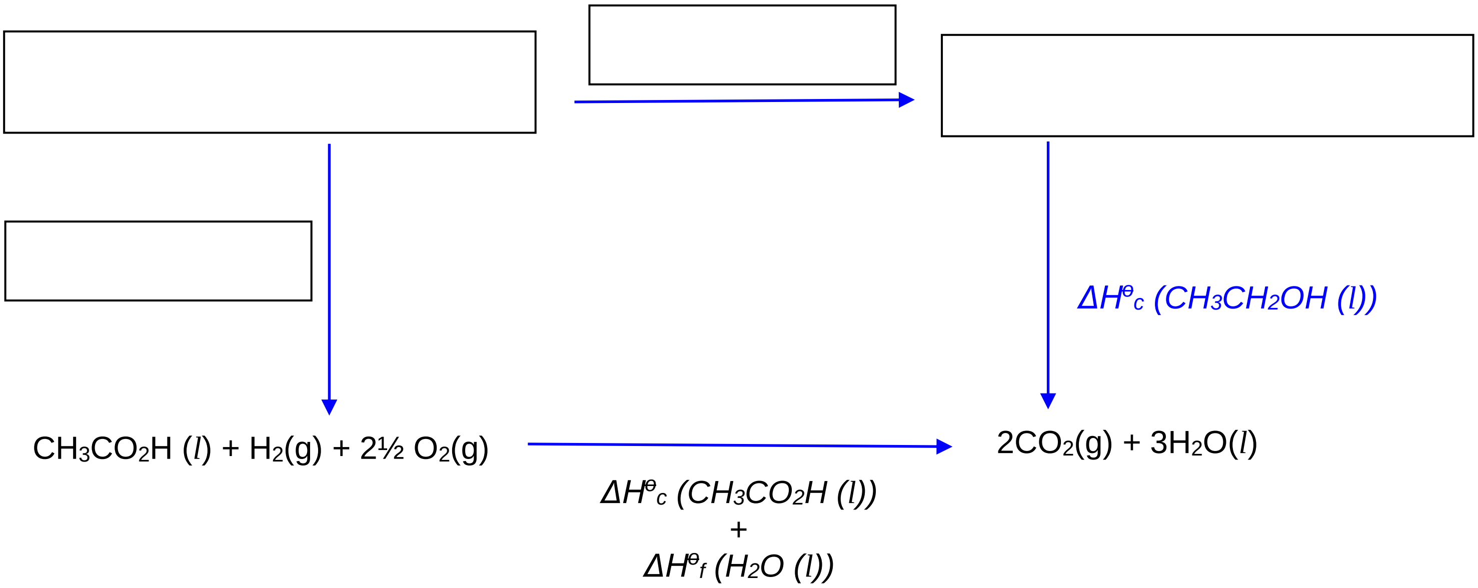
Define the term *standard enthalpy change of formation* of liquid ethanoic acid, CH_3CO_2H (*l*).

....

.... [1]

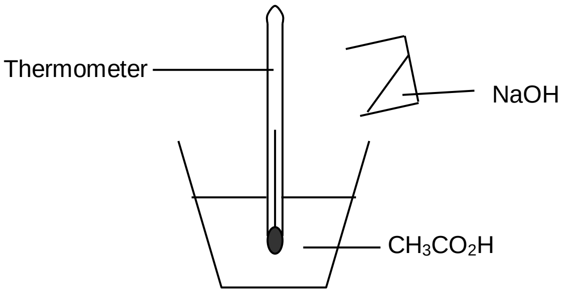
(c) Using the enthalpy change values given below, complete the energy cycle and calculate the standard enthalpy change of formation for ethanoic acid, CH_3CO_2H (*l*).

$\Delta H^{\ominus}_f$ (CH_3CH_2OH (*l*)) = – 278 kJ mol^{-1}
$\Delta H^{\ominus}_c$ (CH_3CH_2OH (*l*)) = – 1371 kJ mol^{-1}
$\Delta H^{\ominus}_c$ (CH_3CO_2H (*l*)) = – 876 kJ mol^{-1}
$\Delta H^{\ominus}_f$ (H_2O (*l*)) = – 286 kJ mol^{-1}



[4]

(d) The ethanoic acid, CH_3CO_2H can undergo neutralisation with sodium hydroxide, NaOH. A thermochemical experiment was carried out to determine the enthalpy change of neutralisation using the experimental set–up below.



The following results were obtained:

Volume of NaOH added / cm^3	50.0
Volume of CH_3CO_2H added / cm^3	50.0
Concentration of NaOH used / mol dm^{-3}	1.00
Concentration of CH_3CO_2H used / mol dm^{-3}	0.65
Initial temperature of CH_3CO_2H / °C	25.0
Highest temperature reached / °C	28.5
Specific heat capacity of water / J g^{-1} K^{-1}	4.18
Density of water / g cm^{-3}	1.00

(i) Use the results to determine the experimental enthalpy change of neutralisation.

[3]

(ii) The experiment described in **(d)(i)** was repeated using HC*l* instead of CH_3CO_2H, under the same conditions. The enthalpy change of neutralisation was found to be –57.9 kJ mol^{-1}. Apart from heat loss, suggest another reason for the discrepancy between this value and that calculated in **(d)(i)**.

....

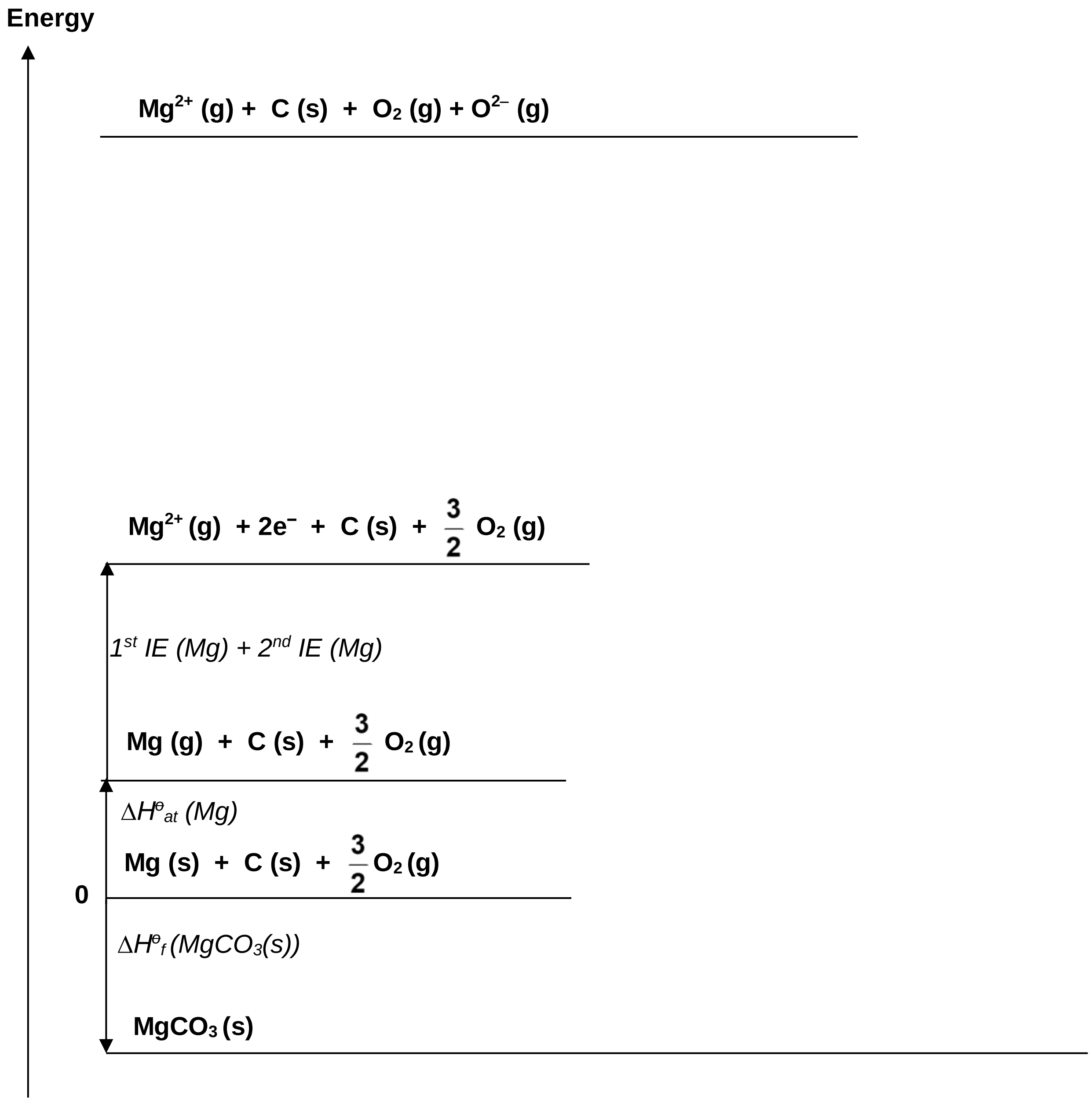
.... [1]

(e) Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, $MgCO_3$ to release carbon dioxide.

Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, $MgCO_3$. [5]

lattice energy of $MgCO_3$ (s)	= –3208 kJ mol^{-1}
standard enthalpy change of atomisation of Mg (s)	= +147 kJ mol^{-1}
sum of 1st and 2nd electron affinity of oxygen	= +702 kJ mol^{-1}
standard enthalpy change of formation of CO_2 (g)	= –393 kJ mol^{-1}
standard enthalpy change of reaction below, $\Delta H^\ominus_r$	= –778 kJ mol^{-1}

$O^{2-}(g) + CO_2(g) \longrightarrow CO_3^{2-}(g)$



[Total: 18]

4 Dragons are able to breathe fire because the parasitic bacteria that live in their lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx.

(a) The gas exhaled by a dragon contains 20 mole % of hydrogen sulfide, H_2S and 15 mole % of oxygen. The average volume of a dragon's lung is 5.1 m^3 and due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is 15 $dm^3\ mol^{-1}$.

(i) Calculate the total amount of gas in moles contained in a dragon's lung.

[1]

(ii) Assuming the temperature of a dragon's lung is 40 °C and the gaseous mixture behaves ideally, use the ideal gas equation and your answer in **(a)(i)** to calculate the internal pressure in the lung experienced by a dragon.

[1]

(iii) The actual pressure in the dragon's lung is lower than the value calculated in **(a)(ii)**. Account for the discrepancy observed.

....

....

....

.... [1]

(iv) Write a balanced equation for the reaction that describes the burning of gas exhaled by the dragon. Hence, calculate the additional moles of oxygen required for the complete combustion of one exhalation of the dragon.

[3]

(b) The parasitic bacteria in the dragon's lung produces a protein molecule **A** which speeds up the formation of flammable gases.

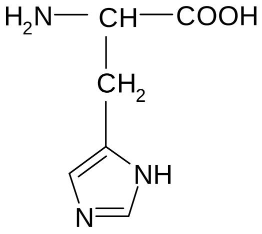
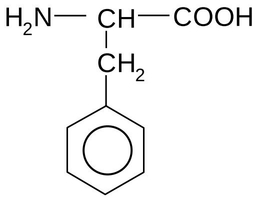
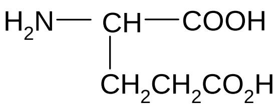
In the study of the structure of **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using the first enzyme:	Digestion using the second enzyme:
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

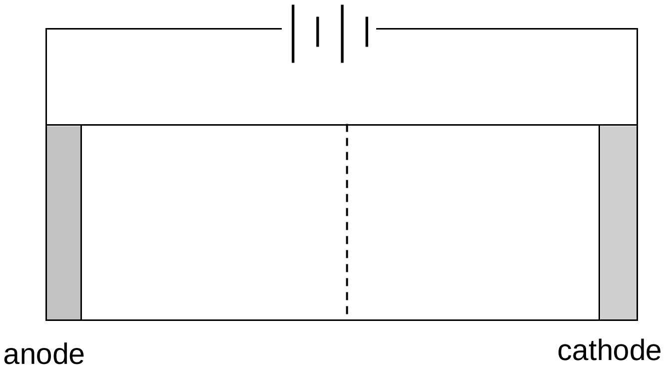
(i) Write out the amino acid sequence of the smallest polypeptide **A**.

.... [2]

(ii) A tripeptide, his-phe-glu, obtained from **A** was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino acids	 his	 phe	 $H_2N-CH(CH_2CH_2CO_2H)-COOH$ glu
Isoelectric point	7.58	5.48	3.10

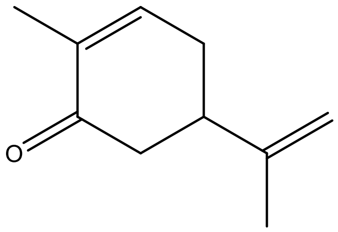
Indicate the relative positions of the amino acids on the diagram below.



[2]

[Total: 10]

5 Carvone is a chemical found naturally in essential oils extracted from the seeds of two common herbs, spearmint and dill.



Carvone

Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

(a) State the type of stereoisomerism carvone can exhibit.

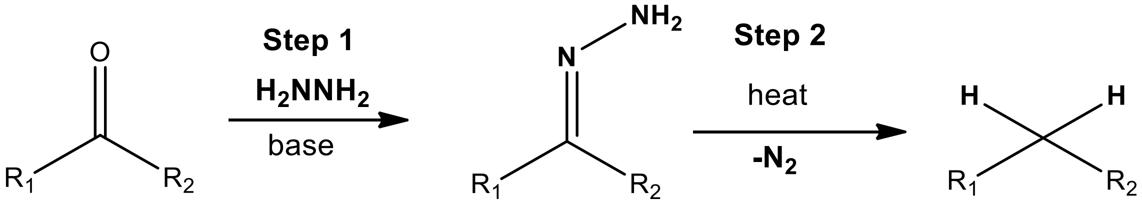
.... [1]

(b) Draw the two stereoisomers of carvone.

[1]

(c) Carvone undergoes reduction with different reagents and conditions to form different products. One notable reduction method is the ***Wolff-Kishner reduction*** whereby the ketone functional group in carvone reacts with hydrazine, N_2H_4, in the presence of a strong base to form limonene, $C_{10}H_{16}$, a major component in the oil of citrus fruit peels.

The general reaction sequence of the ***Wolff-Kishner reduction*** is shown below.

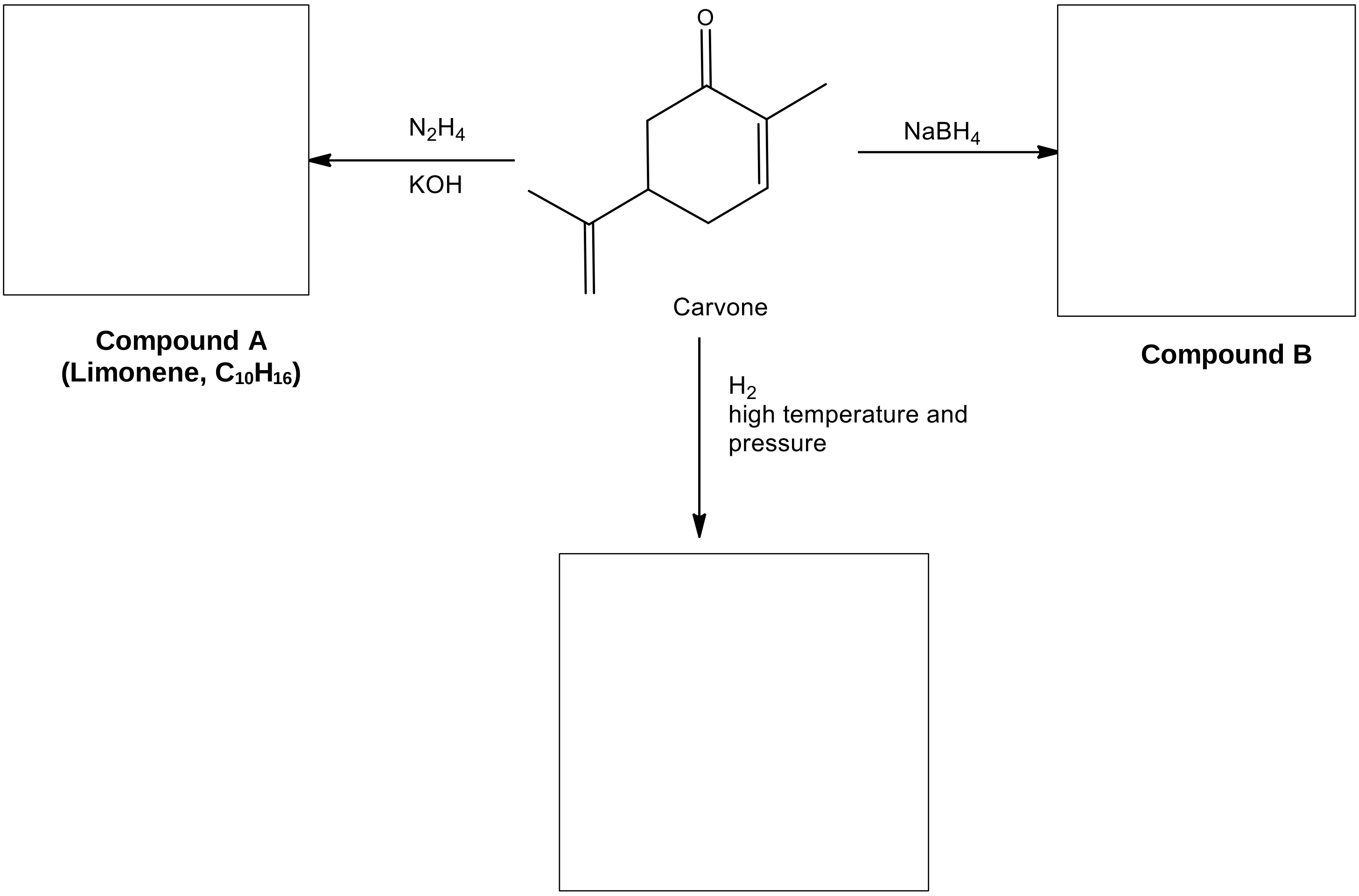


The ***Wolff-Kishner reduction*** is unsuitable for base-sensitive reactants.

(i) Suggest the type of reaction in **Step 1**.

.... [1]

(ii) The following reaction scheme shows the various reduction reactions of carvone. Suggest the structural formulae of compounds **A**, **B** and **C** in the boxes below.



Compound C

[3]

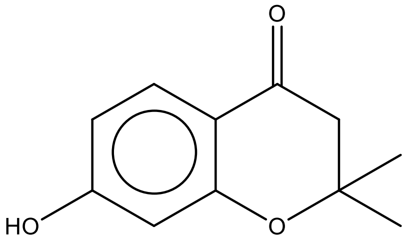
(iii) Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: ....

	Observations:	Products:
Carvone		
Limonene		

[3]

(iv) Suggest a reason why the following compound is unlikely to undergo the ***Wolff-Kishner reduction*** despite the presence of a ketone functional group.

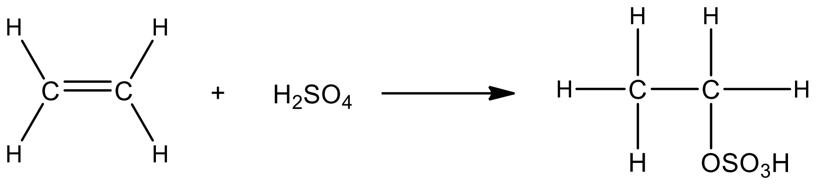


………………………………………………………………………………………………

………………………... [1]

[Total: 10]

6 When fuming sulfuric acid reacts with alkenes, electrophilic addition occurs to form alkyl hydrogensulfates. This is exemplified by the reaction involving ethene below.



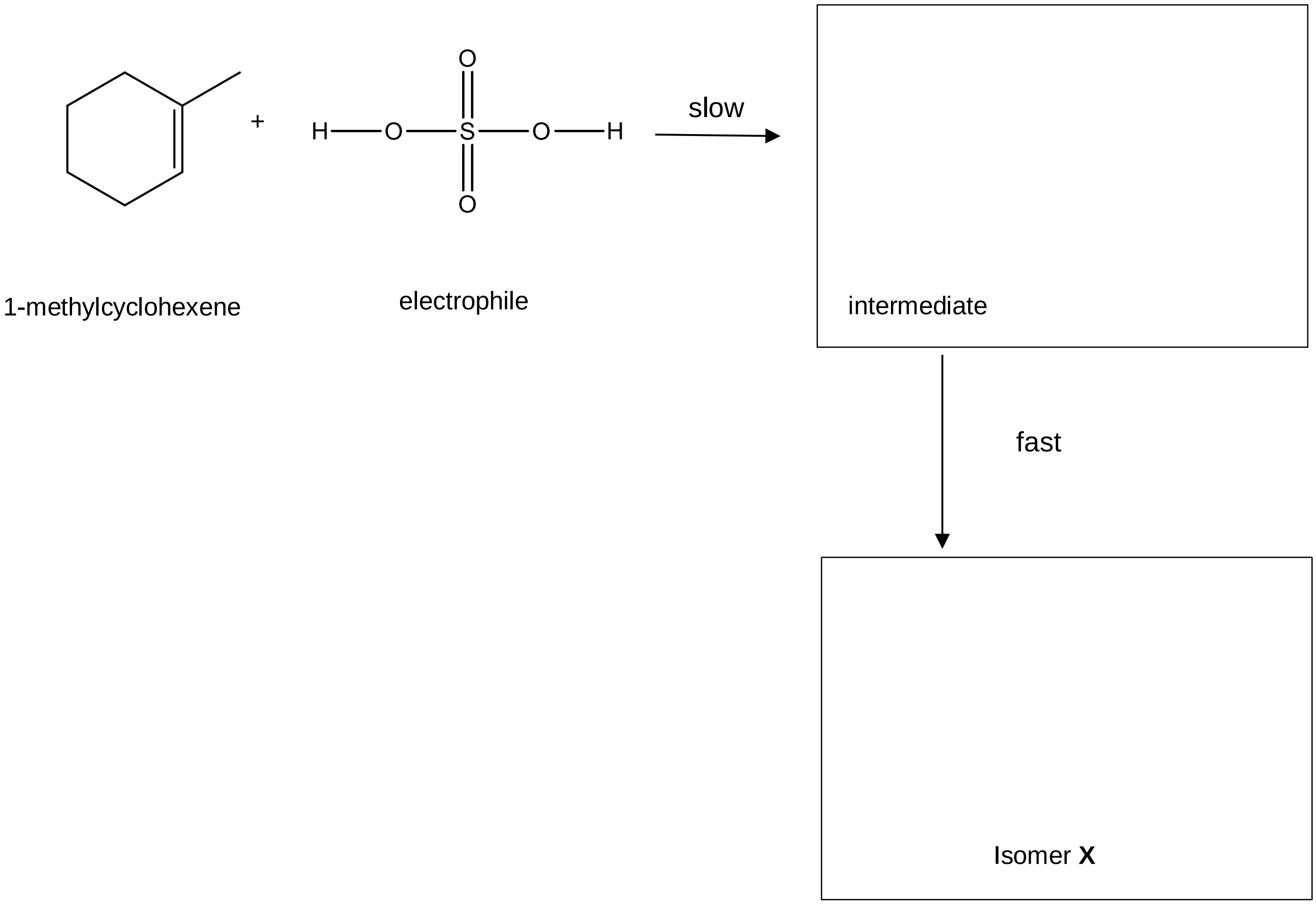
When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers **X** and **Y** are formed, with isomer **X** being the major product.

(a) Name and define the type of isomerism exhibited by isomers **X** and **Y**.

……………………………………………………………………………………………………

……………………………………………………………………………………………………[2]

(b) Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form **X**. Show the structure of the intermediate, the movement of the electron pairs and the structure of **X**.



[4]

(c) Explain why benzene does not undergo addition reactions with fuming sulfuric acid.

……………………………………………………………………………………………………

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…………………………………………………………………………………………………… [2]

[Total: 8]

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Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 30 August 2019

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.

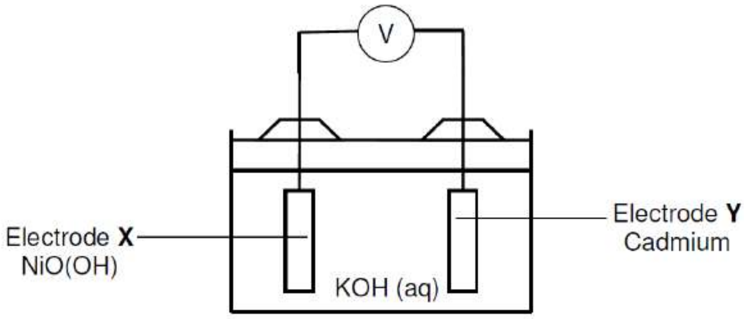
This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** Chemical energy can be directly converted to electrical energy in batteries and fuel cells. Fuel cells require a continuous source of fuel and oxygen to sustain the chemical reaction, whereas in batteries, the chemical energy is usually derived from reactions of metals or metal oxides present in the battery.

The nickel-cadmium (NiCd) battery is a rechargeable battery used in many devices such as handphones and laptops. A simplified diagram of the NiCd electrochemical cell is as shown:



Electrode **X** is made of a solid nickel compound, NiO(OH), and electrode **Y** is made of solid cadmium. The electrolyte is aqueous potassium hydroxide. During discharge, $Ni(OH)_2(s)$ and $Cd(OH)_2(s)$ are formed at the respective electrodes.

(i) Construct the half-equations at the electrodes of this alkaline NiCd electrochemical cell. Hence, give the balanced overall equation for the reaction that occurs during discharge. [2]

(ii) Write a cell representation for the NiCd electrochemical cell, indicating clearly the direction of electron flow in the external circuit. [2]

(iii) NiCd batteries can be recharged by applying a current across the two electrodes. How long would it take to recharge a NiCd battery at a current of 2.0 A, if 5.6 g of cadmium was converted to $Cd(OH)_2$? [2]

(b) Methane gas, CH_4, is the simplest alkane used to power a fuel cell. The methane-oxygen fuel cell has recently been shown to be an efficient source of electrical energy. In the simplest version of this fuel cell, an acid is used as the electrolyte and methane undergoes reaction at one of the electrodes while oxygen undergoes reaction at the other electrode.

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O \qquad E^\theta = +0.17\text{ V}$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

(i) By using the half-equations above and relevant data from the *Data Booklet,* calculate the E^θ_{cell} of this fuel cell. [1]

(ii) Draw a fully labelled diagram of the electrochemical cell you could use to measure this E^{θ}_{cell}. [3]

(c) An alternative fuel used in fuel cells is dimethyl oxalate, $(CH_3)_2C_2O_4$, which is obtained by the esterification of ethanedioic acid, $H_2C_2O_4$, with methanol, CH_3OH. The ethanedioate ion, $C_2O_4^{2-}$, is commonly found in ionic salts such as $\mathbf{X}C_2O_4$. When these ethanedioate salts, $\mathbf{X}C_2O_4$, are oxidised by acidified potassium manganate(VII), $KMnO_4$, both the $\mathbf{X}^{2+}$ and $C_2O_4^{2-}$ ions are oxidised. Carbon dioxide gas is formed as one of the products in the reaction.

(i) Write a balanced equation for the reaction between MnO_4^- and $C_2O_4^{2-}$ under acidic conditions. [1]

(ii) 25.0 cm^3 of 0.1 mol dm^{-3} $\mathbf{X}C_2O_4$ solution was titrated with 0.1 mol dm^{-3} of acidified $KMnO_4$. Determine the volume of $KMnO_4$ needed to oxidise $C_2O_4^{2-}$ only. [2]

(iii) Given that 15.00 cm^3 of acidified $KMnO_4$ was required to completely oxidise 25.0 cm^3 of 0.1 mol dm^{-3} $\mathbf{X}C_2O_4$ solution, and using your answer in **(c)(ii)**, find the oxidation state of **X** in the product. [3]

(d) Potassium manganate(VII), $KMnO_4$, can be used to oxidise alkenes in different ways. Alkene **P**, C_8H_{16}, reacts with hot acidified $KMnO_4$ to form one organic product only, which gives a yellow precipitate with hot aqueous alkaline iodine. **P** also reacts with cold alkaline $KMnO_4$ to form an optically inactive diol, **Q**. When **P** is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including **R**, $C_8H_{14}Cl_2$, which does not have any chiral carbon. When **R** is reacted with ethanolic NaOH, compound **S**, C_8H_{12}, is the only product formed. **S** produces two compounds, CO_2 and CH_3COCO_2H in equimolar amounts when it is oxidised by hot acidified $KMnO_4$.

(i) Suggest the structural formulae for compounds **P**, **Q**, **R** and **S**. [4]

(ii) Draw the structural formula of an isomer of **R**, $C_8H_{14}Cl_2$, that could give **S** on dehydrochlorination. [1]

(iii) Suggest, with a reason, the number of stereoisomers for compound **S**. [1]

[Total:22]

2 With the prospect that fossil fuels will become increasingly scarce in the future, many compounds are being considered for use in internal combustion engines. One of these is DME or dimethyl ether, CH_3OCH_3. DME is a gas which can be synthesised from methanol. Methanol can be obtained from biomass, such as plant waste from agriculture.

(a) Write a balanced equation to define the term *standard enthalpy change of combustion*, $\Delta H_c^{\ominus}$, of DME. [1]

(b) A 0.31 g sample of DME was completely burnt in air. The heat produced raised the temperature of 200 g of water by 11.7 °C. Assume no heat losses occurred during this experiment.

(i) Use relevant data from the *Data Booklet* to calculate the amount of heat released in this experiment. [1]

(ii) Hence calculate the enthalpy change of combustion, $\Delta H_c^{\ominus}$, of DME. [1]

(c) **(i)** Use the bond energies given in the *Data Booklet* to calculate another value for the *enthalpy change of combustion*, $\Delta H_c^{\ominus}$, of DME. [2]

(ii) Suggest a reason for the discrepancy, if any, between this $\Delta H_c^{\ominus}$ value and that calculated in **(b)(ii)**. [1]

(d) DME may be synthesised from methanol according to the following equation.

$$2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l) \qquad \Delta H^{\ominus} = +7.10\ \text{kJ mol}^{-1}$$

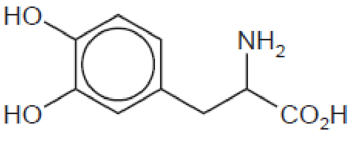
(i) The entropy change for this reaction, $\Delta S^{\ominus}$, is +83.62 J K^{-1} mol^{-1}.
Explain the significance of the sign of $\Delta S^{\ominus}$. [1]

(ii) Use the value of $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ given above to calculate a value for the standard Gibbs Free energy, $\Delta G^{\ominus}$, for this reaction. [1]

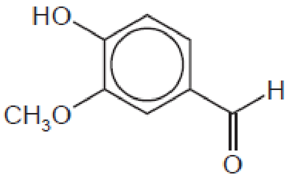
(iii) By considering the effect of temperature on the spontaneity of this reaction, suggest and explain whether high or low temperature should be used to produce DME. [2]

(iv) Explain, in molecular terms, how the rate of the above reaction is affected by changing the concentration of methanol. [2]

(e) Methanol is also a reagent to synthesise vanillin. Vanillin is an important raw material for the production of L-DOPA used in the treatment of Parkinson's disease.



L-DOPA



vanillin

A student carried out some reactions with samples of L-DOPA and vanillin using reagents **X**, **Y** and **Z**.

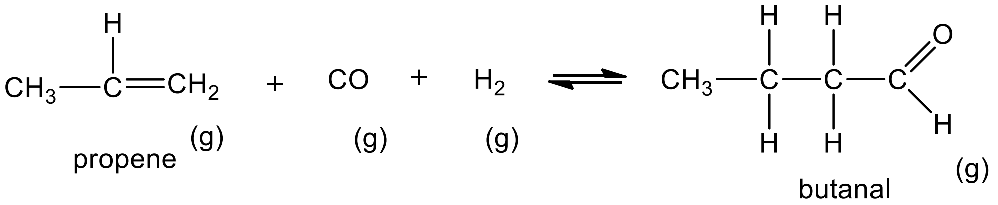
- Reagent **X** reacted with L-DOPA **and** with vanillin.
- Reagent **Y** reacted with L-DOPA but **not** with vanillin.
- Reagent **Z** reacted with vanillin but **not** with L-DOPA.

Assume that the CH_3O– group in vanillin is inert and does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products formed in each case. [7]

[Total: 19]

3 **(a)** The hydroformylation reaction is an industrial process for the production of aldehydes from alkenes. For example, butanal can be synthesised from propene, C_3H_6, as follows:



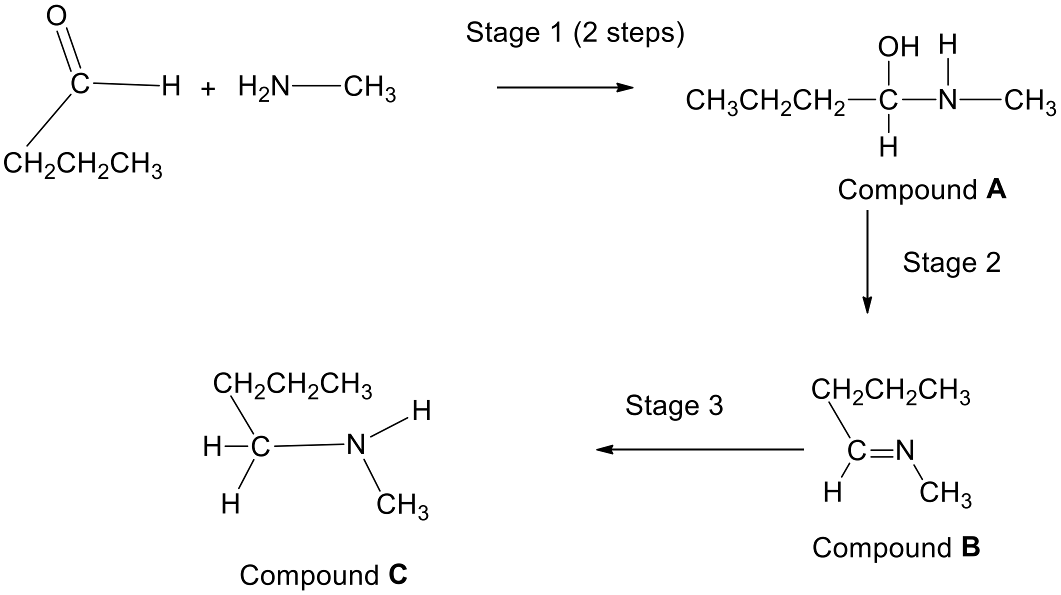
(i) Write an expression for K_p of the reaction, including units. [2]

(ii) Given that the magnitude of K_p for the above reaction is 775, deduce what the K_p value indicates about the position of equilibrium. Hence, state the sign of $\Delta G^{\ominus}$ for the reaction. [2]

(iii) Given that the above reaction is exothermic, suggest, with a reason, the effect of an increased temperature on the amount of butanal formed at equilibrium. [1]

(iv) The mechanism of hydroformylation of propene resembles the electrophilic addition of alkenes and can result in the formation of two isomeric products. Apart from butanal, suggest the structure of the other isomer that can be formed. [1]

(b) In the Leuckart-Wallach reaction, a carbonyl compound reacts with a primary amine to form a secondary amine.



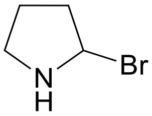
(i) Stage 1 occurs in 2 steps. The first step involves a nucleophilic attack while in the second step, a proton transfer occurs within the intermediate to form the alcohol group.

Name and outline the 2-step mechanism for Stage 1, to form Compound **A**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

(ii) Compound **B** undergoes reduction in Stage 3. Describe the change in oxidation state of carbon which occurs in this stage. [1]

(iii) Unlike primary amines, amides cannot be used in the Leuckart-Wallach reaction. Explain why this is so. [1]

(iv) 2-bromopyrrolidine, a cyclic amine, 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]

(v) State and explain the relative basicities of 2-bromopyrrolidine and compound **C**. [2]

(c) Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds are given in the table below.

Compound	Structure	Dipole moment	Boiling point / °C
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	x	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS. [2]

(ii) Predict a value for the dipole moment of COSe, x, and explain. [1]

(iii) Aside from the common oxides, carbon forms a series of straight-chained reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space. Suggest a displayed structure of tricarbon monoxide. Indicate clearly any lone pairs of electrons present in your structure. [1]

(iv) Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.
Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms. [1]

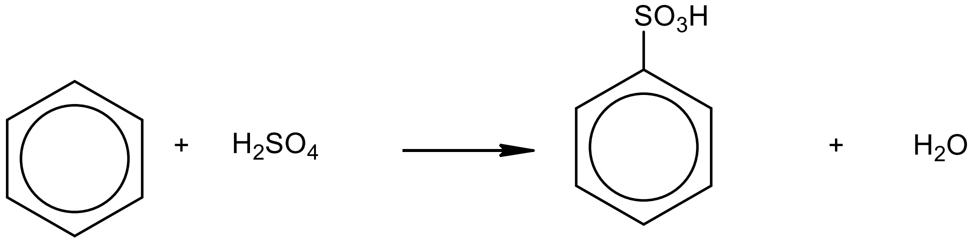
[Total: 19]

Section B

Answer **one** question from this section.

4 **(a)** Benzene is a widely used starting organic compound to synthesize other chemicals, such as benzenesulfonic acid and 2-methylphenol.

Benzenesulfonic acid can be produced by heating benzene under reflux with concentrated sulfuric acid for several hours. This process is similar to the nitration of benzene.

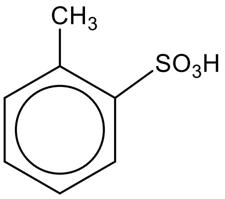


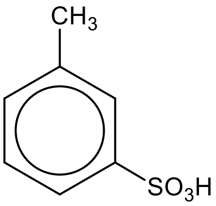
benzenesulfonic acid

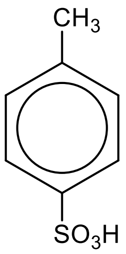
The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

(i) Describe the mechanism for the above reaction. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]

(ii) Similarly, methylbenzene also reacts with concentrated sulfuric acid to form a mixture of the three isomers, in equilibrium.

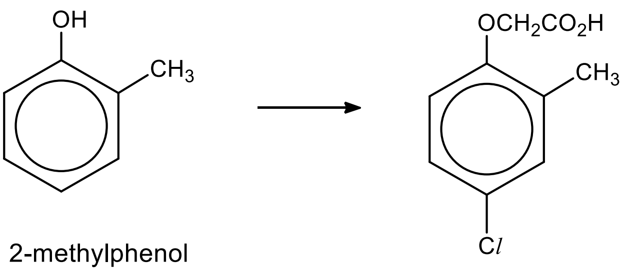






Suggest why there is a lower concentration of 1,2-isomer than that of 1,4-isomer in the equilibrium mixture. [1]

(iii) The chlorinated compound MCPA, widely used as a weed killer, can be synthesized from 2-methylphenol.



2-methylphenol

MCPA

Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [5]

(b) The chemical reactions of benzene sometimes require iron as a catalyst. Iron is a hard grey transition metal which is resistant to corrosion at ordinary temperatures. In contrast, calcium is a fairly soft, silvery-grey Group 2 metal which quickly tarnishes in air.

(i) By considering relevant electronic configurations, explain why the atomic radius of iron is smaller than that of calcium, even though iron has more electrons. [2]

(ii) Iron can exist in different oxidation states whereas calcium does not. Explain why. [2]

(iii) Explain why iron(II) complexes are green in colour. [3]

(iv) Iron(III) ions catalyse the reaction between I^- ions and $S_2O_8^{2-}$ ions through homogeneous catalysis.
Explain why iron(III) ions can be described as a homogeneous catalyst. By considering relevant $E^\ominus$ values from the *Data Booklet*, show by means of balanced equations, how the iron(III) ions carry out its role in this reaction. [3]

[Total: 20]

5 **(a)** Aluminium oxide, Al_2O_3, and aluminium chloride, $AlCl_3$, are widely used in various industrial and commercial applications.

(i) Aluminium oxide has a melting point of 2072 °C while aluminium chloride sublimes at 180 °C. Explain the difference in melting points in terms of structure and bonding in each compound. [2]

(ii) Describe the reactions, if any, of aluminium oxide and aluminium chloride with water, suggesting the pH of the resulting solutions and writing equations, where appropriate. [4]

(b) The reaction between chlorine gas and hot sodium hydroxide is as follows.

$$3Cl_2 + 6NaOH \rightarrow 5\,NaCl + NaClO_3 + 3H_2O$$

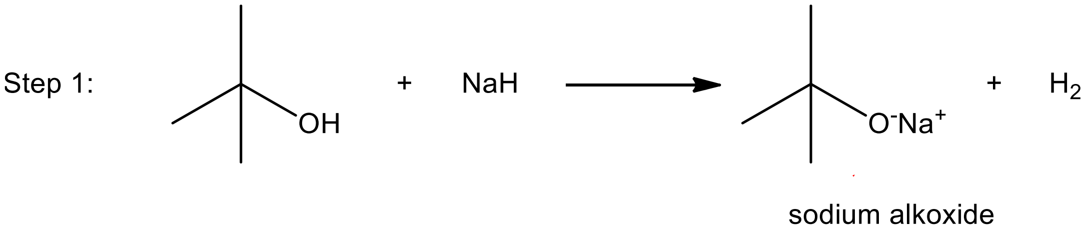
(i) State the type of reaction occuring. [1]

(ii) State the change in oxidation numbers of chlorine that occur during this reaction. [2]

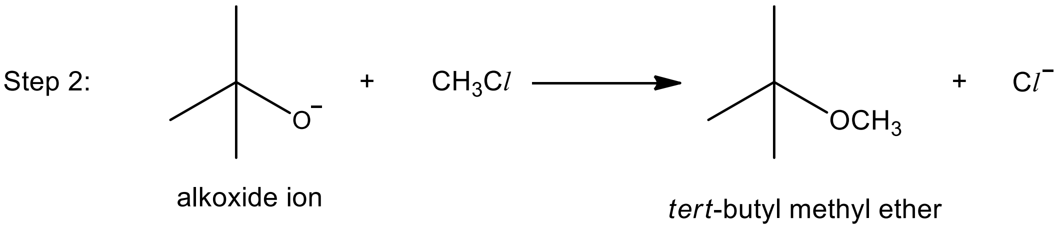
(c) Ethers are a class of organic compounds that has two organic groups bonded to the same oxygen atom, R-O-R'. The organic groups could be alkyl and aryl groups. Williamson synthesis could be used to synthsise ethers by a reaction between primary alkyl halides and metal alkoxides.

A typical example of the Williamson synthesis is a two-step reaction to synthesize *tert*-butyl methyl ether.

The first step of the reaction involved the preparation of sodium alkoxide in the presence of sodium hydride, NaH.



The second step of the reaction involved the reaction between the alkoxide ion and the primary alkyl halide.

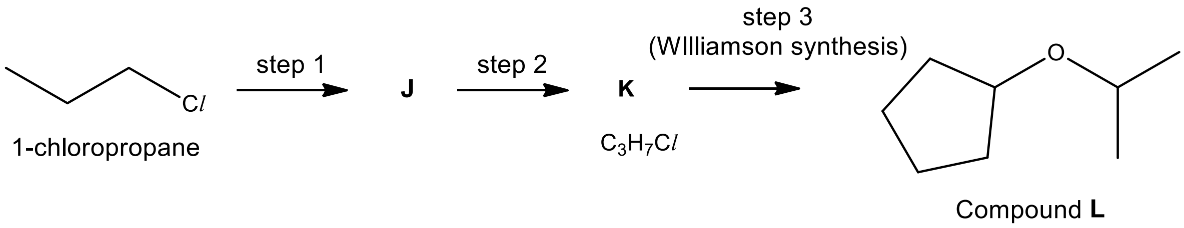


(i) Suggest the role of sodium hydride in step 1. [1]

(ii) Suggest the type of reaction which occurs in step 2. [1]

(iii) Suggest why primary alkyl halide is used in Williamson synthesis instead of secondary or tertiary alkyl halide. [1]

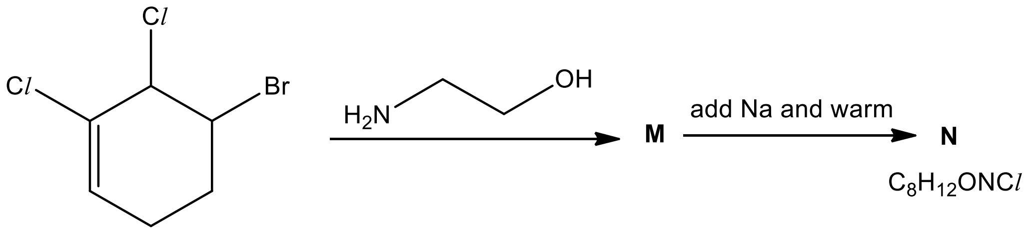
(iv) The following scheme shows a three-step synthesis of compound **L** from 1-chloropropane. Given that step 3 involves Williamson synthesis, suggest the reagents and conditions you would use for each step and identify the intermediates **J** and **K**.



[5]

(d) **(i)** Using monohalogenethanes, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds with respect to hydrolysis. [1]

(ii) There are other methods to synthesise ethers. A cyclic ether **N** could be formed as shown below. Predict the outcomes of the following transformations, drawing the structures of the intermediate **M** and the product **N**.



[2]

[Total: 20]

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Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/04

Paper 4 Practical

19 August 2019

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 and class in the boxes 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 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.

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	**16**
2	**14**
3	**13**
4	**12**
Total	**55**

This document consists of **15** printed pages and **1** blank page.

[Turn over

1 Determination of the percentage by mass of iron(II) sulfate in an iron tablet

Iron tablets, taken for the prevention and treatment of iron deficiency, are health supplements readily available in pharmacies. These iron tablets contain iron(II) sulfate, which is a soluble form of iron. Assuming that all the iron in the tablets is in the form of Fe^{2+}, it is possible to estimate the iron content by titration against potassium manganate(VII).

The equation for this reaction is

$$5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

You are provided with the following.

FA 1 contains 5 iron tablets, crushed to a powder.
FA 2 is 0.00500 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
deionised water

In this experiment, you will determine the percentage of iron(II) sulfate heptahydrate, $FeSO_4.7H_2O$, present in the iron tablets **FA 1**.

(a) Preparation of FA 3, a solution of $FeSO_4.7H_2O$.

- Use a measuring cylinder to transfer about 100 cm^3 of 1.0 mol dm^{-3} sulfuric acid into a conical flask.
- Determine accurately the mass of the crushed iron tablets used, **FA 1**, and record your readings in the space below.

mass of the crushed iron tablets used = …………… g

- Add all the crushed tablets, **FA 1**, to the sulfuric acid.
- **Warm** the mixture gently, **do not overheat**, and stir for about two minutes.
- Allow the flask to cool for around five minutes.
- Filter the mixture into a 250 cm^3 volumetric flask. Ensure that no solution is lost. Note: The filtration takes time. **Proceed to Question 2 whilst the mixture is filtering.**
- Wash out the conical flask with deionised water and add the washings through the filter into the volumetric flask.
- Make up the contents of the flask to the 250 cm^3 mark with deionised water. Stopper and mix the contents thoroughly to obtain a homogeneous solution.
- Label this solution **FA 3**.

(b) **Titration of FA 3 with FA 2**

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Use a measuring cylinder to add about 25.0 cm^3 of 1.0 mol dm^{-3} sulfuric acid to the conical flask.
- Titrate with **FA 2** until the appearance of a first permanent pale-pink colour.
- Record your titration results in the space below. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration as many times as necessary to obtain reliable results.

Titration Results

[6]

From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** = …………….............… [1]

(c) **(i)** Calculate the amount of MnO_4^- ions contained in the mean titre.

amount of MnO_4^- ions =……………………....… [1]

(ii) Calculate the amount of Fe^{2+} ions that reacted with the MnO_4^- ions calculated in **(c)(i)**.

amount of Fe^{2+} ions =……………………...… [1]

(iii) Calculate the amount of Fe^{2+} ions in the five crushed tablets, **FA 1**.

amount of Fe^{2+} ions in **FA 1** =……………………...… [1]

(iv) Calculate the mass of $FeSO_4.7H_2O$ in **one** tablet.
[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

mass of $FeSO_4.7H_2O$ in one tablet =……………………...… [2]

(v) Hence calculate the percentage by mass of $FeSO_4.7H_2O$ in **one** tablet.

percentage by mass of $FeSO_4.7H_2O$ in one tablet =……………………

[2]

(d) Explain why in the procedure described in **(a)**, the volume of sulfuric acid was measured using a measuring cylinder rather than a burette.

…………………………………………………………………………………………………

…………………………………………………………………………………………………… [1]

(e) To confirm the formula of iron(II) sulfate heptahydrate in the tablet, a student dissolved one of the tablets in nitric acid and added a few drops of barium nitrate to the filtrate.

State the observation expected from this chemical test. Give your reasoning.

…………………………………………………………………………………………………

…………………………………………………………………………………………………… [1]

[Total: 16]

2 Determination of the enthalpy change for the reaction of citric acid with $NaHCO_3(aq)$

Antacid, taken for quick relieve of occasional heartburn, is also readily available in pharmacies. Antacid contains mainly citric acid and sodium hydrogencarbonate, which react when in contact with water to give carbon dioxide.

In this experiment, you will determine the enthalpy change when citric acid reacts with sodium hydrogencarbonate.

You are provided with the following.

FA 4 is 0.8 mol dm^{-3} citric acid.
FA 5 is solid sodium hydrogencarbonate, $NaHCO_3$.

(a) Method

You will carry out the following experiment **twice**.

- Weigh between 6.5 g and 7.0 g of **FA 5** in a dry weighing bottle.
- Use a pipette to transfer 50.0 cm^3 of **FA 4** into the plastic cup supported in a 250 cm^3 beaker.
- Place the thermometer in the acid in the plastic cup and record its initial temperature.
- Carefully add the weighed sample of **FA 5**, in *small portions*, into the acid in the plastic cup. Stir the mixture carefully with the thermometer.
- Record the lowest temperature reached.
- Reweigh the weighing bottle and any residual **FA 5**.

Record in a single table, in the space given on **page 7**,

- all measurements of mass and temperature, and
- the temperature fall, ΔT.

Empty and rinse the plastic cup.

Repeat the experiment and calculate the mean value of

- ΔT, and
- mass of **FA 5** added.

Results

mean value of ΔT =……………………...…

mean mass of FA 5 added =……………………...…

[4]

(b) Citric acid is a tribasic acid; i.e. one mole of the acid reacts with three moles of sodium hydrogencarbonate.

(i) Write a balanced equation, with state symbols, to show how citric acid reacts with sodium hydrogencarbonate in the experiment. You may use H_3A to represent citric acid.

....… [1]

(ii) Calculate the heat energy when **FA 5** was added to the acid.

[Assume that 4.3 J are required to raise the temperature of 1.0 cm^3 of any solution by 1.0 °C.]

heat energy =…………..…. J [1]

(iii) In the experiment carried out in **2(a)**, excess citric acid was used. Using your answer to **2(b)(i)**, calculate the amount of citric acid that has reacted with the mean mass of **FA 5** added. [A_r: Na, 23.0; O, 16.0; C, 12.0; H, 1.0]

amount of citric acid = ... mol [2]

(iv) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of citric acid reacts with sodium hydrogencarbonate. Your answer should include the appropriate sign.

enthalpy change, ΔH = ... kJ mol^{-1} [2]

(v) Explain the significance of the sign you have given in **2(b)(iv)** and how it is related to your experimental results.

....

.... [1]

(c) Explain why **FA 5** is added in *small portions* in the procedure described in **2(a)**.

....

.... [1]

(d) A student repeated the experiment described in **2(a)** on another day when the room temperature was much higher. Suggest how this higher room temperature would affect the value of ΔT. Give your reasoning.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

[Total: 14]

3 Planning

The reaction between an acid and a metal hydroxide is exothermic. By using this fact, it is possible to determine the equivalence point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration*.

In the experiment, the temperature is monitored as portions of acid are progressively added to a fixed volume of the alkali until the equivalence point is reached and passed. 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 until they intersect.

(a) In a thermometric titration where an acid is run into an alkali, state and explain how you would recognise that the equivalence point has been passed.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

(b) In this question, you are required to write a plan for a thermometric titration in which citric acid is added to 25.0 cm^3 of aqueous sodium hydroxide.

You are provided with the following materials.

- 2.00 mol dm^{-3} sodium hydroxide, NaOH
- 0.8 mol dm^{-3} citric acid
- equipment normally found in a school laboratory

(i) Using the information given above, show that the volume of citric acid required to reach the equivalence point is 20.90 cm^3.
You may use H_3A to represent citric acid, which is a tribasic acid.

[1]

(ii) Outline how you would carry out the proposed thermometric titration using only the materials provided.

In your plan, you should include

- brief, but specific, details of the apparatus you would use, considering the levels of precision they offer;
- measurements you would make to allow for a suitable graph to be drawn in **3(b)(iii)**, in order to determine the value of $\Delta H_n^{\ominus}$ for this reaction; and
- how you would recognise that the equivalence point had been passed.

Outline your plan as a series of numbered steps.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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……………………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [4]

(iii) Sketch, on the axes provided, the graph you would expect to obtain using information in **3(b)(i)** and the measurements you planned to make in **3(b)(ii)**. Label clearly the axes. You should also indicate on your graph,

- the equivalence point, and
- the maximum temperature rise, ΔT_1.

[3]

(iv) Write an ionic equation to represent the enthalpy change of neutralisation, ΔH_n.

…………………………………………………………………………………………… [1]

(v) Given that ΔT_1 is 11.0 °C and using the information in **3(b)(i)**, determine the value of $\Delta H_n^{\ominus}$ for this reaction.

$\Delta H_n^{\ominus}$ =………………… kJ mol^{-1} [2]

[Total: 13]

4 Inorganic Analysis

You are provided with three solutions, **FA 6**, **FA 7** and **FA 8**, each containing one cation and one anion.

Identification of the anions in FA 6, FA 7 and FA 8.

One or more of the solutions contains a halide ion.

(a) From the *Qualitative Analysis Notes* on page 15, you are to select and use

(i) one reagent to precipitate any halide ion that is present,

(ii) a second reagent to confirm the identity of any halide ion present.

Since the solutions are coloured, you will need to remove traces of solution from the precipitate.

Record the tests performed, the practical procedures used and the observations made for each of the solutions.

Present this information as clearly as possible in a single table in the space below.

[4]

(b) Use your observations to identify any halide ions present in the solutions, **FA 6**, **FA 7** and **FA 8**, and state which ion is present in which solution.

....

....

....

[1]

Identification of the cations in FA 6, FA 7 and FA 8.

(c) Using aqueous NaOH and aqueous NH_3, it is possible to identify two of the cations present and to draw conclusions about the nature of the remaining cation.

Carry out tests with these reagents and record the observations made for each of the solutions.

Test	**FA 6**	**FA 7**	**FA 8**
1. Add aqueous NaOH dropwise until no further change is seen.			
2. Add aqueous NH_3 dropwise until no further change is seen.			

[4]

(d) Use your observations in **4(c)** to identify two of the cations present and state which of the solutions contain those cations.

The cation contained in **FA** .... is ....

Evidence:

....

The cation contained in **FA** .... is ....

Evidence:

....

[2]

(e) From your observations in **4(c)**, what conclusion can you draw about the general nature of the third cation? Explain your answer.

....

.... [1]

[Total: 12]

Qualitative Analysis Notes
[*ppt. = precipitate*]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, A*l* $^{3+}$(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

Tuesday 3 September 2019

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

WORKED SOLUTIONS

1 In a titration experiment, 15 cm^3 of 0.10 mol dm^{-3} phosphorous acid, H_3PO_3 was found to react with 10 cm^3 of 0.30 mol dm^{-3} sodium hydroxide. Using this information, deduce the formula of the salt formed in this neutralisation process.

A NaH_2PO_3

B Na_2HPO_3

C Na_3PO_3

D Na_3PO_4

Concept: MCS, Acid-base reaction
Answer: B

Amount of H_3PO_3 used in experiment = 0.015 x 0.10 = 1.50 x 10^{-3} mol

Amount of NaOH neutralised = 0.010 x 0.30 = 3.00 x 10^{-3} mol

$H_3PO_3 \equiv 2\ NaOH$

2 mol of NaOH neutralise 2 mol of H^+

1 mol of H^+ is left unreacted in 1 mol H_3PO_3 (since $H_3PO_3 \equiv 3H^+$)

Salt formed contains 1 mol of H^+

2 50 cm^3 of a mixture of ethene and propane gas were exploded in excess oxygen. The volume of the residual gases was found to be 200 cm^3. On being shaken with potassium hydroxide, the final volume was found to be 90 cm^3. What is the composition of the mixture? *(All volumes are measured at r.t.p)*

	volume of ethene	volume of propane
A	10	40
B	20	30
C	30	20
D	40	10

Concept: MCS, calculations involving volume of gases (involving hydrocarbons)
Answer: D

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$
$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

Let vol of ethene (C_2H_4) be x.

∴ vol of propane (C_3H_8) = 50 - x

Vol of CO_2 gas formed in total = $2x + 3(50 - x) = 150 - x$

Change in vol of residual gases after passing through KOH = vol of CO_2 formed

= 200 – 90 = 110 cm^3

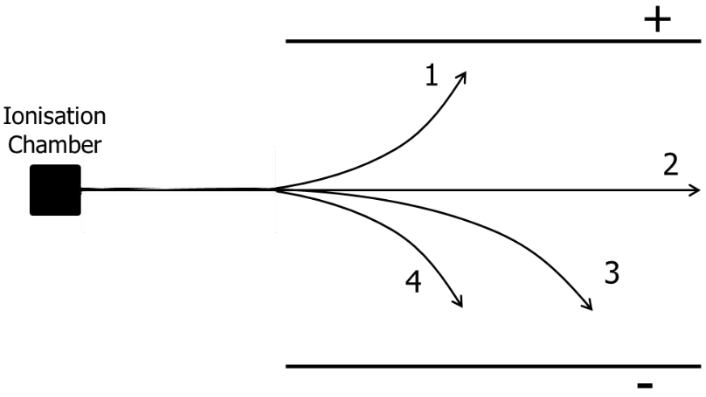
Hence, $150 - x = 110$

x = 40 cm^3 Vol of ethene = 40 cm^3 ; vol of propane = 10 cm^3

3 Plutonium-239 is a radioactive substance that emits a constant stream of α–particles which are similar to the nucleus of ^{4}He.

Rubidium-87 is another radioactive substance that emits β–particles which can be considered as electrons.

A small amount of Plutonium-239 and Rubidium-87 are separately placed in an ionisation chamber to emit a constant stream of radiation and the emitted particles are passed through an electric field.



What would be the path of the emitted particles in the electric field?

	Plutonium-239 (α–particles)	Rubidium-87 (β–particles)
A	1	2
B	1	3
C	4	1
D	3	1

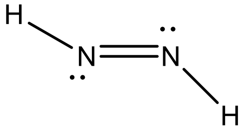
Answer: D

$$\text{Angle of deflection} \propto \frac{\text{charge of ion}}{\text{mass}}$$

Given that alpha particles (α–particles) are similar to the nucleus of He (i.e. $^{4}He^{2+}$) and beta particles (β–particles) can be considered as electrons ($^{0}e^{-}$), α–particles will be deflected towards the negative plate and by a smaller magnitude (due to greater mass no.) than β–particles (towards positive plate).

4 Diazene has a molecular formula of N_2H_2. Given that the nitrogen and hydrogen show their usual valencies, which of the following correctly describes the shape and bond angle around each central atom?

	shape	bond angle
A	bent	110º
B	linear	180º
C	tetrahedral	109º
D	trigonal planar	120º



Concept: Drawing Lewis structure, identify shape and bond angle

Answer: A

Around each N atom, there are 2 bonds pairs and 1 lone pair of electrons. Hence, it is bent around each N atom and the bond angle is between 109º and 120º. Hence, the most appropriate answer is 110º.

5 Which of the following contains delocalised electrons?

1 Graphite
2 Sodium
3 Ethanoate ion
4 Cyclohexene

A 1 and 2 only
B 2 and 3 only
C 1, 2 and 3 only
D 3 and 4 only

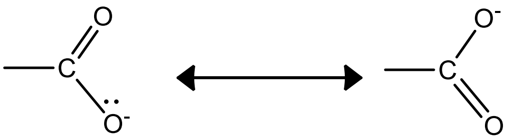
Concept: Structure and bonding, delocalisation of electrons

Answer: C

1: Each C atom is bonded to 3 other C atoms and the remaining electron is delocalised along the layers of carbon atoms.

2: Sodium metal has a giant metallic structure, which has strong electrostatic forces of attraction between the metal ion and the sea of delocalised electrons. The valence electron is involved in delocalisation.

3: The negative charge on oxygen can be delocalised across the sp^2 hybridised carbon.



4: The π electrons are localised between the 2 C in the C=C.

6 Which equation corresponds to the enthalpy change stated?

A	$Ba(OH)_2(aq) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$	Γ $\Delta H^{e}_{\text{neutralisation}}$
B	$Na_2SO_4(s) + aq \rightarrow 2Na^{+}(aq) + SO_4^{2-}(aq)$	Γ $\Delta H^{e}_{\text{solution}}$
C	$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$	Γ $\Delta H^{e}_{\text{formation}}$
D	$Br_2(l) \rightarrow 2Br(g)$	Γ $\Delta H^{e}_{\text{atomisation}}$

Ans: B
From definitions of various enthalpy changes
Errors in options given:
Γ $\Delta H^{e}_{\text{neutralisation}}$ **– only 1 mol of H_2O formed (not 2 mol)**
Γ $\Delta H^{e}_{\text{formation}}$ **– only 1 mol of compound formed (not 8 mol)**
Γ $\Delta H^{e}_{\text{atomisation}}$ **– breaking of bonds in gaseous phase (not liquid phase)**

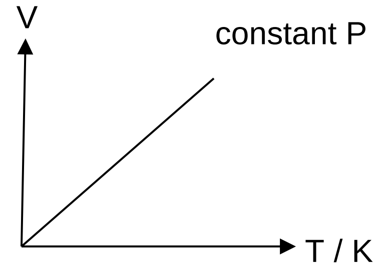
7 In which of the following processes will ΔS be negative?

A Photosynthesis
B Electrolysis of water
C Boiling of water
D Dissociation of solid $MgSO_4$ in water

Ans: A
A: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ ΔS=-ve
B: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ OR $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ΔS=+ve
C: phase change from liquid to solid ΔS=+ve
D: $MgSO_4 + aq \rightarrow MgSO_4(aq)$ ΔS=+ve

8 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas?
(P = pressure, ρ = density, V = volume, T = temperature).

1

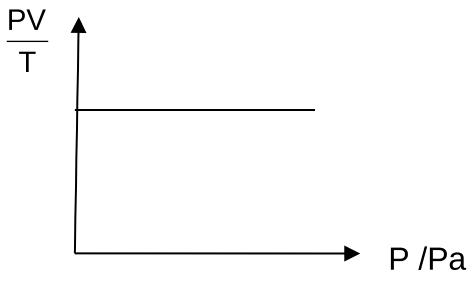


PV = nRT(K)

$V = \frac{nR}{P}T(K)$

V ∝ T(K) (∴ linear line passing through origin)

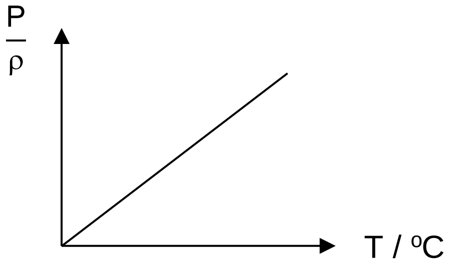
2



PV = nRT

$\frac{PV}{T}$ = nR (constant, ∴ horizontal line)

3



A 1 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

$$PV = nRT(K)$$

$$P = \frac{\rho}{M_r}RT(K)$$

$$\frac{P}{\rho} = \frac{RT(K)}{M_r}$$

$$\frac{P}{\rho} = \frac{R(T(^{o}C)+273)}{M_r}$$

$$\frac{P}{\rho} = \frac{RT(^{o}C)}{M_r} + \frac{273R}{M_r}$$

Plotting P/ρ vs T(°C) will give a linear line with a y-intercept of $\frac{273R}{M_r}$

9 A sample of HBr gas was decomposed in a sealed container at temperature T. The decomposition equation is given below.

$$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g) \qquad \Delta H \text{ is positive}$$

Which of the following statements is **false**?

A Equal amounts of H_2 and Br_2 are formed at equilibrium.

B When a catalyst is added, the rates of the forward and reverse reactions are increased by the same extent.

C The K_c will decrease if reaction is carried out at higher temperature.

D The equilibrium position is unaffected when the volume of the container is decreased.

Concept: Le Chatelier's Principle, Calculating K_c, mole fraction

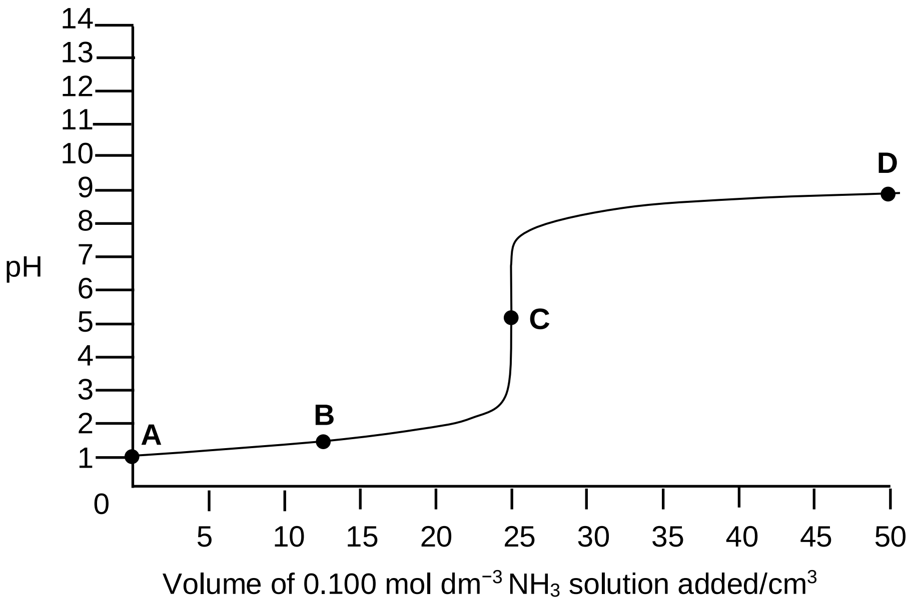
When the temperature is increased, the position of equilibrium shifts to the right to favour the forward reaction which is heat-absorbing/endothermic. K_c will increase.

$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

Since the number of mole of gases on both sides of the equation are the same, there would be no change in equilibrium position when the volume of container is decreased and the pressure is increased. Hence Option D is true.

10 The pH changes when 0.100 mol dm^{-3} $NH_3(aq)$ is added dropwise to 25.0 cm^3 of 0.100 mol dm^{-3} HC*l* as shown below.

At which point on the graph does pOH = pK_b, where K_b is the base dissociation constant of the weak base?



Concept: Chemistry of Aqueous Solutions, interpreting titration curve

Answer: D

For pOH = pK_b, [NH_4^+] = [NH_3]

HC*l* + NH_3 → NH_4C*l*

At **A**, species present: HC*l*

At **B**, species present: HC*l* and NH_4C*l*

At equivalence point **C**, NH_4^+ ion hydrolyses in water, $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

At **D**,

n_{NH3} = 25.00/1000 x 0.100
= 2.5 x 10^{-3} mol

n_{NH4Cl} formed = 25.0/1000 x 0.100
= 2.5 x 10^{-3} mol

At **D**, [NH_4^+] = [NH_3]

11 Ammonia usually reacts as a base. In which reaction does it behave as an acid?

1 $Hg_2Cl_2 + 2NH_3 \rightarrow Hg + HgCl(NH_2) + NH_4^+ + Cl^-$
2 $Cu^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$
3 $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

Answer: D

Option 1: NH_3 donate a H^+ to form NH_2^-. ➔ Bronsted-Lowry acid

Option 2: The 4 NH_3 donate a pair of electrons each to the Cu^{2+} to form an adduct through the formation of a dative bond. (complex formation – covered in JC2 Transition Metals) ➔ Lewis base

Option 3: Ammonia accepts a H^+ from HCl to form ammonium ion (NH_4^+). ➔ Bronsted-Lowry base

12 The table shows experimental results obtained for the reaction of hydrogen peroxide with acidified iodide ions to liberate iodine.

initial concentrations of reactants / mol dm^{-3}			*initial rate of formation of iodine* / mol dm^{-3} s^{-1}
$[H_2O_2]$	$[I^-]$	$[H^+]$	
0.010	0.010	0.010	2.0×10^{-6}
0.030	0.010	0.010	6.0×10^{-6}
0.030	0.020	0.010	1.2×10^{-5}
0.030	0.020	0.020	1.2×10^{-5}

What can be deduced from these results?

1 The rate equation for the reaction can be written: rate = $k[H_2O_2][I^-]$.
2 The reaction is zero order with respect to acid.
3 The units of rate constant is mol^{-2} dm^{6} s^{-1}.
4 Both hydrogen peroxide and iodide ions are involved in the rate-determining step.

A 1 and 2 only
B 3 and 4 only
C 1, 2 and 4
D 2, 3 and 4

Ans: C

Comparing expt 1 and 2, $[I^-]$ and $[H^+]$ kept constant, when $[H_2O_2]$ is tripled, initial rate is also tripled. ∴ reaction is 1st order w.r.t. H_2O_2.

Comparing expt 2 and 3, $[H_2O_2]$ and $[H^+]$ kept constant, when $[I^-]$ is doubled, initial rate is also doubled. ∴ reaction is 1st order w.r.t. I^-.

Comparing expt 3 and 4, $[H_2O_2]$ and $[I^-]$ kept constant, when $[H^+]$ is doubled, initial rate is unchanged. ∴ reaction is zero order w.r.t. H^+. (statement 2)

Hence, rate equation is rate = $k[H_2O_2][I^-]$ (statement 1) and only H_2O_2 and I^- are involved in the rate-determining step. (statement 4)

From experiment 1,

units of *k* $= \dfrac{\text{rate}}{[H_2O_2][I^-]} = \dfrac{\text{mol dm}^{-1}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$

$= \text{mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}$ **(not statement 3)**

13 The mechanism for a certain reaction is given below:

$$2P \longrightarrow R \text{ (fast)}$$
$$R + Q \rightleftharpoons S \text{ (slow)}$$
$$S + Q \longrightarrow P_2Q_2 \text{ (fast)}$$

What conclusion can be drawn from the above mechanism?

A The rate equation is rate = $k[P]^2[Q]$.

B The overall order of reaction is 2.

C The units of the rate constant, k, is $\text{mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}$.

D The half-life of [Q] is halved when [Q] is doubled,

Overall equation: $2\mathbf{P} + 2\mathbf{Q} \rightarrow \mathbf{P_2Q_2}$
From here, we can conclude that **R** and **S** are intermediates and should not appear in the rate equation.

The second step of the reaction mechanism, $\mathbf{R} + \mathbf{Q} \rightleftharpoons \mathbf{S}$ is a slow step.
Hence, Rate = k [**R**] [**Q**].

Since R is the intermediate formed from 2 moles of **P**, Rate = k $[\mathbf{P}]^2$ [**Q**]
Thus overall order of reaction is 3.

Rate constant **k** has the units of $\dfrac{mol dm^{-3}s^{-1}}{(mol dm^{-3})^3} = mol^{-2}dm^{6}s^{-1}$

The reaction is first-order with respect to **Q**, hence **Q** has a constant half-life that is independent of [**Q**].

Answer: Option **A**

14 Four elements with atomic numbers from 11 to 17 inclusive have the following properties.

- Chloride of **E** dissolves in water and turns moist blue litmus red.
- Oxide of **F** is amphoteric.
- **G** has the lowest electronegativity among these four elements.
- **H** has the smallest atomic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

A **F**, **G**, **H**, **E**
B **F**, **G**, **E**, **H**
C **G**, **F**, **E**, **H**
D **G**, **F**, **H**, **E**

Concept: The Periodic Table − properties of Period 3 elements (chlorides and oxides)
Answer: C

$MgCl_2$, $AlCl_3$, $SiCl_4$ and PCl_5 dissolves in water to give acidic solutions and hence turn blue litmus red. E could be Mg, Al, Si or P.

Only Al_2O_3 is amphoteric. F is Al.

Across a Period, the electronegativity increases. G is the first element of give E, F, G and H.

Chlorine has the smallest atomic radius. H is chlorine.

15 *Use of Data Booklet is relevant to this question.*
Which statements about the elements chlorine, bromine and iodine are correct?

1 The oxidising power increases from chlorine to iodine.
2 The strength of the covalent bonds in the molecules decreases from chlorine to iodine.
3 The magnitude of the first electron affinity increases from chlorine to iodine.

A 1 only
B 2 only
C 2 and 3 only
D 1, 2 and 3

Concept: The Periodic Table – properties of Group 17
Answer: B

Statement 1: Group 17 elements, X_2, have positive $E^\ominus$ values, which indicates that they are oxidising in nature. They tend to be reduced to form X^- ions.
$Cl_2 + 2e \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V

$Br_2 + 2e \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V
$I_2 + 2e \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

$E^\ominus$ values decreases down the group, which indicates the oxidising power of the elements decreases from Cl_2 to I_2. Hence, Statement 1 is wrong.

Statement 2:

$Cl—Cl$ BE = 244 kJ mol^{-1}
$Br—Br$ BE = 193 kJ mol^{-1}
$I—I$ BE = 151 kJ mol^{-1}

Down the group, as the size of the halogen atom increases, the X—X bond length increases and is weaker. Hence, Statement 2 is correct.

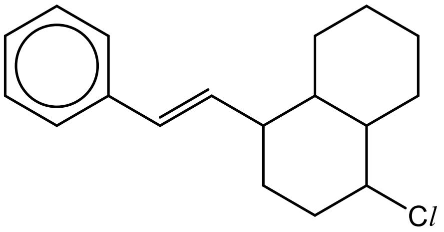
Statement 3:

First electron affinity is the energy released when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous anions. First EA is always negative because it is an exothermic reaction, attraction is formed between nucleus and the incoming electron and hence energy is released.

$X(g) + e \rightleftharpoons X^-(g)$

Down the group, the size of halogen atom increases, the attraction between the nucleus and the incoming electron is weaker. Hence, less energy is released. Magnitude of the first EA decreases from Cl to I.

16 How many stereoisomers does compound **Q** exhibit?



Compound **Q**

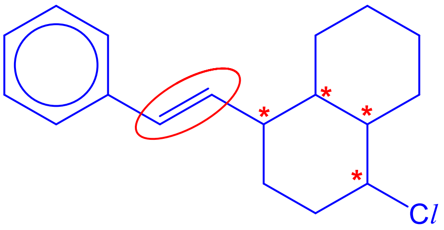
A 2 **B** 5 **C** 16 **D** 32

Concept: Identification of chiral centres and C=C that can exhibit cis/trans;

Answer: D

Total number of stereoisomers = 2^n *(Note: maximum no. of stereoisomers = 2^n, where n = total no. of C=C bonds that can show Cis-trans isomerism + no. of chiral carbon centres)*

Total number of stereoisomers = 2^5 = 32



17 Which of the following is a **propagation** step in the formation of 1,1-dibromopropane from the reaction between propane and bromine in the presence of ultraviolet light?

A $CH_3CH_2CH_2Br + Br\bullet \rightarrow CH_3CH_2CH_2\bullet + Br_2$

B $CH_3CH_2CH_2\bullet + Br\bullet \rightarrow CH_3CH_2CH_2Br$

C $CH_3CH_2CH_2\bullet + Br_2 \rightarrow CH_3CH_2CHBr\bullet + HBr$

D $CH_3CH_2CHBr\bullet + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br\bullet$

Concept: Alkane, Free Radical Substitution

Answer: D

Propagation (generation of new radicals in each step):

Highly reactive bromine radicals **react with propane molecules** and abstract one **hydrogen atom leaving a propyl radical**

$CH_3CH_2CH_3 + Br\bullet \longrightarrow CH_3CH_2CH_2\bullet + HBr$

Regeneration of bromine free radical by propyl radical

$CH_3CH_2CH_2\bullet + Br_2 \longrightarrow CH_3CH_2CH_2Br + Br\bullet$

Regenerated bromine free radical reacts with 1-bromopropane and process **repeats** with 1-bromopropyl radical

$CH_3CH_2CH_2Br + Br\bullet \longrightarrow CH_3CH_2CHBr\bullet + HBr$

$$\boxed{CH_3CH_2CHBr\bullet + Br_2 \longrightarrow CH_3CH_2CHBr_2 + Br\bullet}$$

18 Methane is a greenhouse gas but is destroyed in the troposphere by the action of hydroxyl radicals.

$$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$$

Which statement about this reaction is correct?

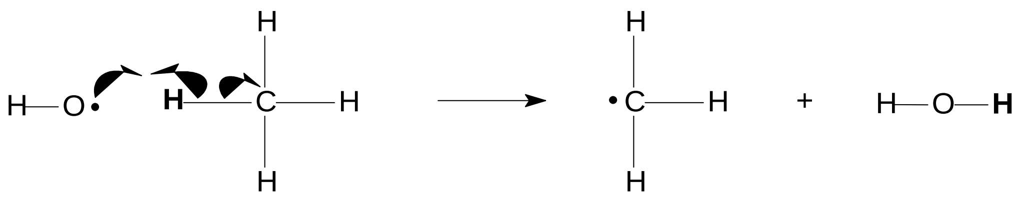
A The reaction involves homolytic fission and σ bond formation.

B The reaction involves heterolytic fission and σ bond formation.

C The reaction involves heterolytic fission and π bond formation.

D The total number of electrons in the two reacting species is 20.

Answer: A



The reaction involves the breaking of a C–H covalent bond in CH_4 with one of the bonded electrons going to each atom, forming two radicals (•CH_3 and •H) ⇒ homolytic fission
The unpaired electron in the hydrogen radical (•H) and that in the hydroxyl radical (•OH) then pair up to form a σ bond (O–H bond).

(<u>Note:</u> Heterolytic fission is the breaking of a covalent bond with both of the bonded electrons going to one of the atoms, forming a cation and an anion.)

The total number of electrons in the two reacting species is 9(•OH) + 10(CH_4) = 19. Hence, option D is incorrect.

19 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.

$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "\text{Stage1}"] & CH_3CHO \arrow[r, "\text{Stage2}", "CH_3CH_2OH"'] & CH_3CH(OH)OCH_2CH_3 \arrow[d, "\text{Stage 3}"] \\
 & & CH_3CO_2CH_2CH_3 \\
 & & \text{ethyl ethanoate}
\end{tikzcd}$$

Which process is involved at some stage in this reaction sequence?

A electrophilic addition

B nucleophilic substitution

C nucleophilic addition

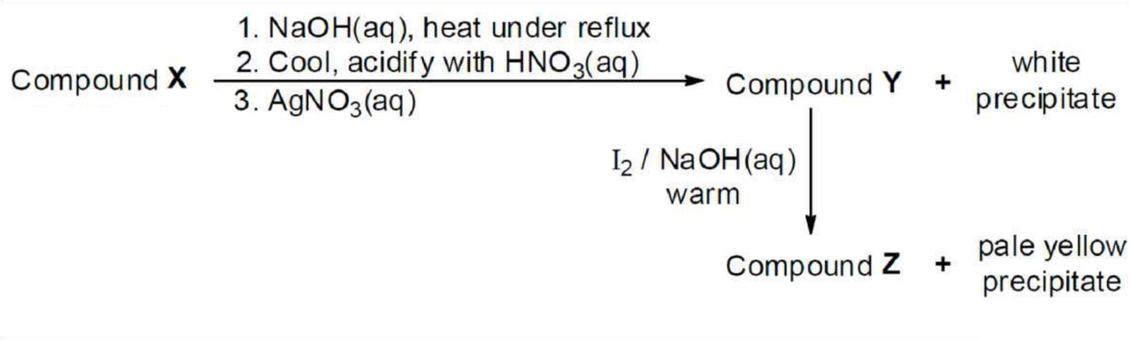
D condensation

Answer: **C**

$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "\substack{\text{oxidation}\\ \text{Stage1}}"] & CH_3CHO \arrow[r, "\substack{\text{nucleophilic addition}\\ \text{Stage2}}", "CH_3CH_2OH"'] & CH_3CH(OH)OCH_2CH_3 \arrow[dd, "\substack{\text{Stage 3}\\ \text{oxidation (C-OH}\\ \text{oxidised to C=O)}}"] \\
\text{primary alcohol} & \text{aldehyde} & \\
 & & CH_3CO_2CH_2CH_3
\end{tikzcd}$$

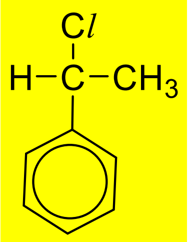
Answer is **C**. Stages 1 and 3 are oxidation whereas stage 2 is nucleophilic addition with CH_3CH_2OH acting as the nucleophile. Stage 2 is not condensation as there is no loss of any molecules.

20 Compound **X** was subjected to the following sequence of reactions.

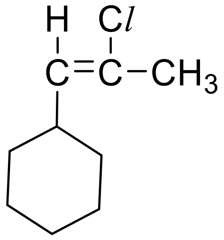


Which of the following could be the structure of **X** ?

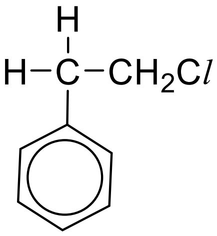
A



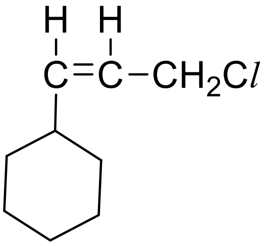
C

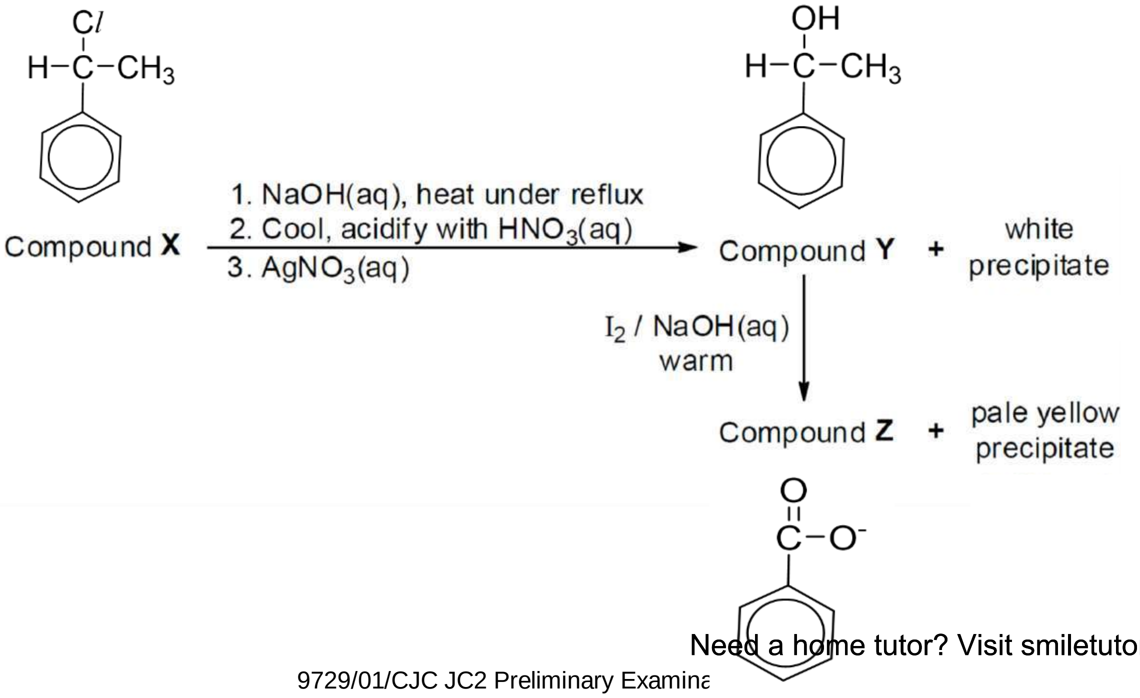


B

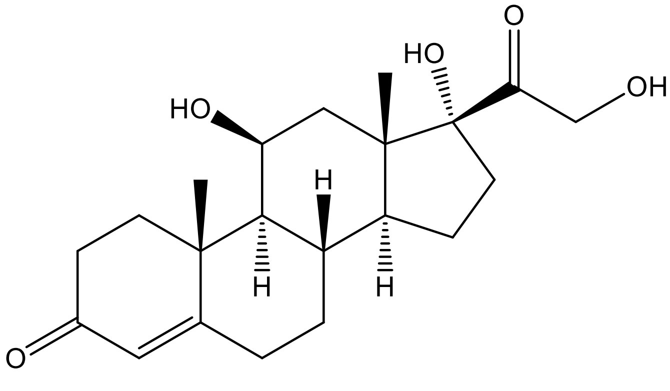


D





21 Hydrocortisone is commonly used as an active ingredient in anti-inflammatory creams and has the following structure.



hydrocortisone

Which of the following statements about hydrocortisone is correct?

A When treated with an excess of hot acidified $KMnO_4$, it forms a compound containing six carbonyl groups.

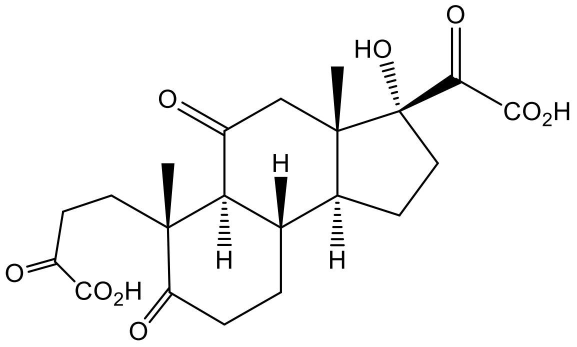
B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C When treated with cold dilute $KMnO_4$, it forms a compound containing two additional hydroxy groups.

D When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing seven hydroxy groups.

Concept: Organic reactions involving oxidation and reduction

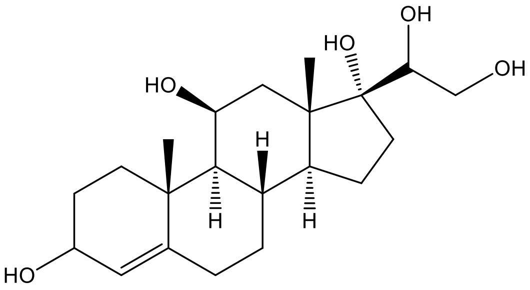
A The C=C, primary and secondary alcohols will undergo oxidation with hot acidified $KMnO_4$ to give the following compound. Only 4 carbonyl groups are formed.



B The compound does not contain $–CH_3CH(OH)$ or $–COCH_3$, hence no yellow precipitate is observed.

C When reacted with cold dilute $KMnO_4$, mild oxidation of the C=C occurs and a diol (2 alcoholic –OH groups) is formed.

D When treated with $NaBH_4$, the following compound is obtained (5 hydroxy groups are present). Note that C=C does not react with $NaBH_4$.



22 Compound **P**, $C_4H_8O_2$, has an unbranched carbon chain. An aqueous solution of **P** has an approximate pH of 3. Compound **Q**, C_3H_8O, is a secondary alcohol.

P and **Q** are reacted together in the presence of a small amount of concentrated sulfuric acid to form **R** as the major organic product.

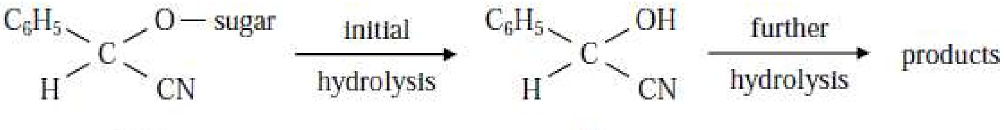
What is the structural formula of **R**?

A $(CH_3)_2CHCO_2CH_2CH_2CH_3$
B $CH_3(CH_2)_2CO_2CH(CH_3)_2$
C $CH_3(CH_2)_2CO_2(CH_2)_2CH_3$
D $(CH_3)_2CHCO_2CH(CH_3)_2$

Ans: B

- **P is butanoic acid, $CH_3(CH_2)_2CO_2H$, which forms an ester with Q (2° alcohol).**
- **ester formed contains butanoate group (∴ either B or C).**
- **since Q is a 2° alcohol, ester formed is not C.**

23 *Amygdalin* is partly responsible for the flavour of almonds. On hydrolysis, it first gives compound **X**, which is then further hydrolysed to give other products.



amygdalin

X

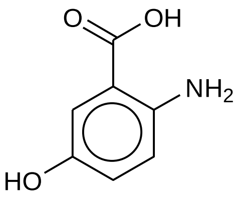
What are the other products formed after further hydrolysis?

A $C_6H_5CH(OH)CO_2H$ and NH_3
B $C_6H_5CH_2OH$ and CO_2 and NH_3
C $C_6H_5CO_2H$ and HCHO and NH_3
D C_6H_5OH and CH_3CN

Ans: A

- **The –CN group is hydrolysed to give the corresponding carboxylic acid and NH_3.**

24 5-hydroxyanthranillic acid (5-HAA) is a tryptophan metabolite that is suspected of generating oxidative stress and neuronal death.

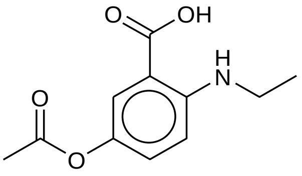


5-HAA

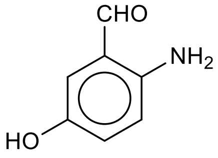
When 5-HAA was reacted with ethanoyl chloride followed by lithium aluminium hydride, $LiAlH_4$, in dry ether, the product was found to give a purple colouration with neutral $FeCl_3$(aq).

Which is a likely product?

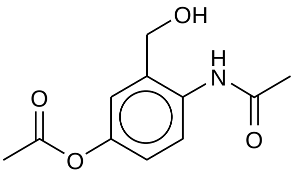
A



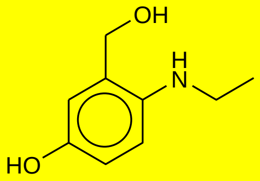
B



C

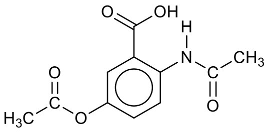


D



Concept: Condensation reactions with amines, phenols, distinguishing test for phenols

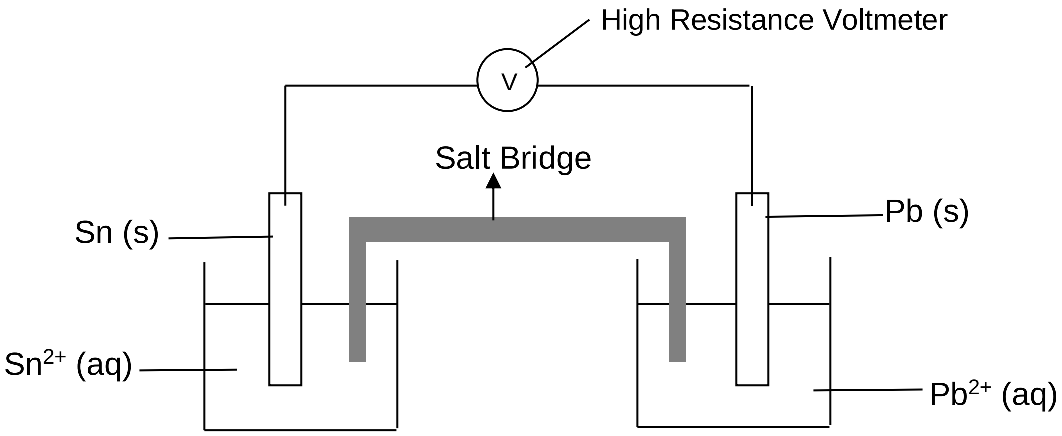
D Ethanoyl chloride undergoes condensation reaction with amines, alcohols and phenols. The intermediate produced contains an amide and an ester.



Lithium aluminium hydride can reduce carboxylic acid (to 1° alcohol), amide (to the corresponding amine) and ester (to the corresponding alcohols or phenol).

Since purple colouration with neutral $FeCl_3$(aq) is observed, this indicates that the phenol is formed from the reduction of esters.

25 Use of the *Data Booklet* is relevant to this question.



A student set up an electrochemical cell as above and made the conclusion listed below. Which of the statements are correct?

1 The reaction is feasible and Pb electrode grows larger with time.
2 Electrons flow from the Sn electrode to the Pb electrode.
3 Sn is the positive electrode while Pb is the negative electrode.
4 Concentrated KC*l* is suitable to be used as salt bridge.

A 1 and 2 only **B** 2 and 3 only **C** 1, 2 and 3 only **D** 1, 2, 3 and 4

Answer: A

Concept: Electrochemical cell setup, predicting feasibility based on $E^{\ominus}_{cell}$
Answer: A (i and ii only)

$Pb^{2+} + 2e \rightleftharpoons Pb$ -0.13 V $E^{\ominus}_{red}$

$Sn^{2+} + 2e \rightleftharpoons Sn$ -0.14 V $E^{\ominus}_{oxd}$

$E^{\ominus}_{cell} = -0.13 - (-0.14) = +0.01$

(reaction is feasible and Pb is formed)

Reduction: $Pb^{2+} + 2e \rightarrow Pb$ …………..Pb is the cathode (+)

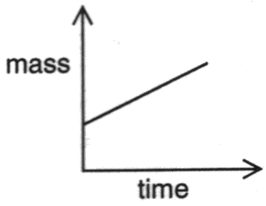
Oxidation: $Sn \rightarrow Sn^{2+} + 2e$ …………..Sn is the anode (-)

Electrons flow from anode to cathode i.e. from Sn to Pb electrode.

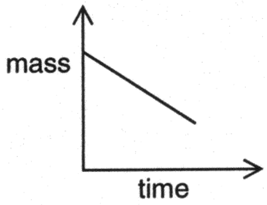
KC*l* is unsuitable to be used as salt bridge as $PbCl_2$ will be precipitated instead.

26 Electrolysis of aqueous copper(II) sulfate was carried out using copper electrodes and a steady current. Which graph shows the change in mass of the cathode with time?

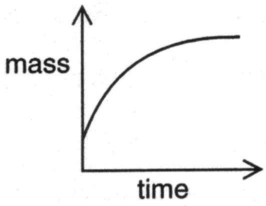
A



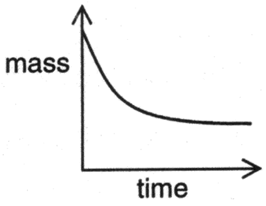
B



C



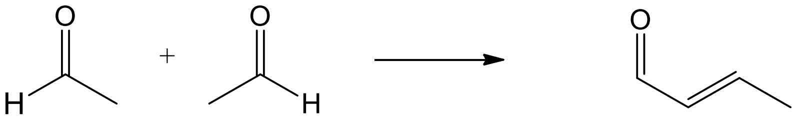
D



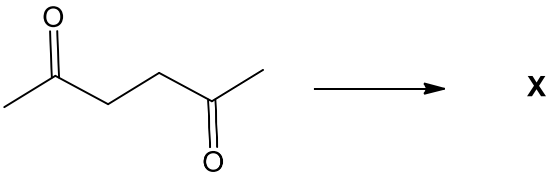
Concept: Electrolysis, mass of substance liberated during electrolysis
Answer: A

Reduction occurs at the cathode
$Cu^{2+} + 2e^{-} \rightarrow Cu$ (cathode mass increases)
Since mass α Q (Faraday's 1st Law Electrolysis)
And Q = I t
Therefore, mass α time

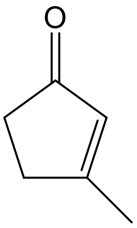
27 Aldol condensation is used in the manufacture of pharmaceuticals. One example of such a reaction is as shown below in the presence of a base.



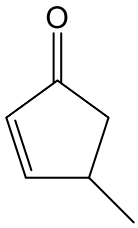
Under similar conditions, what would be the product **X**?



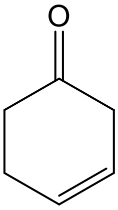
A



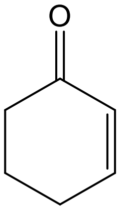
B



C

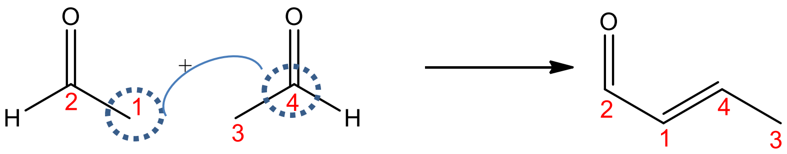


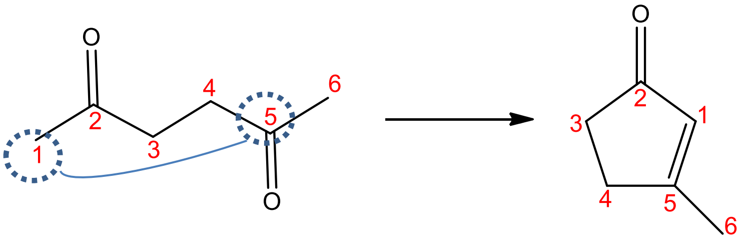
D



Concept: Pattern recognition of novel reaction; predicting structure of product

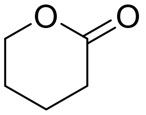
Answer: A



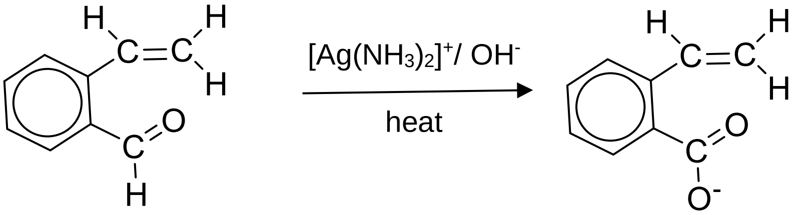


28 Which of the following reactions would yield the product shown?

1 $HO(CH_2)_4COOH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$



2



3 $CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{\text{NaBr(aq)}} CH_3CH_2CH_2Br$

A 1 only

B 2 only

C 1 and 2 only

D 1, 2 and 3 only

Option 1 is correct:
The alcohol and the carboxylic acid functional groups of $HO(CH_2)_4COOH$ undergo condensation reaction to cyclic ester molecule.

Option 2 is correct:
The aromatic aldehyde undergoes mild oxidation with alkaline $[Ag(NH_3)_2]^+$ (Tollen's reagent) to form a carboxylate ion.

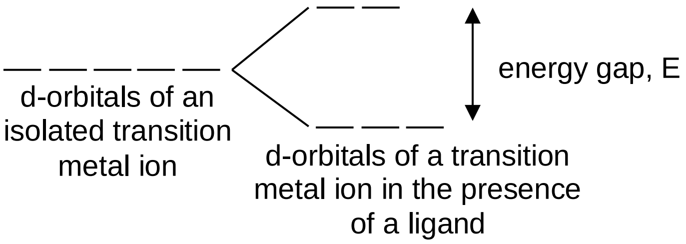
Option 3 is incorrect:
Solid NaBr is needed to react with **conc H_2SO_4** while **heating under reflux** to produce hydrogen bromide, HBr.

$$NaBr(s) + conc.\ H_2SO_4 \rightarrow \mathbf{HBr(g)} + NaHSO_4$$

HBr undergoes nucleophilic substitution reaction with $CH_3CH_2CH_2OH$ to form $CH_3CH_2CH_2Br$

29 *Use of Data Booklet is relevant to this question.*

The following diagram shows how the d–orbitals are split in an octahedral environment.



Some transition metal ions exhibit the ability to change their 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 first, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are first filled, by pairing up if necessary, before the higher energy d–orbitals are used.

Which one of the following transition metal ions is likely to be able to exhibit both spin states?

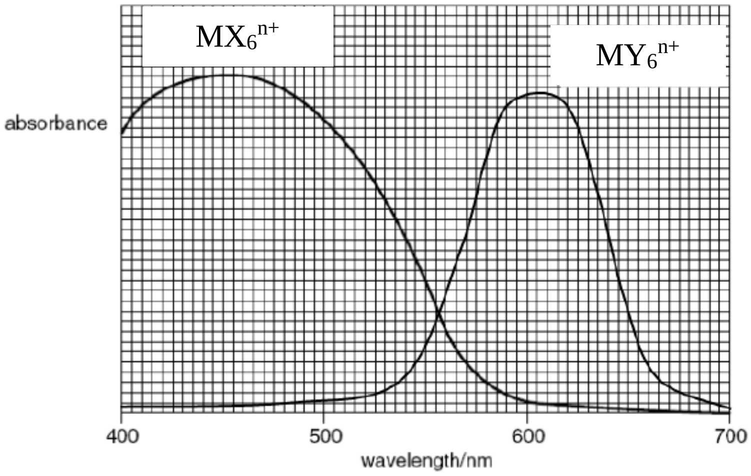
1 Fe^{3+}
2 Cu^{2+}
3 Cr^{3+}
4 Co^{3+}

A 1 only **B** 1 and 4 only **C** 1, 2 and 4 only **D** 2 and 3 only

Answer: B

Fe^{3+}: [Ar] $3d^5$--The high spin and low spin configuration are different. Hence it can show a difference between the two spin states.
Cu^{2+}: [Ar] $3d^9$ -- The high spin and low spin configuration are exactly the same. Hence it cannot show a difference between the two spin states.
Cr^{3+}: [Ar] $3d^3$ --The high spin and low spin configuration are exactly the same. Hence it cannot show a difference between the two spin states.
$Co^{3+:}$ [Ar] $3d^6$ -- The high spin and low spin configuration are different. Hence it can show a difference between the two spin states.

30 The absorbance graph below shows the visible spectra of two complexes of transition metal M, MX_6^{n+} and MY_6^{n+}.



violet	blue	green	yellow	orange	red

High energy

Low energy

What is the colour of each complex and which ligand causes a larger d-orbital splitting?

	Colour of MX_6^{n+}	**Colour of MY_6^{n+}**	**ligand which causes a larger d-orbital splitting**
A	Violet	Orange-red	X
B	Red	Green-blue	X
C	Violet	Orange-red	Y
D	Red	Green-blue	Y

Answer: B

For MX_6^{n+}, it absorbs wavelength at the 400-600 nm region, thus the colour observed will be red.

For MY_6^{n+}, it absorbs wavelength at the 550-650 nm region, thus the colour observed will be green-blue.

Shorter wavelength absorbed means a larger ΔE → Thus, X causes a larger d-orbital splitting.

Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/02

Paper 2 Structured Questions

Friday 23 August 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

WORKED SOLUTIONS

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

1 The Taj Mahal is an ivory-white marble monument in the Indian city of Agra. The famous building is becoming brown and green from environmental pollution. Acid rain accelerates the erosion of marble monuments. Marble consists primarily of calcium carbonate.

(a) You should refer to the following solubility product data to help answer the following questions.

Substance	$CaCO_3$	$CaSO_4$	$BaCO_3$	$BaSO_4$
Solubility product / $mol^2\,dm^{-6}$	1.69×10^{-8}	2.03×10^{-3}	8.28×10^{-9}	8.84×10^{-11}

The pollutant SO_2 dissolves in rainwater to form sulfuric acid. The sulfuric acid slowly converts calcium carbonate into solid calcium sulfate.

(i) Write an equation for the reaction between calcium carbonate and sulfuric acid.

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$

Or $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$ [1]

(ii) By calculating the solubilities of calcium carbonate and calcium sulfate, deduce why acid rain accelerates the erosion of marble.

Calculate the solubility of $CaCO_3$, x:

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp}(CaCO_3) = [Ca^{2+}][CO_3^{2-}]$
$1.69 \times 10^{-8} = x^2$
$x = \underline{1.30 \times 10^{-4}}\ mol\ dm^{-3}$

Calculate the solubility of $CaSO_4$, y:

$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp}(CaSO_4) = [Ca^{2+}][SO_4^{2-}]$
$2.03 \times 10^{-3} = y^2$
$y = \underline{4.51 \times 10^{-2}}\ mol\ dm^{-3}$

Acid rain contains H_2SO_4, which converts $CaCO_3$ into <u>$CaSO_4$, which is more soluble in water</u>.

[3]

The lifespan of Taj Mahal can be extended by treatment with an aqueous mixture of barium hydroxide, $Ba(OH)_2$ and urea, $CO(NH_2)_2$. As this solution soaks into the porous marble, the urea slowly hydrolyses forming ammonia and carbon dioxide. The carbon dioxide released reacts with the barium hydroxide in the mixture forming barium carbonate.

(iii) Write an equation for the reaction between barium hydroxide and carbon dioxide.

$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$ [1]

(iv) By considering the reaction between surface barium carbonate and acid rain, explain how the erosion process can be slowed down.

$BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + CO_2 + H_2O$ or $BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + H_2CO_3$

$BaCO_3$ can react with SO_2 / H_2SO_4 in the air to form a layer of barium sulfate, $BaSO_4$. $BaSO_4$ is the least soluble and hence, slow down the erosion process.

[1]

(b) Group 2 carbonates undergo decomposition in the same way at different temperatures.

(i) Predict and explain the order of decomposition temperatures for the three carbonates, $MgCO_3$, $CaCO_3$ and $BaCO_3$.

Decomposition temperature: $MgCO_3 < CaCO_3 < BaCO_3$

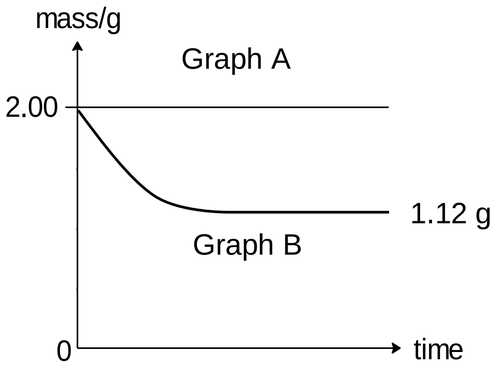
Going down Group 2, size of cation increases from Mg^{2+} to Ba^{2+}.

Hence, **charge density and polarising power of cation decreases from Mg^{2+} to Ba^{2+}.**

Therefore, **the ability of cation to distort the CO_3^{2-} electron cloud**, weakening and break the C−O bond **decreases from Mg^{2+} to Ba^{2+}**

Hence less energy is required to decompose $MgCO_3$ and the decomposition temperature is the lowest. [3]

The graph given below shows the change in mass when 2.00 g of each $CaCO_3$ and $BaCO_3$ were heated separately at a temperature T °C.



(ii) From the shapes of the graphs, identify $CaCO_3$ and $BaCO_3$ in the spaces provided below.

Graph A: **$BaCO_3$**

Graph B: **$CaCO_3$**

[1]

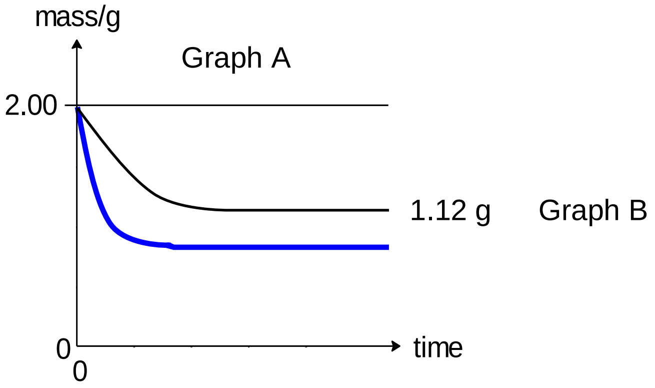
$CaCO_3 \rightarrow CaO + CO_2$

Amount of $CaCO_3$ = 2.00 / 100.1 = 2.00×10^{-2} mol

$CaCO_3 \equiv CaO$

Mass of CaO = $2.00 \times 10^{-2} \times 56.1$ = 1.12 g

(iii) Sketch on the same axes, a graph that would be obtained by heating 2.00 g of magnesium carbonate, $MgCO_3$, at the same temperature, T °C.



[1]

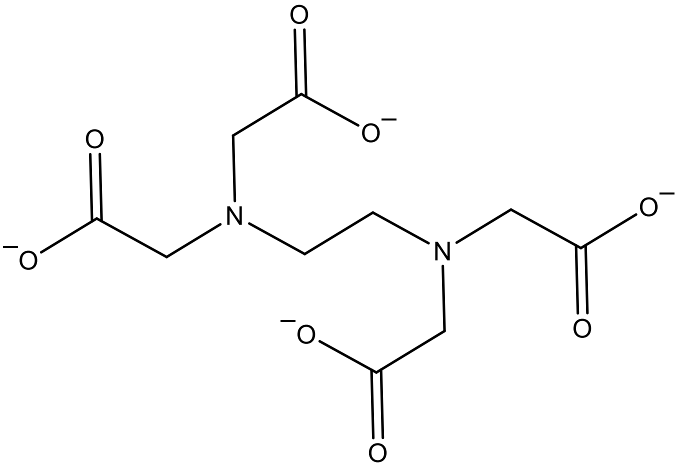
Shorter time to decompose + smaller residual mass

$CaCO_3 \rightarrow CaO + CO_2$
Amount of $CaCO_3$ = 2.00 / 100.1 = 0.0200 mol
$CaCO_3 \equiv CaO$
Mass of CaO = 0.0200 x 56.1 = 1.12 g

Amount $MgCO_3$ = 2.00 / 84.3 = 0.0237 mol
$MgCO_3 \equiv MgO$
Mass of MgO = 0.0237 x 40.3 = 0.955 g
$MgCO_3$ is less thermally stable than $CaCO_3$. Hence, $MgCO_3$ decompose completely faster.

[Total: 11]

2 Hydrogen peroxide is a common bleaching agent used to whiten wood pulp during the manufacture of paper. Transition metal ions such as $Fe^{3+}(aq)$, that are naturally present in wood pulp, would catalyse the decomposition of hydrogen peroxide, and hence reduce the bleaching efficiency. The wood pulp is therefore washed with a chelating agent such as EDTA to remove the transition metal ions before hydrogen peroxide is added.
[EDTA = $(^{-}O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^{-})_2$]



EDTA

(a) **(i)** Any $Fe^{3+}(aq)$ in the wood pulp would form a polydentate complex with EDTA. Give the formula of the complex formed. You may use the abbreviation 'EDTA' in your answer.

$[Fe(EDTA)]^{-}$ .... [1]

(ii) State the coordination number of the complex in **(a)(i)**.

6 .... [1]

(b) **(i)** H_2O and NH_3 are simple molecules. Explain why, at room temperature, H_2O is a liquid while NH_3 is a gas.

H_2O is a liquid due to the presence of more extensive intermolecular hydrogen bonding in H_2O than NH_3. On average, H_2O can form two hydrogen bonds per molecule while NH_3 can only form one hydrogen bond per molecule. More energy is thus required to overcome the hydrogen bonds in H_2O. [2]

Alternative answer:

H_2O is a liquid due to the presence of stronger intermolecular hydrogen bonding in H_2O than NH_3. O is more electronegative than N hence H−O bond is more polar than H−N bond, thus a greater dipole moment of the H−O bond that makes the intermolecular hydrogen bonding stronger. More energy is thus required to overcome the hydrogen bonds in H_2O.

(ii) While EDTA is a polydentate *ligand*, H_2O and NH_3 are examples of monodentate *ligands* in transition metal complexes. Explain what is meant by the term *ligand*.

A ligand is an ion or molecule that has at least one lone pair of electrons that can be donated into the vacant orbitals in the central metal atom or ion to form a dative covalent bond. [1]

(c) Consider the ion $[Cu(H_2O)_6]^{2+}$ present in an aqueous solution of copper(II) sulfate. When a central metal is surrounded by water ligands, it is known as an aqua complex. Addition of NH_3 to the copper(II) sulfate solution brings about a stepwise replacement of the water ligands by ammonia ligands such that the overall equation is shown below.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

The stability constant, K_{stab}, for the above equilibrium is given as:

$$K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2\,]^{2+}}{[Cu(H_2O)_6{}^{2+}][NH_3]^4} = 1 \times 10^{13}\ mol^{-4}\ dm^{12}$$

In the above expression, the square brackets imply concentrations in mol dm^{-3}. Similar to the example shown above for $[Cu(H_2O)_6]^{2+}$, complexes of iron have values of K_{stab} which are measured against the relative stability of the aqua complex of iron.

The following table lists some iron complexes together with their colours and their stability constants.

aqueous complex	colour	K_{stab}
$[Fe(SCN)(H_2O)_5]^{2+}$	deep red	1×10^2
$[FeF_6]^{3-}$	colourless	2×10^{15}
Fe^{3+}(aq) complex with edta	yellow	x
$[Fe(CN)_6]^{3-}$	pale yellow	1×10^{31}

(i) Including equations where appropriate, use the data to explain

- why an addition of KSCN(aq) to a solution of Fe^{3+}(aq) produces a deep red solution.

When KCSN is added, the deep red $[Fe(SCN)(H_2O)_5]^{2+}$ is formed as ligand exchange / displacement takes place OR as position of equilibrium shifts right as shown by the higher K_{stab} value

$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+} + H_2O$ [2]

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- what is observed when KF(aq) is added to the deep red solution mentioned above.

When KF is added, the colourless $[FeF_6]^{3-}$ is formed.

(ligand exchange takes place. $[FeF_6]^{3-}$ is more stable than $[Fe(SCN)(H_2O)_5]^{2+}$ as seen by the larger K_{stab} value.)

$[Fe(SCN)(H_2O)_5]^{2+} + 6F^- \rightleftharpoons [FeF_6]^{3-} + SCN^- + 5H_2O$ [2]

(ii) Deduce if the value of x, the K_{stab} of the Fe^{3+}(aq) complex with EDTA, is expected to be higher or lower than the K_{stab} value of $[FeF_6]^{3-}$.

Higher because chelates tend to be more stable complexes, as the polydentate ligands are able to hold the metal cation more securely. [1]

(Lecture notes)

(iii) Give the electronic configuration of Fe in $[Fe(CN)_6]^{3-}$(aq).

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ or $[Ar]\ 3d^5$ [1]

(iv) $[Fe(CN)_6]^{3-}$(aq) is a weaker oxidising agent than Fe^{3+}(aq). Explain this statement by quoting appropriate $E^\ominus$ values from the *Data Booklet*.

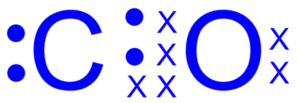
$[Fe(H_2O)_6]^{3+}(aq) + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}(aq)$ $\quad E^\ominus = +0.77$ V

$[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$ $\quad E^\ominus = +0.36$ V

The less positive E^θ value suggests that $[Fe(CN)_6]^{3-}$(aq) has a lower tendency to be reduced to $[Fe(CN)_6]^{4-}$.

(This indicates that CN^- ligand better stabilises Fe^{3+} than H_2O ligand) [2]

(d) **(i)** CO is a toxic gas. Draw the dot-and-cross structure of CO.



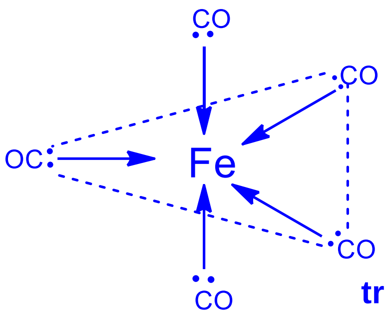
[1]

CO is also a ligand in iron pentacarbonyl, $Fe(CO)_5$. CO binds to the central metal via the carbon atom.

(ii) What is the oxidation state of iron in $Fe(CO)_5$?

0 [1]

(iii) Draw and name the shape of the complex, Fe(CO)$_5$.

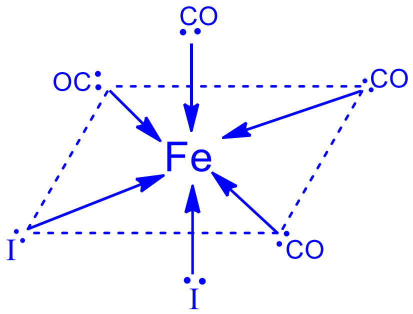


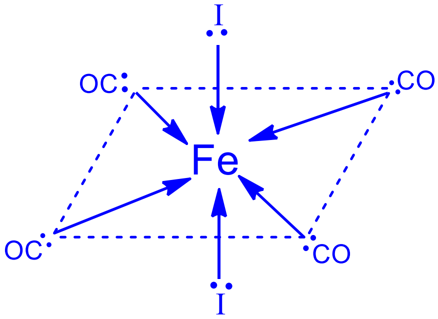
trigonal bipyramidal

[2]

(iv) When iron pentacarbonyl reacts with iodine in hexane solution, iron is oxidised and an octahedral complex, Fe(CO)$_4$I$_2$, is formed.

Isomerism can occur in Fe(CO)$_4$I$_2$ due to different positions of the ligands with respect to the central metal ion. Draw the two isomers of Fe(CO)$_4$I$_2$.





I$^-$ ligand can be either be <u>cis or trans position</u> / I$^-$ ligand can be in <u>opposite positions of the central metal or the same side</u> of the central metal.

[1]

[Total: 18]

3 **(a)** Converting harmful greenhouse gases such as CO_2 into useful chemical commodities, such as methanol, CH_3OH, is gaining traction in green chemistry as it is economically viable and environment–friendly.

A mixture containing 1.0 mol of CO_2 and 3.0 mol of H_2 is allowed to reach *dynamic equilibrium* at 200°C and 55 bar. Under these conditions, 32% CO_2 is converted to methanol, CH_3OH.

$$CO_2\,(g) + 3H_2\,(g) \rightleftharpoons CH_3OH\,(g) + H_2O\,(g)$$

Calculate the equilibrium pressure of each gas and hence calculate the K_p value, with the units for this reaction at 200°C. [4]

	CO_2 (g) +	**$3H_2$ (g)** $\rightleftharpoons$	**CH_3OH(g)** +	**H_2O(g)**
Initial amount / mol	1.0	3.0	0	0
Change / mol	$-\frac{32}{100}\times 1.0 = -0.32$	$-3(0.32) = -0.96$	+0.32	+0.32
Equilibrium amount / mol	**0.68**	**2.04**	**0.32**	**0.32**

Total amount of gaseous particles = 0.68 + 2.04 + 0.32 + 0.32 = 3.36 mol

$$P_{CH_3OH} = P_{H_2O} = \frac{0.32}{3.36}\times 55 = 5.238 \text{ bar}$$

$$P_{CO_2} = \frac{0.68}{3.36}\times 55 = 11.13 \text{ bar}$$

$$P_{H_2} = \frac{2.04}{3.36}\times 55 = 33.39 \text{ bar}$$

$$K_p = \frac{(P_{CH_3OH})\,(P_{H_2O})}{(P_{CO_2})(P_{H_2})^3}$$

$$= \frac{5.238 \times 5.238}{11.13 \times (33.39)^3} = \underline{\mathbf{6.62\ x10^{-5}\ bar^{-2}}}$$

(b) Methanol reacts with carbon monoxide with the help of catalyst to produce ethanoic acid.
Define the term *standard enthalpy change of formation* of liquid ethanoic acid, CH_3CO_2H (*l*). [1]

Standard enthalpy change of formation of liquid ethanoic acid is the **energy change** when **one mole of CH_3CO_2H (*l*)** is **formed from its elements** (i.e. C (s), H_2 (g) and O_2(g)) **at standard conditions of 298K and 1 bar**.

(c) Using the enthalpy change values given below, complete the energy cycle and calculate the standard enthalpy change of formation for ethanoic acid, CH_3CO_2H (*l*).

$\Delta H^\ominus_f$ (CH_3CH_2OH (*l*)) = – 278 kJ mol^{-1}
$\Delta H^\ominus_c$ (CH_3CH_2OH (*l*)) = – 1371 kJ mol^{-1}
$\Delta H^\ominus_c$ (CH_3CO_2H (*l*)) = – 876 kJ mol^{-1}
$\Delta H^\ominus_f$ (H_2O (*l*)) = – 286 kJ mol^{-1} [4]

Given:

$2C(s) + \tfrac{1}{2}O_2(g) + 3H_2(g) \longrightarrow CH_3CH_2OH(l)$ $\Delta H^\ominus_f$ ($CH_3CH_2OH(l)$) = –278 kJ mol^{-1}
$CH_3CH_2OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H^\ominus_c$ ($CH_3CH_2OH(l)$) = –1371 kJ mol^{-1}
$CH_3CO_2H(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ $\Delta H^\ominus_c$ ($CH_3CO_2H(l)$) = – 876 kJ mol^{-1}
$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\ominus_f$ ($H_2O(l)$) = – 286 kJ mol^{-1}

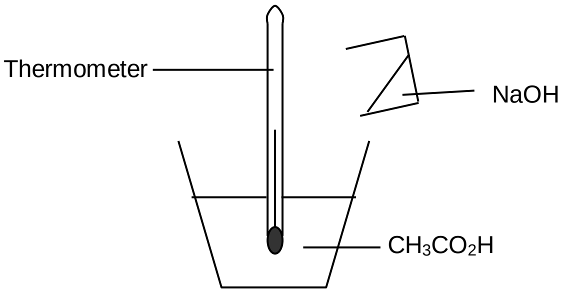
$$\begin{tikzcd}
2C(s) + \tfrac{1}{2}O_2(g) + 3H_2(g) + 3O_2(g) \arrow[r, "\Delta H^\ominus_f(CH_3CH_2OH(l))"] \arrow[d, "\Delta H^\ominus_f(CH_3COOH(l))"'] & CH_3CH_2OH(l) + 3O_2(g) \arrow[d, "\Delta H^\ominus_c(CH_3CH_2OH(l))"] \\
CH_3CO_2H(l) + H_2(g) + 2\tfrac{1}{2}O_2(g) \arrow[r, "\Delta H^\ominus_c(CH_3CO_2H(l)) + \Delta H^\ominus_f(H_2O(l))"'] & 2CO_2(g) + 3H_2O(l)
\end{tikzcd}$$

By Hess's Law,

$\Delta H^\ominus_f$ ($CH_3CO_2H(l)$) + $\Delta H^\ominus_c$ (CH_3CO_2H (*l*)) **+** $\Delta H^\ominus_f$ (H_2O (*l*)) **=** $\Delta H^\ominus_f$ (CH_3CH_2OH (*l*)) + $\Delta H^\ominus_c$ (CH_3CH_2OH (*l*))

$\Delta H^\ominus_f$ ($CH_3CO_2H(l)$) = (–278) + (–1371) – (–876) – (–286)
= – 487 kJ mol^{-1}

(d) The ethanoic acid, CH_3CO_2H can undergo neutralisation with sodium hydroxide, NaOH. A thermochemical experiment was carried out to determine the enthalpy change of neutralisation using the experimental set–up below.



The following results were obtained:

Volume of NaOH added / cm^3	50.0
Volume of CH_3CO_2H added / cm^3	50.0
Concentration of NaOH used / mol dm^{-3}	1.00
Concentration of CH_3CO_2H used / mol dm^{-3}	0.65
Initial temperature of CH_3CO_2H / °C	25.0
Highest temperature reached / °C	28.5
Specific heat capacity of water / J g^{-1} K^{-1}	4.18
Density of water / g cm^{-3}	1.00

(i) Use the results to determine the experimental enthalpy change of neutralisation. [3]

Heat absorbed by the solution, $Q = mc\Delta T = (100 \times 1.00)(4.18)(28.5 - 25.0)$
$= \mathbf{1463\ J}$

Assuming no heat loss to surroundings, i.e. 100% efficiency,

$$\Delta H_n = -\frac{Q'}{n_{H_2O}}$$

No. of moles of $CH_3CO_2H = 0.65 \times \frac{50}{1000} = 0.0325$

No. of moles of NaOH $= 1 \times \frac{50}{1000} = 0.0500$

$\Rightarrow$ CH_3CO_2H is the limiting reagent

Mole ratio: $CH_3CO_2H \equiv H_2O$

No. of moles of H_2O formed = no. of moles of CH_3CO_2H = **0.0325 mol**

$$\Delta H_n = -\frac{Q'}{n_{H_2O}} = \frac{\mathbf{-1463}}{\mathbf{0.0325}} = \underline{\mathbf{-45.0\ kJ\ mol^{-1}}}$$

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(ii) The experiment described in **(d)(i)** was repeated using HC*l* instead of CH_3CO_2H, under the same conditions. The enthalpy change of neutralisation was found to be –57.9 kJ mol^{-1}. Apart from heat loss, suggest another reason for the discrepancy between this value and that calculated in **(d)(i)**. [1]

The value calculated in (d)(i) is less exothermic, as CH_3CO_2H, as a weak acid, only *dissociates partially* in solution.

Some of the heat released from the neutralisation is used to **promote further dissociation of CH_3CO_2H molecules** (energy is used to break the O–H bonds in the remaining CH_3CO_2H molecules to form more $H^+(aq)$ for neutralisation). Hence the overall enthalpy change is less exothermic.

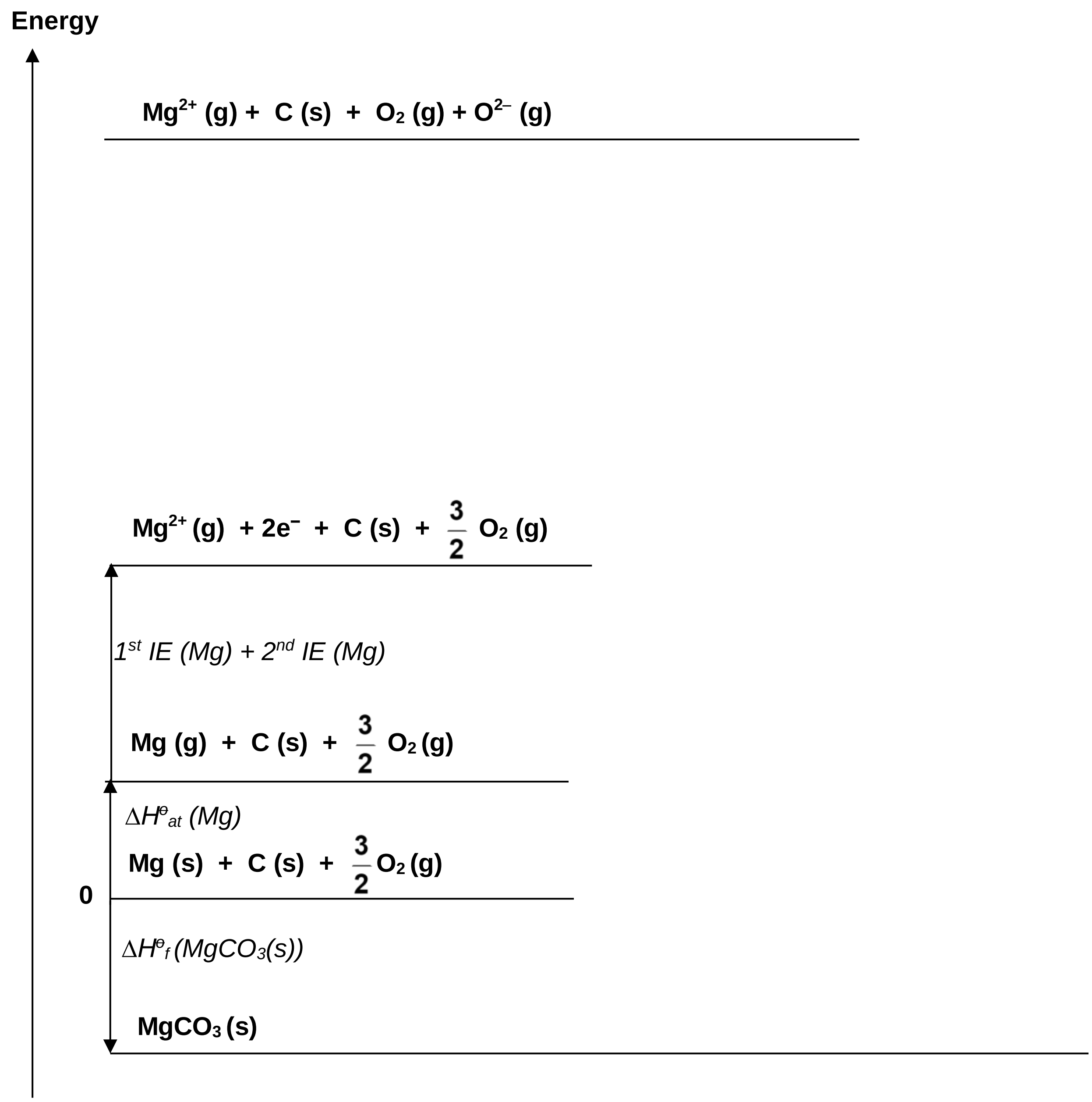
(e) Like many acids, ethanoic acid reacts with basic carbonates such as magnesium carbonate, $MgCO_3$ to release carbon dioxide.

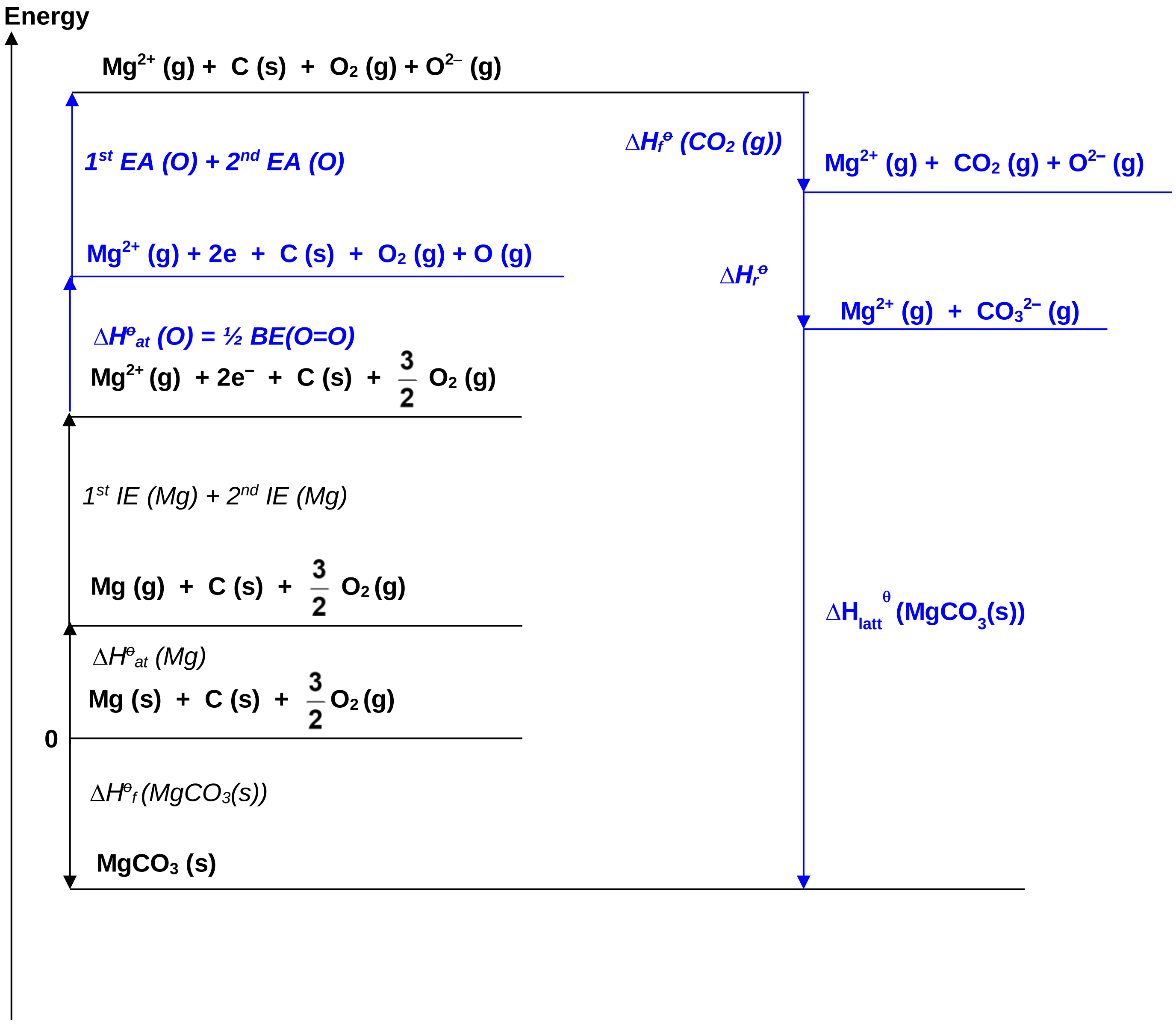
Using the following data and relevant data from the *Data Booklet*, complete the following energy level diagram and use it to determine the standard enthalpy change of formation of magnesium carbonate, $MgCO_3$.

lattice energy of $MgCO_3$ (s)	= –3208 kJ mol^{-1}
standard enthalpy change of atomisation of Mg (s)	= +147 kJ mol^{-1}
sum of 1st and 2nd electron affinity of oxygen	= +702 kJ mol^{-1}
standard enthalpy change of formation of CO_2 (g)	= –393 kJ mol^{-1}
standard enthalpy change of reaction below, $\Delta H^\ominus_r$	= –778 kJ mol^{-1}

$O^{2-}(g) + CO_2(g) \longrightarrow CO_3^{2-}(g)$

[5]


Energy
$Mg^{2+}(g) + C(s) + O_2(g) + O^{2-}(g)$
$Mg^{2+}(g) + 2e^- + C(s) + \frac{3}{2}O_2(g)$
1st IE (Mg) + 2nd IE (Mg)
$Mg(g) + C(s) + \frac{3}{2}O_2(g)$
$\Delta H^\ominus_{at}$ (Mg)
$Mg(s) + C(s) + \frac{3}{2}O_2(g)$
0
$\Delta H^\ominus_f(MgCO_3(s))$
$MgCO_3(s)$



By Hess' Law,
ΔH_f ($MgCO_3$ (s)) =
ΔH_{at}^θ(Mg) + 1st IE (Mg) + 2nd IE (Mg) + ½ BE(O=O) + 1st EA(O) + 2nd EA (O) + ΔH_f^θ(CO_2) + ΔH_r^θ + ΔH_{latt}^θ($MgCO_3$)

ΔH_f ($MgCO_3$ (s)) = +147 + 736 + 1450 + ½(496) + 702 + (–393) + (–778) + (–3208)
= $\underline{\mathbf{-1096\ kJ\ mol^{-1}}}$

[Total: 18]

4 Dragons are able to breathe fire because the parasitic bacteria that live in their lungs produce flammable gases. If a dragon exhales sharply, the gas can ignite due to the friction against the rough walls of the larynx.

(a) The gas exhaled by a dragon contains 20 mole % of hydrogen sulfide, H_2S and 15 mole % of oxygen.

The average volume of a dragon's lung is 5.1 m^3 and due to the high pressures experienced when a dragon exhales, the molar volume of the gas contained in their lungs is 15 dm^3 mol^{-1}.

(i) Calculate the total amount of gas in moles contained in a dragon's lung.

Total amount of gas = 5.1 x 10^3 / 15

= 340 mol

[1]

(ii) Assuming the temperature of a dragon's lung is 40 °C and the gaseous mixture behaves ideally, use the ideal gas equation and your answer in **(a)(i)** to calculate the internal pressure in the lung experienced by a dragon.

Let p to be the internal pressure in the dragon's lung

pV = nRT

p x 5.1 = 340 x 8.314 x (40 + 273)

p = 173 x 10^3 Pa

[1]

(iii) The actual pressure in the dragon's lung is lower than the value calculated in **(a)(ii)**. Account for the discrepancy observed.

The calculated value in part (a)(ii) is based on the assumption gases in the dragon's lung are ideal gases. However, they behave as real gases.

There are significant intermolecular forces of attractions between these gas molecules. Hence, these gases exert smaller amount of force on the walls of the lung.

The actual pressure is expected to be smaller than that calculated by ideal gas equation.

[1]

(iv) Write a balanced equation for the reaction that describes the burning of gas exhaled by the dragon. Hence, calculate the additional moles of oxygen required for the complete combustion of one exhalation of the dragon.

$H_2S + (3/2)O_2 \rightarrow SO_2 + H_2O$

Amount of H_2S gas = 340 x 0.2 = 68 mol

Amount of O_2 gas contained in the dragon's lung = 340 x 0.15

= 51 mol

$H_2S \equiv (3/2)O_2$

The amount of O_2 gas required for complete combustion

= 68 x 3/2 = 102 mol

The additional moles of O_2 required = 102 – 51 = 51 mol

[3]

(b) The parasitic bacteria in the dragon's lung produces a protein molecule **A** which speeds up the formation of flammable gases.

In the study of the structure of **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using the first enzyme:	Digestion using the second enzyme:
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

(i) Write out the amino acid sequence of the smallest polypeptide **A**.

From 2nd enzyme: gly−asp−gly−thr

From 1st enzyme: his-phe-gly asp-gly thr-phe-leu

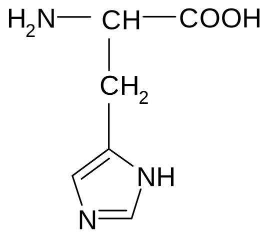
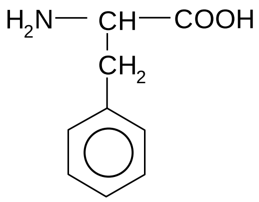
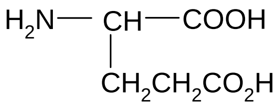
From 2nd enzyme: his-phe phe-leu-ser

From 1st enzyme: ser-pro-glu

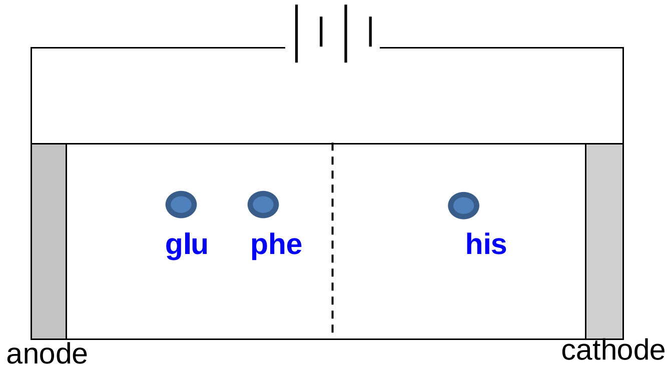
his−phe−gly−asp−gly−thr−phe−leu−ser−pro−glu

[2]

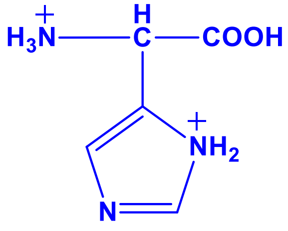
(ii) A tripeptide, his-phe-glu, obtained from **A** was further hydrolysed. The resulting solution was added to an excess of a buffer solution of pH 6.5 and placed at the centre of the plate. A potential difference was then applied across the plate.

Amino acids	 his	 phe	 $H_2N-CH(CH_2CH_2CO_2H)-COOH$ glu
Isoelectric point	7.58	5.48	3.10

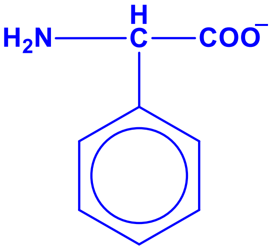
Indicate the relative positions of the amino acids on the diagram below.



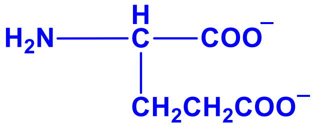
At pH 6.5,



his



phe



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

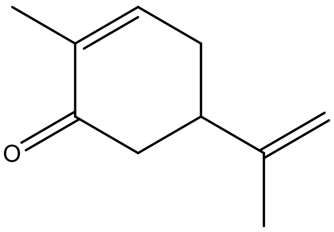
glu

[2]

Positively charged species will migrate to the cathode (negative electrode)
Negatively charged species will migrate to the anode (positive electrode)

[Total: 10]

5 Carvone is a chemical found naturally in essential oils extracted from the seeds of two common herbs, spearmint and dill.



Carvone

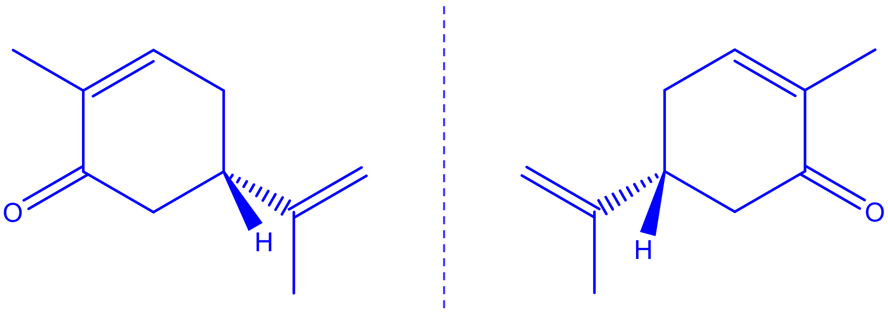
Two stereoisomers of carvone are responsible for the distinctively different flavor and smell of the two herbs.

(a) State the type of stereoisomerism carvone can exhibit.

Optical isomerism / enantiomerism

.... [1]

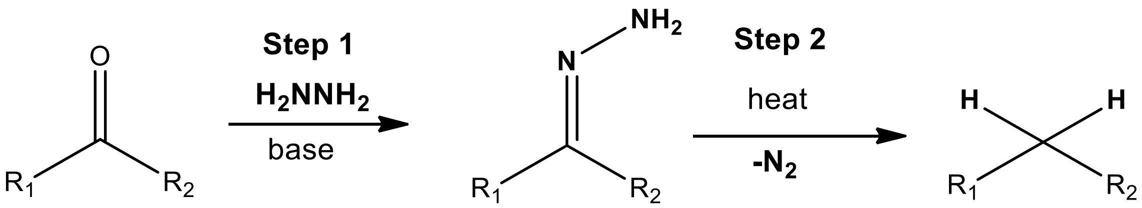
(b) Draw the two stereoisomers of carvone.



[1]

(c) Carvone undergoes reduction with different reagents and conditions to form different products. One notable reduction method is the ***Wolff-Kishner reduction*** whereby the ketone functional group in carvone reacts with hydrazine, N_2H_4, in the presence of a strong base to form limonene, $C_{10}H_{16}$, a major component in the oil of citrus fruit peels.

The general reaction sequence of the ***Wolff-Kishner reduction*** is shown below.

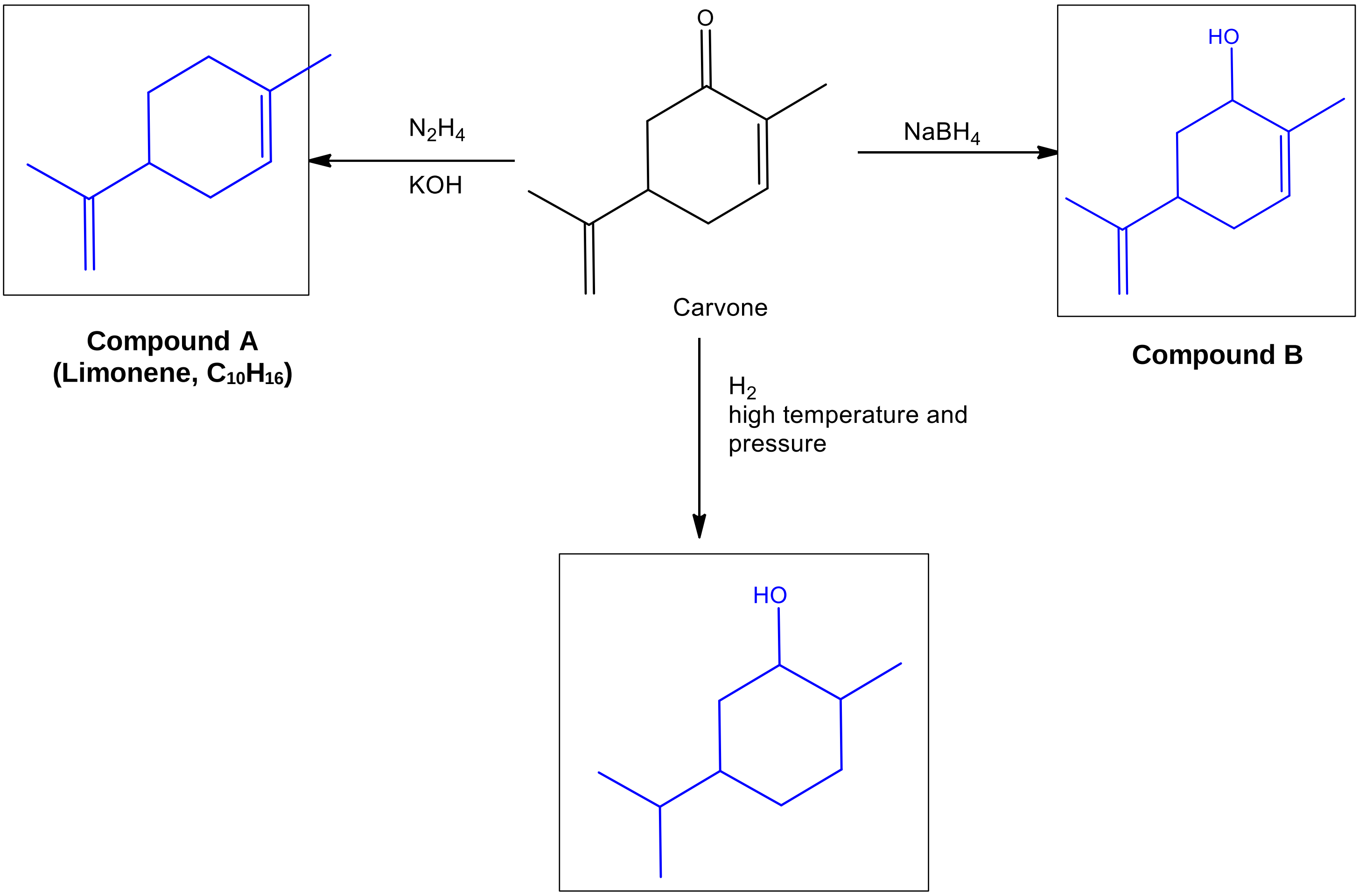


The ***Wolff-Kishner reduction*** is unsuitable for base-sensitive reactants.

(i) Suggest the type of reaction in **Step 1**.

Condensation / Addition-Elimination ....[1]

(ii) The following reaction scheme shows the various reduction reactions of carvone. Suggest the structural formulae of compounds **A**, **B** and **C** in the boxes below.



Compound A
(Limonene, $C_{10}H_{16}$)

Compound B

Compound C [3]

(iii) Suggest a simple chemical test that could distinguish between carvone and limonene. State the observations expected for each compound and the products (if any) that gives the observations.

Reagents and conditions: 2, 4-dinitrophenylhydrazine, heat ....

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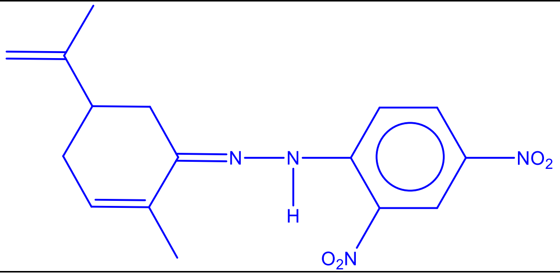
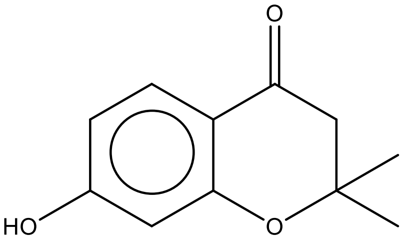
	Observations:	Products:
Carvone	**Orange ppt formed**	
Limonene	**No orange ppt formed**	**N.A.**

[3]

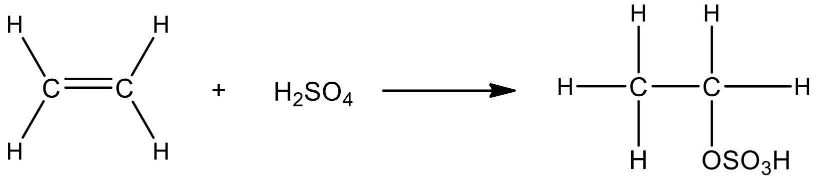
(iv) Suggest a reason why the following compound is unlikely to undergo the ***Wolff-Kishner reduction*** despite the presence of a ketone functional group.



Presence of <u>acidic</u> phenolic group which would react with the base used in step 1 [1]

[Total: 10]

6 When fuming sulfuric acid reacts with alkenes, electrophilic addition occurs to form alkyl hydrogensulfates. This is exemplified by the reaction involving ethene below.



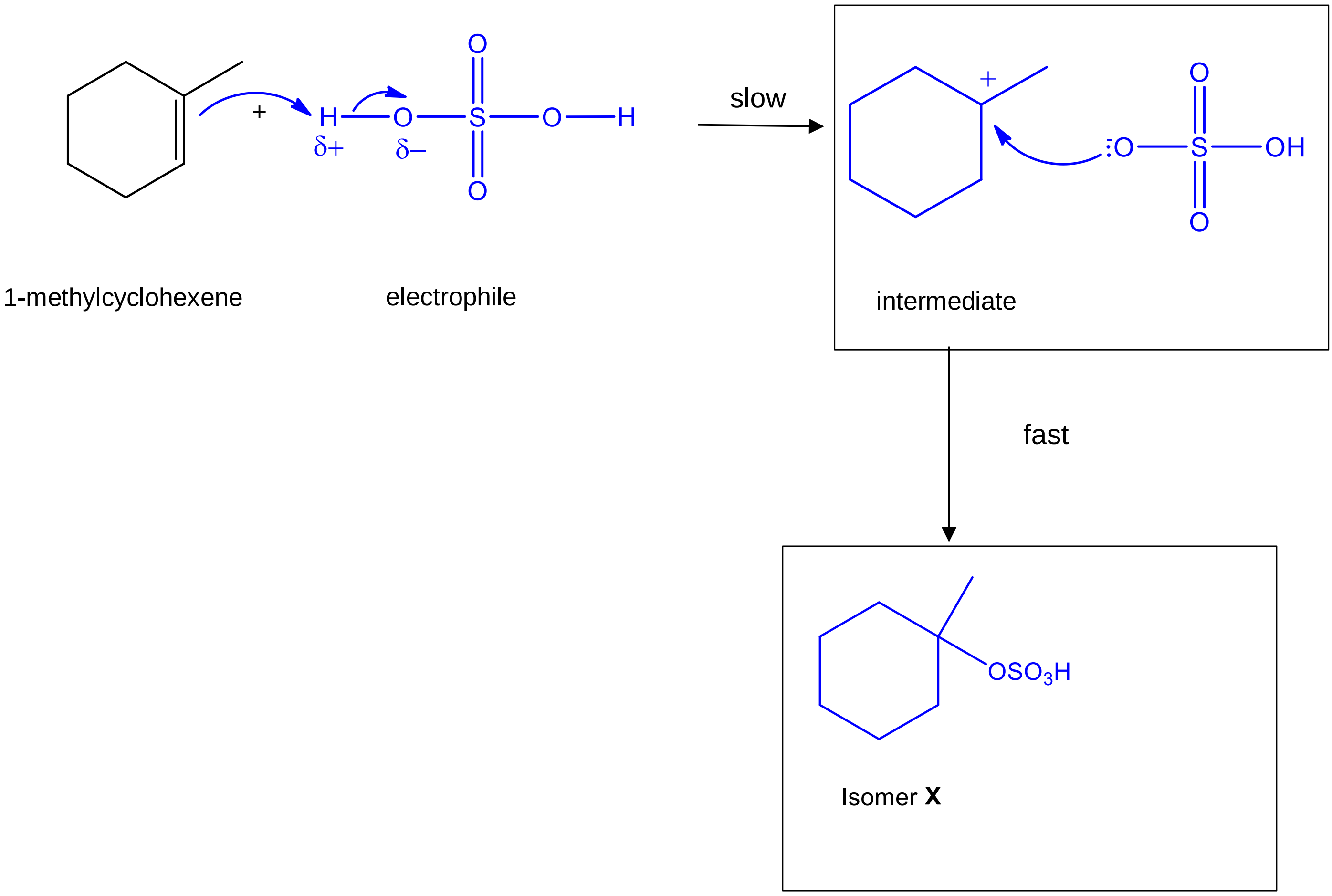
When 1-methylcyclohexene reacts with fuming sulfuric acid, a mixture of two isomers **X** and **Y** are formed, with isomer **X** being the major product.

(a) Name and define the type of isomerism exhibited by isomers **X** and **Y**.

Positional/Constitutional isomerism

Constitutional isomers have the same molecular formula but different structural formula. In addition, positional isomers have the same substituents / functional groups, but at different positions (-OSO_3H). [2]

(b) Complete the following to suggest a mechanism for the reaction between 1-methylcyclohexene and sulfuric acid to form **X**. Show the displayed structure of H_2SO_4, the structure of the intermediate, the movement of the electron pairs and the structure of **X**. [4]



(c) Explain why benzene does not undergo addition reactions with fuming sulfuric acid.

Benzene contains a ring of delocalised π electrons which leads to extra stability (resonance stability),
hence to maintain the stability of benzene, it would not undergo addition reaction which will lead to breaking the ring of delocalised π electrons and giving less stable products due to loss of resonance stability. [2]

[Total: 8]

Catholic Junior College

JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/03

Paper 3 Free Response

Friday 30 August 2019

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

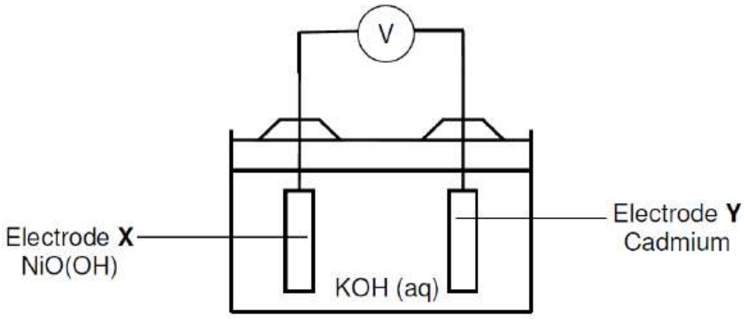
WORKED SOLUTIONS

Section A

Answer **all** the questions in this section.

1 **(a)** Chemical energy can be directly converted to electrical energy in batteries and fuel cells. Fuel cells require a continuous source of fuel and oxygen to sustain the chemical reaction, whereas in batteries, the chemical energy is usually derived from reactions of metals or metal oxides present in the battery.

The nickel-cadmium (NiCd) battery is a rechargeable battery used in many devices such as handphones and laptops. A simplified diagram of the NiCd electrochemical cell is as shown:



Electrode **X** is made of a solid nickel compound, NiO(OH), and electrode **Y** is made of solid cadmium. The electrolyte is aqueous potassium hydroxide. During discharge, $Ni(OH)_2$(s) and $Cd(OH)_2$(s) are formed at the respective electrodes.

(i) Construct the half-equations at the electrodes of this alkaline NiCd electrochemical cell. Hence, give the balanced overall equation for the reaction that occurs during discharge. [2]

Electrode X:
$NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Electrode Y:
$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

Overall equation:
$Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

(ii) Write a cell representation for the NiCd electrochemical cell, indicating clearly the direction of electron flow in the external circuit. [2]

e^- flow

Cd(s), $Cd(OH)_2$(s) // NiO(OH)(s), $Ni(OH)_2$(s)

(iii) NiCd batteries can be recharged by applying a current across the two electrodes. How long would it take to recharge a NiCd battery at a current of 2.0 A, if 5.6 g of cadmium was converted to $Cd(OH)_2$? [2]

Moles of Cd converted = 5.6 / 112.4 = 0.0498 mol
Moles of electrons required = 0.0498 x 2 = 0.0996 mol

Total charge required = 0.0996 x 96500 = 9615 C
Time required = 9615 / 2.0 = 4807 s (or 80.1 min)

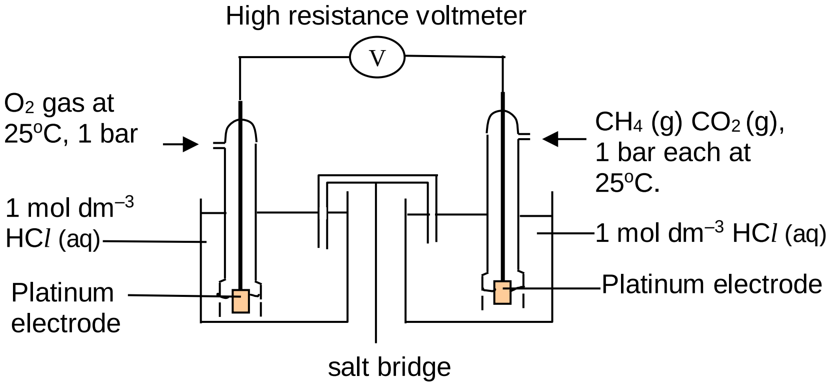
(b) Methane gas, CH_4, is the simplest alkane used to power a fuel cell. The methane-oxygen fuel cell has recently been shown to be an efficient source of electrical energy. In the simplest version of this fuel cell, an acid is used as the electrolyte and methane undergoes reaction at one of the electrodes while oxygen undergoes reaction at the other electrode.

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O \qquad E^\theta = +0.17\ V$$
$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

(i) By using the half–equations above and relevant data from the *Data Booklet,* calculate the E^θ_{cell} of this fuel cell. [1]

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^\theta = +1.23\ V$
$E^\theta_{cell} = 1.23 – (0.17) = +1.06\ V$

(ii) Draw a fully labelled diagram of the electrochemical cell you could use to measure this E^θ_{cell}. [3]



(c) An alternative fuel used in fuel cells is dimethyl oxalate, $(CH_3)_2C_2O_4$, which is obtained by the esterification of ethanedioic acid, $H_2C_2O_4$, with methanol, CH_3OH. The ethanedioate ion, $C_2O_4^{2-}$, is commonly found in ionic salts such as **X**C_2O_4. When these ethanedioate salts, **X**C_2O_4, are oxidised by acidified potassium manganate(VII), $KMnO_4$, both the **X**$^{2+}$ and $C_2O_4^{2-}$ ions are oxidised. Carbon dioxide gas is formed as one of the products in the reaction.

(i) Write a balanced equation for the reaction between MnO_4^- and $C_2O_4^{2-}$ under acidic conditions. [1]

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(ii) 25.0 cm^3 of 0.1 mol dm^{-3} **X**C_2O_4 solution was titrated with 0.1 mol dm^{-3} of acidified $KMnO_4$. Determine the volume of $KMnO_4$ needed to oxidise $C_2O_4^{2-}$ only. [2]

Moles of $C_2O_4^{2-}$ ions = 0.025 x 0.1 = 0.0025 mol
Since $C_2O_4^{2-}$: MnO_4^- is 5 : 2,
Moles of MnO_4^- needed to oxidise $C_2O_4^{2-}$ = 0.0025 x 2/5 = 0.001 mol
Volume of MnO_4^- needed = (0.001 / 0.1) x 1000 = 10 cm^3

(iii) Given that 15.00 cm^3 of acidified $KMnO_4$ was required to completely oxidise 25.0 cm^3 of 0.1 mol dm^{-3} **X**C_2O_4 solution, and using your answer in **(c)(ii)**, find the oxidation state of **X** in the product. [3]

Volume of MnO_4^- ions needed to oxidise X^{2+} ions = 15 – 10 = 5 cm^3

Moles of MnO_4^- ions = (5 / 1000) x 0.1 = 0.0005 mol

From Data Booklet, $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$

Moles of electrons gained by MnO_4^- = 0.0005 x 5 = 0.0025 mol

Moles of **X**$^{2+}$ions = 0.025 x 0.1 = 0.0025 mol

Therefore, mole ratio of **X**$^{2+}$: e = 1 : 1

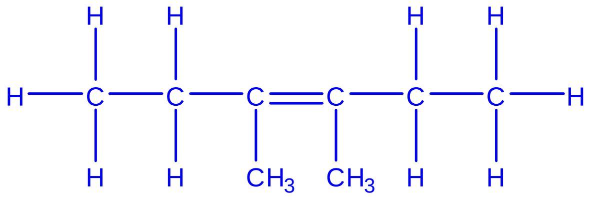
Since 1 mole of X^{2+} loses 1 mole of electrons,

Oxidation state of **X** in the product = +3

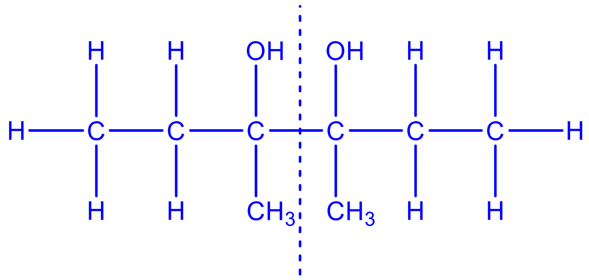
(d) Potassium manganate(VII), $KMnO_4$, can be used to oxidise alkenes in different ways. Alkene **P**, C_8H_{16}, reacts with hot acidified $KMnO_4$ to form one organic product only, which gives a yellow precipitate with hot aqueous alkaline iodine. **P** also reacts with cold alkaline $KMnO_4$ to form an optically inactive diol, **Q**. When **P** is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including **R**, $C_8H_{14}Cl_2$, which does not have any chiral carbon. When **R** is reacted with ethanolic NaOH, compound **S**, C_8H_{12}, is the only product formed. **S** produces two compounds, CO_2 and CH_3COCO_2H in equimolar amounts when it is oxidised by hot acidified $KMnO_4$.

(i) Suggest the structural formulae for compounds **P**, **Q**, **R** and **S**. [4]

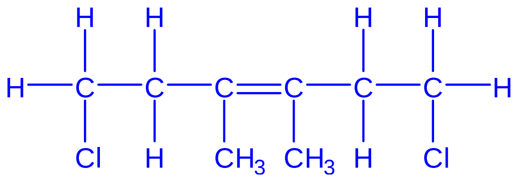
P :



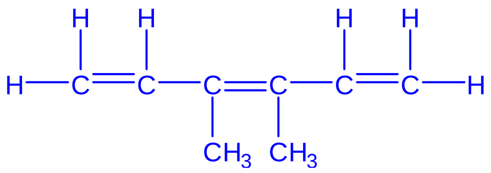
Q :



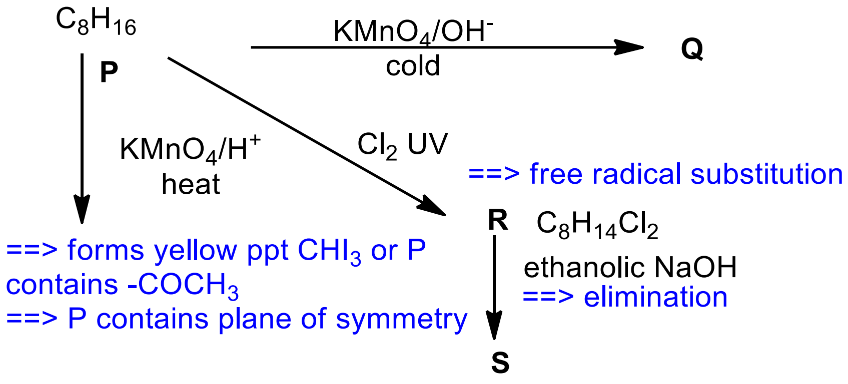
R :



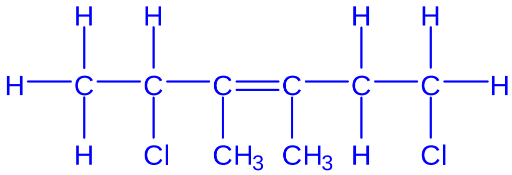
S :



$CH_2=CH-C(CH_3)=C(CH_3)-CH=CH_2$

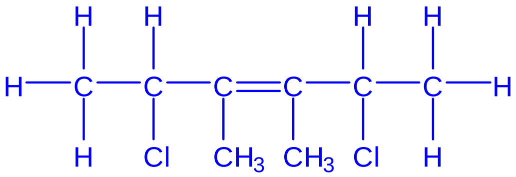


(ii) Draw the structural formula of an isomer of **R**, $C_8H_{14}Cl_2$, that could give **S** on dehydrochlorination. [1]



$CH_3-CHCl-C(CH_3)=C(CH_3)-CH_2-CH_2Cl$

or



$CH_3-CHCl-C(CH_3)=C(CH_3)-CHCl-CH_3$

(iii) Suggest, with a reason, the number of stereoisomers for compound **S**. [1]

There is 1 alkene double bond that is capable of exhibiting cis-trans isomerism as there are 2 different groups attached to each C atom across C=C double bond; no of stereoisomers= **2**.

[Total:22]

2 With the prospect that fossil fuels will become increasingly scarce in the future, many compounds are being considered for use in internal combustion engines. One of these is DME or dimethyl ether, CH_3OCH_3. DME is a gas which can be synthesised from methanol. Methanol can be obtained from biomass, such as plant waste from agriculture.

(a) Write a balanced equation to define the term *standard enthalpy change of combustion*, $\Delta H_c^\ominus$, of DME. [1]

$CH_3OCH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

(b) A 0.31 g sample of DME was completely burnt in air. The heat produced raised the temperature of 200 g of water by 11.7 °C. Assume no heat losses occurred during this experiment.

(i) Use relevant data from the *Data Booklet* to calculate the amount of heat released in this experiment. [1]

heat released $= mc\,\Delta T$

$= 200 \times 4.18 \times 11.7$

$= 9781$ J (or 9.78 kJ)

(ii) Hence calculate the enthalpy change of combustion, $\Delta H_c^\ominus$, of DME. [1]

M_r of DME, $CH_3OCH_3 = 2(12.0) + 6(1.0) + 16.0 = 46.0$

0.31 g of DME produce 9.78 kJ

$\therefore\ \Delta H_c^\ominus$ of DME $= -\frac{9.78 \times 46.0}{0.31} = -1451$ kJ mol^{-1}

(c) **(i)** Use the bond energies given in the *Data Booklet* to calculate another value for the *enthalpy change of combustion*, $\Delta H_c^\ominus$, of DME. [2]

$CH_3OCH_3(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Bonds broken	(ΔH_1/ kJ mol^{-1})	Bonds formed	(ΔH_2/ kJ mol^{-1})
2 C–O	2(+360)	4 C=O	4(–805)
6 C–H	6(+410)	6 O–H	6(–460)
3 O=O	3(+496)		

$\therefore\ \Delta H_c^\ominus = 2(+360) + 6(+410) + 3(+496) + 4(-805) + 6(-460)$

$= -1312$ kJ mol^{-1}

(ii) Suggest a reason for the discrepancy, if any, between this $\Delta H_c^\ominus$ value and that calculated in **(b)(ii)**. [1]

This $\Delta H_c^\ominus$ value is less exothermic than that calculated in (b)(ii) because bond energies given in Data Booklet are average values and do not relate to any specific compound.

(d) DME may be synthesised from methanol according to the following equation.

$$2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l) \qquad \Delta H^{\ominus} = +7.10 \text{ kJ mol}^{-1}$$

(i) The entropy change for this reaction, $\Delta S^{\ominus}$, is +83.62 J K^{-1} mol^{-1}.
Explain the significance of the sign of $\Delta S^{\ominus}$. [1]

$\Delta S^{\ominus}$ is positive, which shows that the reaction proceeds with an increase in disorderliness due to the increase in number of moles of gas from 0 mol to 1 mol.

(ii) Use the value of $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ given above to calculate a value for the standard Gibbs Free energy, $\Delta G^{\ominus}$, for this reaction. [1]

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus} \\ &= +7.10 - (298)(+83.62 \times 10^{-3}) \\ &= -17.82 \text{ kJ mol}^{-1}\end{aligned}$$

(iii) By considering the effect of temperature on the spontaneity of this reaction, suggest and explain whether high or low temperature should be used to produce DME. [2]

As temperature decreases, the term $(-T\Delta S^{\ominus})$ becomes less negative and so, $\Delta G^{\ominus}$ will become less negative; and the reaction is less spontaneous.

OR

As temperature increases, the term $(-T\Delta S^{\ominus})$ becomes more negative and so, $\Delta G^{\ominus}$ will become more negative; and the reaction is more spontaneous.

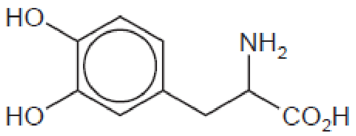
- To ensure that the reaction remains spontaneous ($\Delta G^{\ominus} < 0$), the production of DME should be carried out at high temperature.

(iv) Explain, in molecular terms, how the rate of the above reaction is affected by changing the concentration of methanol. [2]

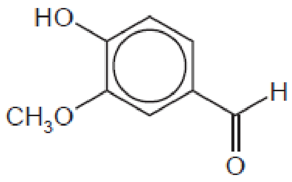
- rate of reaction increases when concentration of methanol is increased due to increase in frequency of collisions between methanol molecules which are now closer together, and this increases the number of successful/effective collisions.

OR rate of reaction decreases when concentration of methanol is decreased due to decrease in frequency of collisions between methanol molecules which are now further apart, and this reduces the number of successful collisions.

(e) Methanol is also a reagent to synthesise vanillin. Vanillin is an important raw material for the production of L-DOPA used in the treatment of Parkinson's disease.



L-DOPA



vanillin

A student carried out some reactions with samples of L-DOPA and vanillin using reagents **X**, **Y** and **Z**.

- Reagent **X** reacted with L-DOPA **and** with vanillin.
- Reagent **Y** reacted with L-DOPA but **not** with vanillin.
- Reagent **Z** reacted with vanillin but **not** with L-DOPA.

Assume that the $CH_3O–$ group in vanillin is inert and does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products formed in each case. [7]

- Reagent X: for <u>phenol</u> - any one of aq. Br_2; NaOH, Na, $RCOCl$; OR

  $LiAlH_4$ for reduction of carboxylic acid & aldehyde

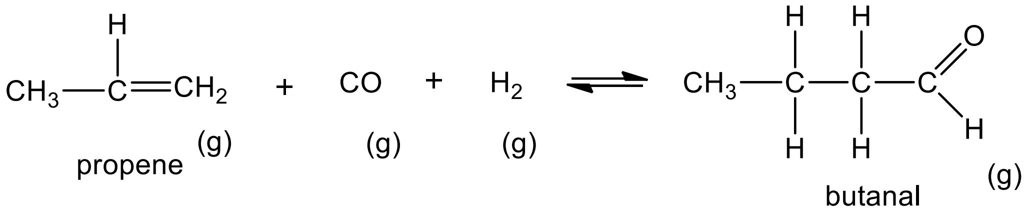
- Reagent Y: for <u>carboxylic acid</u> - any one of Na_2CO_3; $NaHCO_3$, $SOCl_2$, PCl_5, ROH + H_2SO_4; OR

  for <u>amines</u> - any one of HCl, CH_3Cl

- Reagent Z: for <u>aldehyde</u> - any one of Tollens' reagent, 2,4-dinitrophenylhydrazine; acidified $K_2Cr_2O_7$, HCN + trace NaCN/NaOH, $NaBH_4$

[Total: 19]

3 **(a)** The hydroformylation reaction is an industrial process for the production of aldehydes from alkenes. For example, butanal can be synthesised from propene, C_3H_6, as follows:



(i) Write an expression for K_p of the reaction, including units. [2]

$$K_p = \frac{p_{CH_3CH_2CH_2CHO}}{(p_{CH_3CH=CH_2})(p_{CO})(p_{H_2})} \text{ atm}^{-2} \text{ or Pa}^{-2}$$

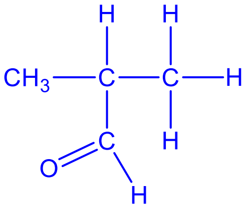
(ii) Given that the magnitude of K_p for the above reaction is 775, deduce what the K_p value indicates about the position of equilibrium. Hence, state the sign of $\Delta G^{\ominus}$ for the reaction. [2]

As K_p is large, and thus position of equilibrium lies very much to the right.
$\Delta G^{\ominus}$ is negative.

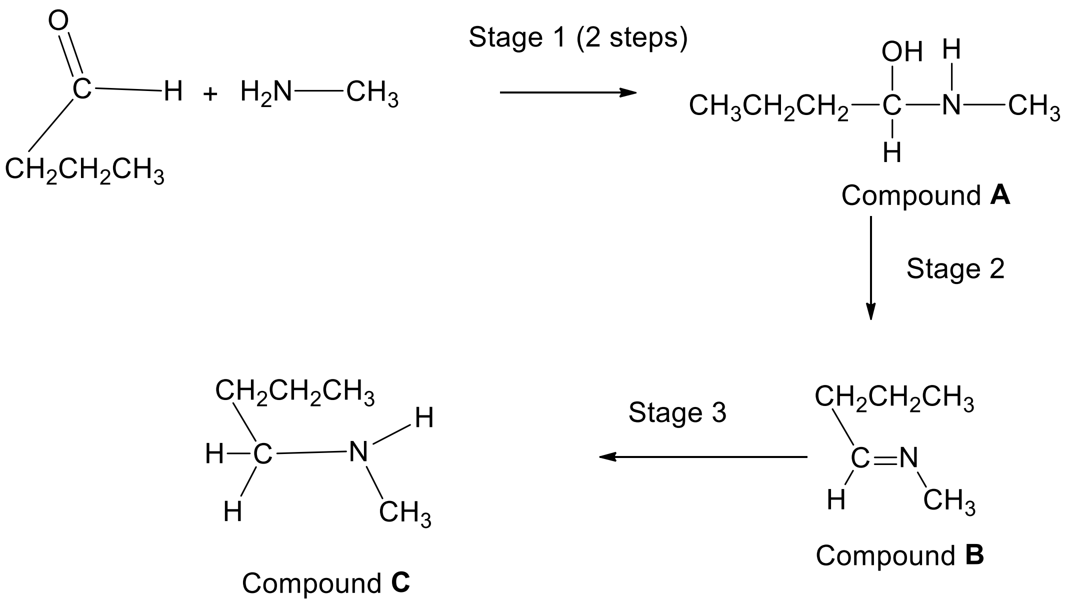
(iii) Given that the above reaction is exothermic, suggest, with a reason, the effect of an increased temperature on the amount of butanal formed at equilibrium. [1]

When the temperature is increased, the position of equilibrium shifts to the left as the reverse reaction is endothermic and absorbs heat. Thus, the amount of butanal at equilibrium decreases.

(iv) The mechanism of hydroformylation of propene resembles the electrophilic addition of alkenes and can result in the formation of two isomeric products. Apart from butanal, suggest the structure of the other isomer that can be formed. [1]



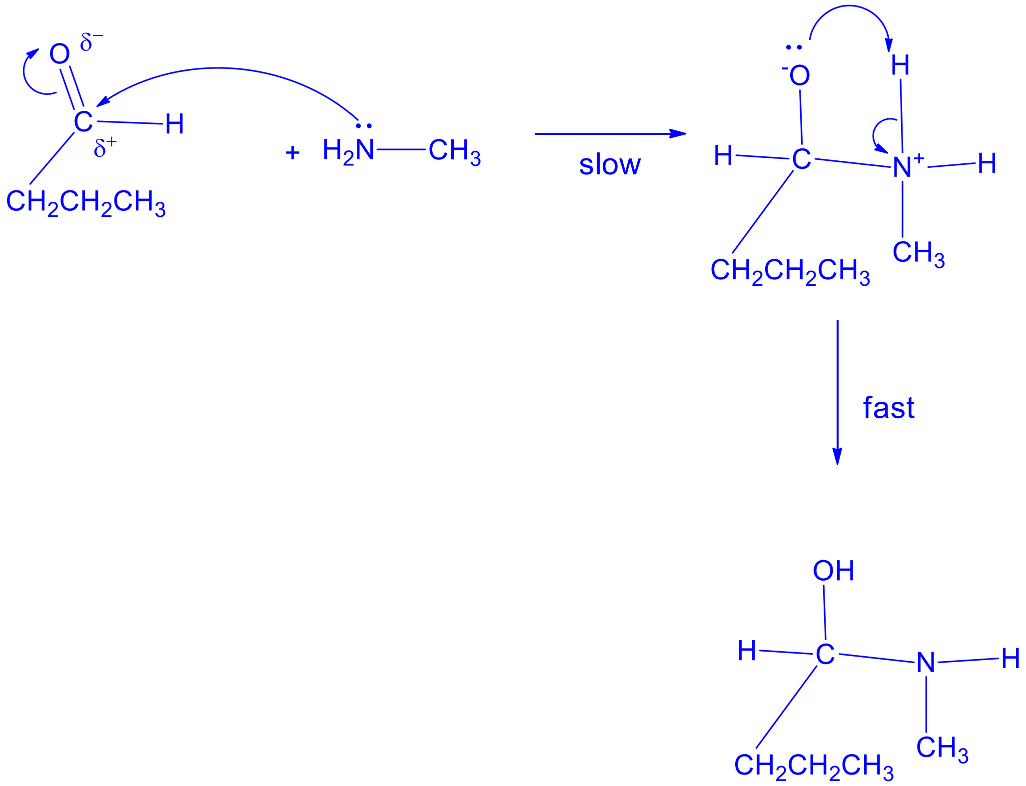
(b) In the Leuckart-Wallach reaction, a carbonyl compound reacts with a primary amine to form a secondary amine.



(i) Stage 1 occurs in 2 steps. The first step involves a nucleophilic attack while in the second step, a proton transfer occurs within the intermediate to form the alcohol group.

Name and outline the 2-step mechanism for Stage 1, to form Compound **A**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

Nucleophilic Addition



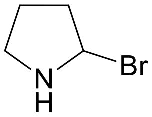
(ii) Compound **B** undergoes reduction in Stage 3. Describe the change in oxidation state of carbon which occurs in this stage. [1]

There is a decrease in oxidation number of the C (of the C=N) from +1 to -1

(iii) Unlike primary amines, amides cannot be used in the Leuckart-Wallach reaction. Explain why this is so. [1]

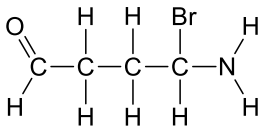
In amides, the lone pair of electrons on the nitrogen atom can delocalise into the π electron cloud of the adjacent C=O bond/electron-withdrawing C=O group. Hence, the lone pair of electrons is not available for donation/less available to accept a proton and unable to act as a nucleophile in Stage 1.

(iv) 2-bromopyrrolidine, a cyclic amine, 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]



(v) State and explain the relative basicities of 2-bromopyrrolidine and compound **C**. [2]

2-bromopyrrolidine is a weaker base than compound C. 2-bromopyrrolidine has an electron-withdrawing Br atom, and thus the lone pair of electrons on nitrogen is less available for donation to a proton .

(c) Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds are given in the table below.

Compound	Structure	Dipole moment	Boiling point / °C
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	x	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS. [2]

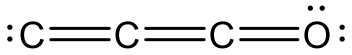
Both CS_2 and COS have simple molecular structures. CS_2 has a larger number of electrons (or larger electron cloud) than COS. More energy is required to overcome the stronger instantaneous dipole-induced dipole attractions between CS_2 molecules than the permanent dipole-permanent dipole attractions between COS molecules. Hence, CS_2 has a higher boiling point.

(ii) Predict a value for the dipole moment of COSe, x, and explain. [1]

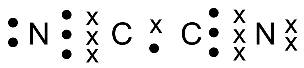
0.73 (> 0.71)

C=S bond is more polar than C=Se (since S is more electronegative than Se). There is smaller difference in the dipole moment of C=O and C=S as compared to that between C=O and C=Se.

(iii) Aside from the common oxides, carbon forms a series of straight-chained reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space. Suggest a displayed structure of tricarbon monoxide. Indicate clearly any lone pairs of electrons present in your structure. [1]



(iv) Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.
Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms. [1]



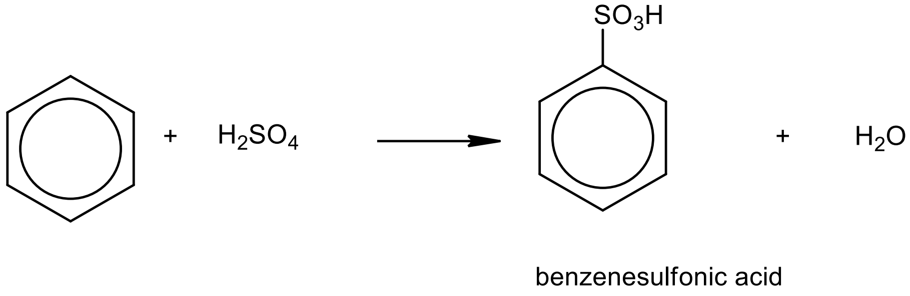
[Total: 19]

Section B

Answer **one** question from this section.

4 **(a)** Benzene is a widely used starting organic compound to synthesize other chemicals, such as benzenesulfonic acid and 2-methylphenol.

Benzenesulfonic acid can be produced by heating benzene under reflux with concentrated sulfuric acid for several hours. This process is similar to the nitration of benzene.

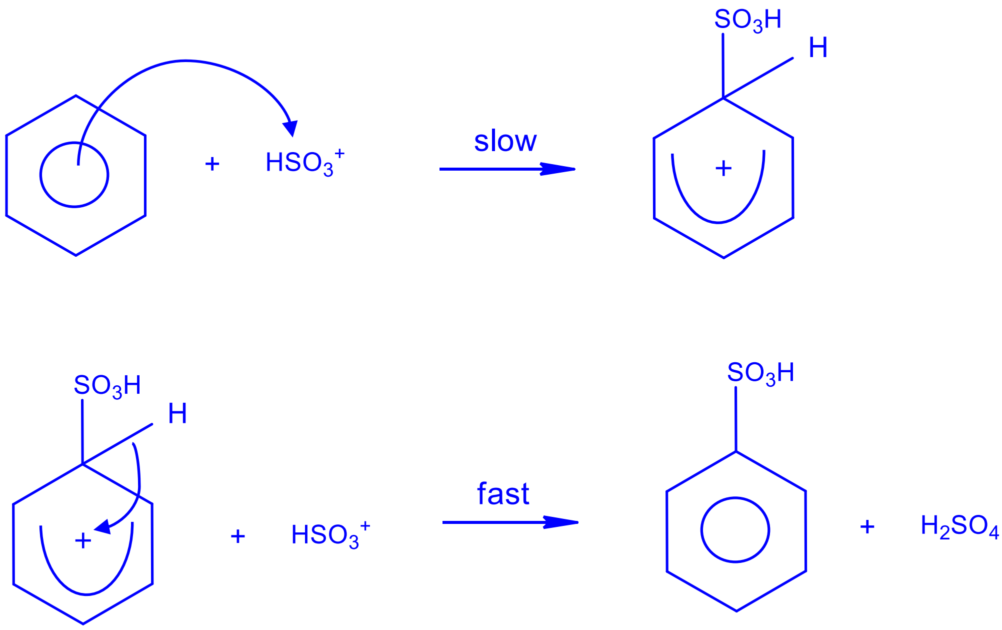


The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

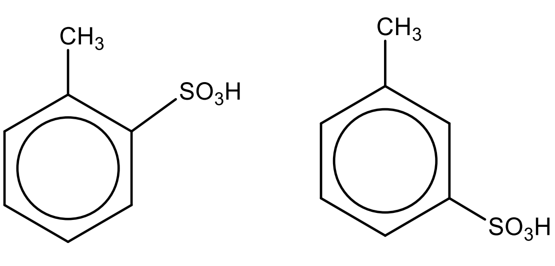
(i) Describe the mechanism for the above reaction. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]

Electrophilic substitution

$H_2SO_4 + H_2SO_4 \rightarrow HSO_3^+ + H_2O + HSO_4^-$



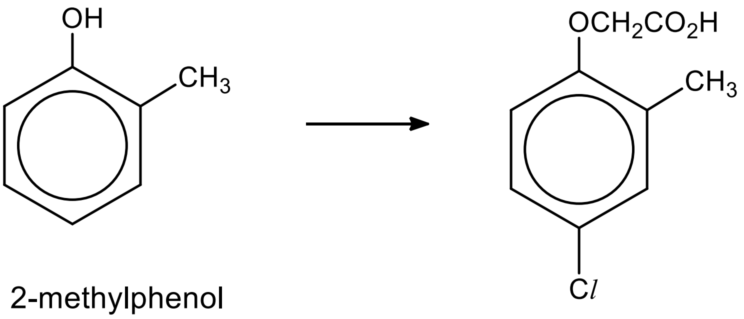
(ii) Similarly, methylbenzene also reacts with concentrated sulfuric acid to form a mixture of the three isomers, in equilibrium.



Suggest why there is a lower concentration of 1,2-isomer than that of 1,4-isomer in the equilibrium mixture. [1]

This may be due to steric hindrance of $-CH_3$ group, as the $-CH_3$ group may have electrostatic repulsion with the large incoming SO_3H^+ group.

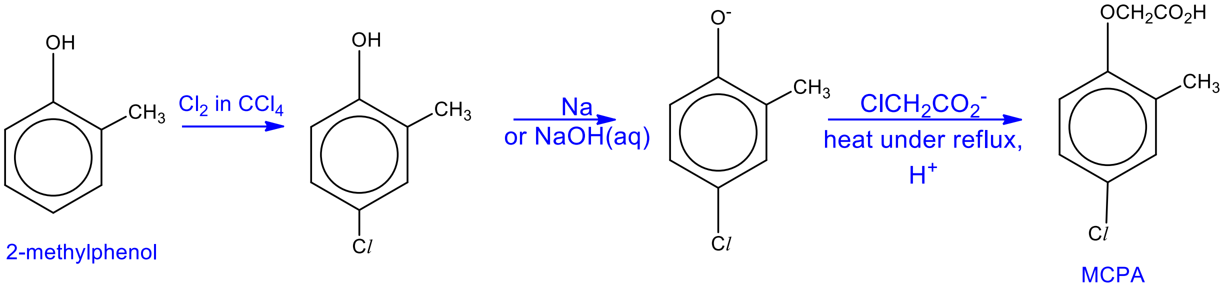
(iii) The chlorinated compound MCPA, widely used as a weed killer, can be synthesized from 2-methylphenol.



2-methylphenol

MCPA

Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [5]



(b) The chemical reactions of benzene sometimes require iron as a catalyst. Iron is a hard grey transition metal which is resistant to corrosion at ordinary temperatures. In contrast, calcium is a fairly soft, silvery-grey Group 2 metal which quickly tarnishes in air.

(i) By considering relevant electronic configurations, explain why the atomic radius of iron is smaller than that of calcium, even though iron has more electrons. [2]

Ca: [Ar] $4s^2$ Fe: [Ar] $3d^6 4s^2$
The atomic radius of iron is smaller (0.126nm) than that of Ca (0.197 nm).
Iron has a higher nuclear charge (due to greater no. of protons) and relatively poor shielding effect by the 3d electrons, the outermost 4s electrons are more strongly attracted by the nucleus.

(ii) Iron can exist in different oxidation states whereas calcium does not. Explain why. [2]

The 3d and 4s electrons are of similar energy so different number of 3d and 4s electrons can be removed to form ions of similar stability, giving rise to variable oxidation states.

However, for s-block elements, only the valence s electrons can be removed. A lot of energy is required to remove the inner shell p electrons as they are more closely bound by the nucleus. Thus, s-block elements have fixed oxidation states.

(iii) Explain why iron(II) complexes are green in colour. [3]

In the **presence of ligands**, **the partially-filled degenerate d orbitals in Fe^{2+} become non-degenerate** and split into **two groups of non-degenerate d orbitals with a small energy gap.**
When exposed to visible light, d electron in a d orbital of lower energy absorbs energy in the **red region** and is **promoted** to a higher energy d* orbital. This is called ***d-d* electronic transition***, where d* is the higher energy orbital.
The **complementary colour** of red, i.e. green, is **not absorbed** and thus green is seen as the colour of the complex.

(iv) Iron(III) ions catalyse the reaction between I^- ions and $S_2O_8^{2-}$ ions through homogeneous catalysis.
Explain why iron(III) ions can be described as a homogeneous catalyst. By considering relevant $E^\ominus$ values from the *Data Booklet*, show by means of balanced equations, how the iron(III) ions carry out its role in this reaction. [3]
Fe^{3+} operates in the same phase as the reactants (iodide and peroxodisulfate) and is regenerated.

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(aq)$
$E^\ominus = +0.77 - (+0.54) = +0.23V$
$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$
$E^\ominus = +2.01 - (+0.77) = +1.24V$

[Total: 20]

5 (a) Aluminium oxide, Al_2O_3, and aluminium chloride, $AlCl_3$, are widely used in various industrial and commercial applications.

(i) Aluminium oxide has a melting point of 2072 °C while aluminium chloride sublimes at 180 °C. Explain the difference in melting points in terms of structure and bonding in each compound. [2]

Aluminium oxide has a giant ionic structure while aluminium chloride has a simple molecular structure.

A larger amount of energy is needed to overcome the stronger ionic bonds (electrostatic force of attraction) between Al^{3+} ions and O^{2-} ions than the weaker instantaneous dipole-induced dipole attractions between aluminium chloride molecules.

(ii) Describe the reactions, if any, of aluminium oxide and aluminium chloride with water, suggesting the pH of the resulting solutions and writing equations, where appropriate. [4]

For Al_2O_3: Does not dissolve in water, **pH of resultant solution= 7**

For $AlCl_3$:

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

The Al^{3+} ion has a high charge density (higher charge and smaller radius compared to Na^+) The small, highly polarizing Al^{3+} cation then weakens the O-H bonds of the water molecules in its sphere of coordination and results in the release of H^+ ions in the solution. **pH of solution of $AlCl_3$ ≈ 3**

(b) The reaction between chlorine gas and hot sodium hydroxide is as follows.

$$3Cl_2 + 6NaOH \rightarrow 5\,NaCl + NaClO_3 + 3H_2O$$

(i) State the type of reaction occuring. [1]

Disproportionation

(ii) State the change in oxidation numbers of chlorine that occur during this reaction. [2]

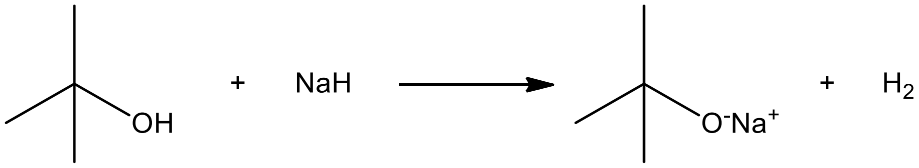
The oxidation number of Cl is decreased from 0 in Cl_2 to -1 in Cl^- (reduction) and increased from 0 in Cl_2 to +5 in ClO_3^- (oxidation).

(c) Ethers are a class of organic compounds that has two organic groups bonded to the same oxygen atom, R-O-R'. The organic groups could be alkyl and aryl groups. Williamson synthesis could be used to synthsise ethers by a reaction between primary alkyl halides and metal alkoxides.

A typical example of the Williamson synthesis is a two-step reaction to synthesize *tert*-butyl methyl ether.

The first step of the reaction involved the preparation of sodium alkoxide in the presence of sodium hydride, NaH.

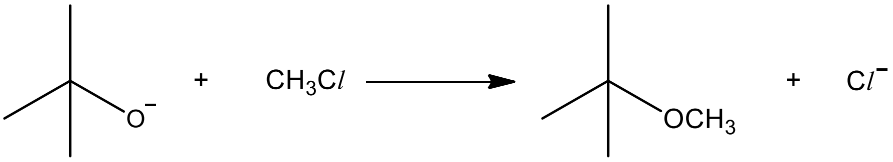
Step 1:



sodium alkoxide

The second step of the reaction involved the reaction between the alkoxide ion and the primary alkyl halide.

Step 2:



alkoxide ion

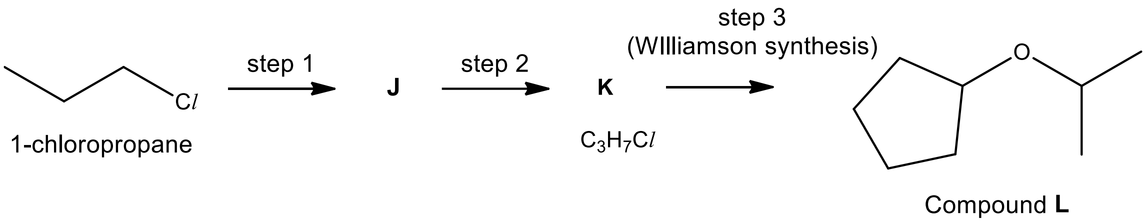
tert-butyl methyl ether

(i) Suggest the role of sodium hydride in step 1. [1]
Base

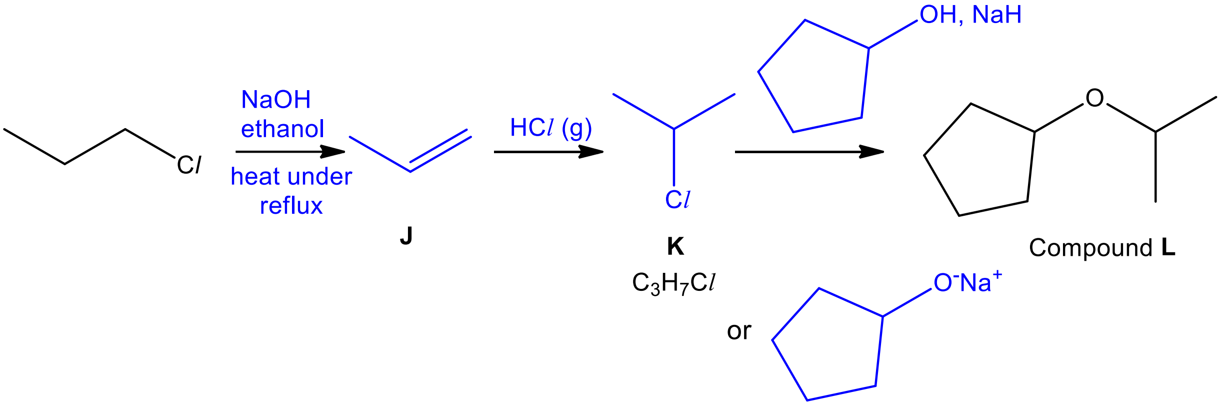
(ii) Suggest the type of reaction which occurs in step 2. [1]
S_N2 nucleophilic substitution

(iii) Suggest why primary alkyl halide is used in Williamson synthesis instead of secondary or tertiary alkyl halide. [1]
The alkoxide, which acts as a nucleophile has 3 bulky substituents. Only a primary alkyl halide that has smaller hydrogen atoms compared to bulky alkyl groups in secondary or tertiary alkyl halide will cause less steric hindrance and allow the bulky nucleophile to attack the carbon centre easily from the rear.

(iv) The following scheme shows a three-step synthesis of compound **L** from 1-chloropropane. Given that step 3 involves Williamson synthesis, suggest the reagents and conditions you would use for each step and identify the intermediates **J** and **K**.



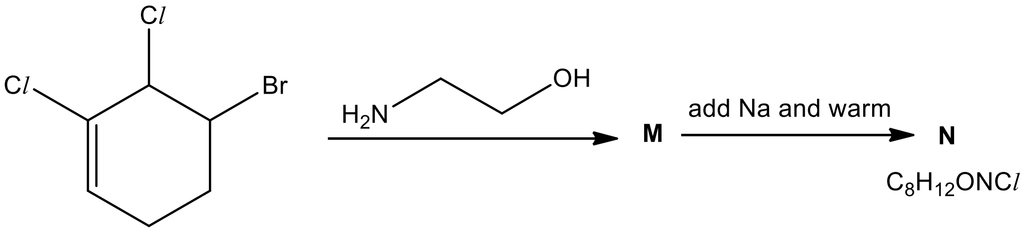
[5]



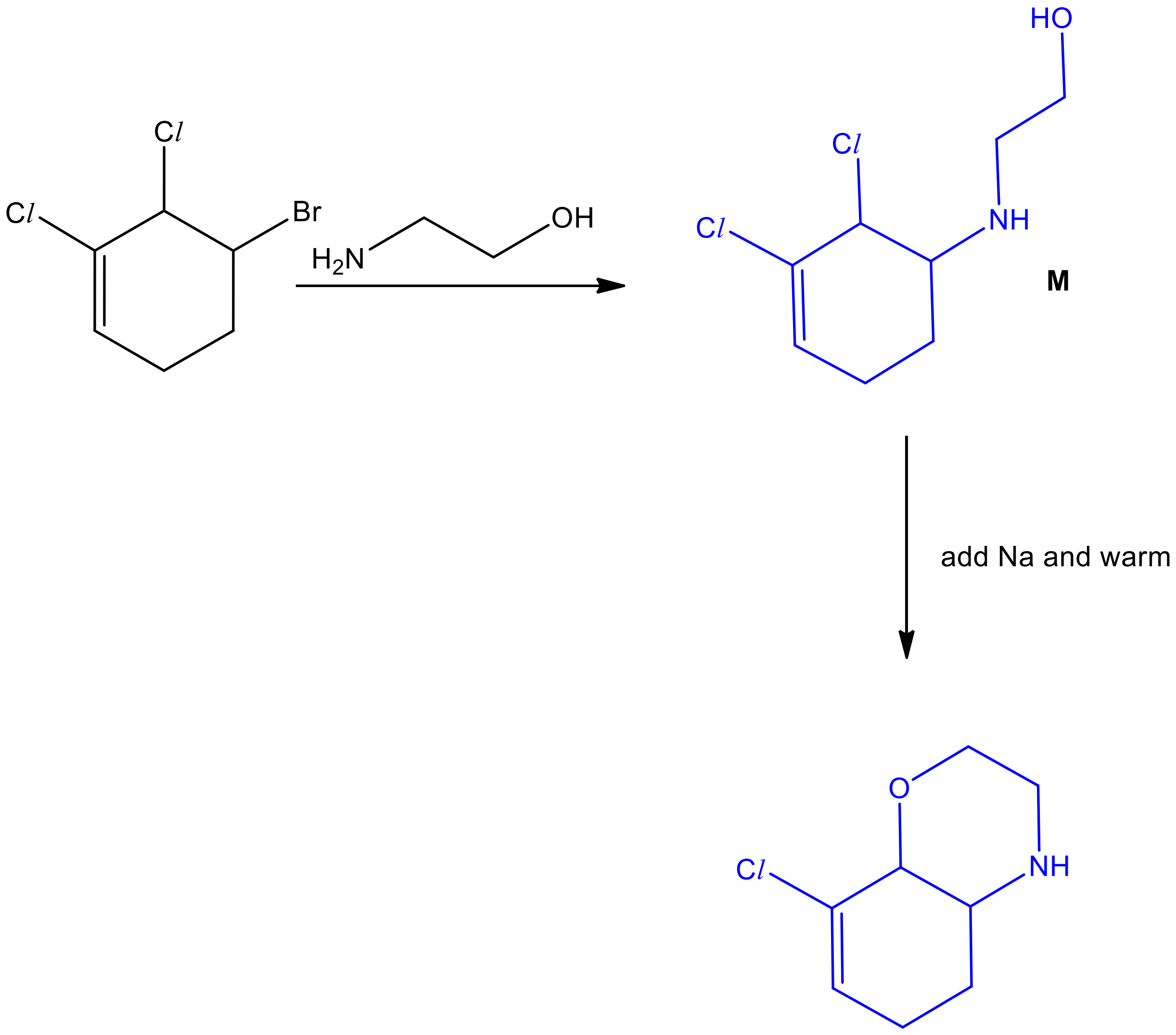
(d) **(i)** Using monohalogenethanes, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds with respect to hydrolysis. [1]

Bromoethane is more reactive towards hydrolysis (nucleophilic substitution) as C-Br bond is weaker and thus requires less energy to break the bond.

(ii) There are other methods to synthesise ethers. A cyclic ether **N** could be formed as shown below. Predict the outcomes of the following transformations, drawing the structures of the intermediate **M** and the product **N**.



[2]



M

N

$C_8H_{12}ONCl$

[Total: 20]

Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/04

Paper 4 Practical

19 August 2019

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 and class in the boxes 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 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.

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	**16**
2	**14**
3	**13**
4	**12**
Total	**55**

This document consists of **15** printed pages and **1** blank page.

[Turn over

1 Determination of the percentage by mass of iron(II) sulfate in an iron tablet

Iron tablets, taken for the prevention and treatment of iron deficiency, are health supplements readily available in pharmacies. These iron tablets contain iron(II) sulfate, which is a soluble form of iron. Assuming that all the iron in the tablets is in the form of Fe^{2+}, it is possible to estimate the iron content by titration against potassium manganate(VII).

The equation for this reaction is

$$5Fe^{2+}(aq) + MnO_4^{-}(aq) + 8H^{+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

You are provided with the following.

FA 1 contains 5 iron tablets, crushed to a powder.
FA 2 is 0.00500 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
deionised water

In this experiment, you will determine the percentage of iron(II) sulfate heptahydrate, $FeSO_4.7H_2O$, present in the iron tablets **FA 1**.

(a) Preparation of FA 3, a solution of $FeSO_4.7H_2O$.

- Use a measuring cylinder to transfer about 100 cm^3 of 1.0 mol dm^{-3} sulfuric acid into a conical flask.
- Determine accurately the mass of the crushed iron tablets used, **FA 1**, and record your readings in the space below.

mass of container + **FA 1** / g	**m_2**
mass of container + residual **FA 1** / g	**m_1**
mass of **FA 1** used / g	**$m_2 - m_1$**

mass of the crushed iron tablets used = …………… g

- Add all the crushed tablets, **FA 1**, to the sulfuric acid.
- **Warm** the mixture gently, **do not overheat**, and stir for about two minutes.
- Allow the flask to cool for around five minutes.
- Filter the mixture into a 250 cm^3 volumetric flask. Ensure that no solution is lost. Note: The filtration takes time. **Proceed to Question 2 whilst the mixture is filtering.**
- Wash out the conical flask with deionised water and add the washings through the filter into the volumetric flask.
- Make up the contents of the flask to the 250 cm^3 mark with deionised water. Stopper and mix the contents thoroughly to obtain a homogeneous solution.
- Label this solution **FA 3**.

(b) **Titration of FA 3 with FA 2**

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 3** into a conical flask.
- Use a measuring cylinder to add about 25.0 cm^3 of 1.0 mol dm^{-3} sulfuric acid to the conical flask.
- Titrate with **FA 2** until the appearance of a first permanent pale-pink colour.
- Record your titration results in the space below. Make certain that the recorded results show the precision of your practical work.
- Repeat the titration as many times as necessary to obtain reliable results.

Titration Results

	1	**2**
final burette reading / cm^3		
initial burette reading / cm^3		
volume of FA 2 used / cm^3	V_1	V_2
	✓	✓

[6]

From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

average titre = $\frac{V_1+V_2}{2}$

= ……… cm^3

volume of **FA 2** = ……………............. [1]

(c) **(i)** Calculate the amount of MnO_4^- ions contained in the mean titre.

mol of MnO_4^- = cV = 0.00500 × $\frac{\text{average titre}}{1000}$

= ……….. mol

amount of MnO_4^- ions =……………….………..…. [1]

(ii) Calculate the amount of Fe^{2+} ions that reacted with the MnO_4^- ions calculated in **(c)(i)**.

mol of Fe^{2+} reacted = 5 × mol of MnO_4^-
= 5 × ans to (b)(i)
= ……….. mol

amount of Fe^{2+} ions =…………..………...… [1]

(iii) Calculate the amount of Fe^{2+} ions in the five crushed tablets, **FA 1**.

mol of Fe^{2+} in 5 crushed tablets = mol of Fe^{2+} in 250 cm^3 solution
= $\frac{250}{25.0}$ × ans to (b)(ii)
= …………. mol

amount of Fe^{2+} ions in **FA 1** =…………..………...… [1]

(iv) Calculate the mass of $FeSO_4.7H_2O$ in **one** tablet.
[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

M_r of $FeSO_4.7H_2O$ = 55.8 + 32.1 + 4(16.0) + 7[2(1.0) + 16.0] = 277.9

mass of $FeSO_4.7H_2O$ in 5 tablets = nM_r = ans to (b)(iii) x 277.9
= …………. g

∴ mass of $FeSO_4.7H_2O$ in 1 tablet = $\frac{1}{5}$ x above ans
= …………. g

mass of $FeSO_4.7H_2O$ in one tablet =…………..………...… [2]

(v) Hence calculate the percentage by mass of $FeSO_4.7H_2O$ in **one** tablet.

% by mass of $FeSO_4.7H_2O$ in 1 tablet = $\frac{5 \times \text{ans to (b)(iv)}}{\text{mass of FA1}}$ x 100

= ………. %

percentage by mass of $FeSO_4.7H_2O$ in one tablet =……………………

[2]

(d) Explain why in the procedure described in **(a)**, the volume of sulfuric acid was measured using a measuring cylinder rather than a burette.

- **sulfuric acid is in excess and so, its volume need not be measured precisely.**

……………………………………………………………………………………………… [1]

(e) To confirm the formula of iron(II) sulfate heptahydrate in the tablet, a student dissolved one of the tablets in nitric acid and added a few drops of barium nitrate to the filtrate.

State the observation expected from this chemical test. Give your reasoning.

- **white ppt of $BaSO_4$ formed confirmed the presence of SO_4^{2-} ion.**

……………………………………………………………………………………………… [1]

[Total: 16]

2 Determination of the enthalpy change for the reaction of citric acid with $NaHCO_3(aq)$

Antacid, taken for quick relieve of occasional heartburn, is also readily available in pharmacies. Antacid contains mainly citric acid and sodium hydrogencarbonate, which react when in contact with water to give carbon dioxide.

In this experiment, you will determine the enthalpy change when citric acid reacts with sodium hydrogencarbonate.

You are provided with the following.

FA 4 is 0.8 mol dm^{-3} citric acid.
FA 5 is solid sodium hydrogencarbonate, $NaHCO_3$.

(a) Method

You will carry out the following experiment **twice**.

- Weigh between 6.5 g and 7.0 g of **FA 5** in a dry weighing bottle.
- Use a pipette to transfer 50.0 cm^3 of **FA 4** into the plastic cup supported in a 250 cm^3 beaker.
- Place the thermometer in the acid in the plastic cup and record its initial temperature.
- Carefully add the weighed sample of **FA 5**, in *small portions*, into the acid in the plastic cup. Stir the mixture carefully with the thermometer.
- Record the lowest temperature reached.
- Reweigh the weighing bottle and any residual **FA 5**.

Record in a single table, in the space given on **page 7**,

- all measurements of mass and temperature, and
- the temperature fall, ΔT.

Empty and rinse the plastic cup.

Repeat the experiment and calculate the mean value of

- ΔT, and
- mass of **FA 5** added.

Results

	Expt 1	**Expt 2**
mass of weighing bottle + **FA 5** / g	**m_1**	**m_3**
mass of weighing bottle + residual **FA 5** / g	**m_2**	**m_4**
mass of **FA 5** used / g	**$m_1 - m_2$**	**$m_3 - m_4$**
initial temperature / °C	**T_1**	**T_3**
lowest temperature / °C	**T_2**	**T_4**
temperature fall, ΔT / °C	**$T_1 - T_2$**	**$T_3 - T_4$**

- **mean value of $\Delta T = \frac{(T_1-T_2)+(T_3-T_4)}{2}$ = …… °C**
- **mean mass of FA 5 added = $\frac{(m_1-m_2)+(m_3-m_4)}{2}$ = ……… g**

mean value of ΔT =…………………….…..

mean mass of FA 5 added =…………………….…..

[4]

(b) Citric acid is a tribasic acid; i.e. one mole of the acid reacts with three moles of sodium hydrogencarbonate.

(i) Write a balanced equation, with state symbols, to show how citric acid reacts with sodium hydrogencarbonate in the experiment. You may use H_3A to represent citric acid.

$H_3A(aq) + 3NaHCO_3(s) \rightarrow Na_3A(aq) + 3H_2O(l) + 3CO_2(g)$……………………… [1]

(ii) Calculate the heat energy when **FA 5** was added to the acid.

[Assume that 4.3 J are required to raise the temperature of 1.0 cm^3 of any solution by 1.0 °C.]

heat absorbed = mc ΔT
= 50 × 4.3 × mean ΔT
= …………… J

heat energy =…………..…. J [1]

(iii) In the experiment carried out in **2(a)**, excess citric acid was used. Using your answer to **2(b)(i)**, calculate the amount of citric acid that has reacted with the mean mass of **FA 5** added. [A_r: Na, 23.0; O, 16.0; C, 12.0; H, 1.0]

M_r of $NaHCO_3$ = 23.0 + 1.0 + 12.0 + 3(16.0) = 84.0

mol of $NaHCO_3$ used = $\frac{\text{mean mass of FA5}}{84.0}$

= ……… mol

mol of citric acid reacted = $\frac{1}{3}$ × mol of $NaHCO_3$

= $\frac{1}{3}$ × above answer

= ………… mol

amount of citric acid = ... mol [2]

(iv) Calculate the enthalpy change, in kJ mol^{-1}, when 1 mol of citric acid reacts with sodium hydrogencarbonate. Your answer should include the appropriate sign.

$$\Delta H = + \frac{\text{ans to (b)(ii)}}{\text{ans to (b)(iii)}}$$

= + ……… kJ mol^{-1}

enthalpy change, ΔH = ... kJ mol^{-1} [2]

(v) Explain the significance of the sign you have given in **2(b)(iv)** and how it is related to your experimental results.

- **+ sign because the reaction is endothermic (or heat is absorbed in the reaction or temperature falls during the reaction)**

.... [1]

(c) Explain why **FA 5** is added in *small portions* in the procedure described in **2(a)**.

- **to prevent excessive effervescence / acid spray which results in loss of solution.**

.... [1]

(d) A student repeated the experiment described in **2(a)** on another day when the room temperature was much higher. Suggest how this higher room temperature would affect the value of ΔT. Give your reasoning.

no effect on ΔT due to higher initial and higher final (minimum) temperature

.... [2]

[Total: 14]

3 Planning

The reaction between an acid and a metal hydroxide is exothermic. By using this fact, it is possible to determine the equivalence point of a neutralisation reaction without the use of an indicator. This process is known as *thermometric titration*.

In the experiment, the temperature is monitored as portions of acid are progressively added to a fixed volume of the alkali until the equivalence point is reached and passed. 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 until they intersect.

(a) In a thermometric titration where an acid is run into an alkali, state and explain how you would recognise that the equivalence point has been passed.

- **Since reaction is exothermic, temperature of the mixture increases until the equivalence point is reached.**
- **Beyond the equivalence point, temperature of the mixture decreases as no further reaction takes place and the acid added is at a lower temperature than the mixture.**

.... [2]

(b) In this question, you are required to write a plan for a thermometric titration in which citric acid is added to 25.0 cm^3 of aqueous sodium hydroxide.

You are provided with the following materials.

- 2.00 mol dm^{-3} sodium hydroxide, NaOH
- 0.8 mol dm^{-3} citric acid
- equipment normally found in a school laboratory

(i) Using the information given above, show that the volume of citric acid required to reach the equivalence point is 20.90 cm^3.
You may use H_3A to represent citric acid, which is a tribasic acid.

Since citric acid is tribasic, $H_3A \equiv 3NaOH$ [OR $H_3A + 3NaOH \rightarrow Na_3A + 3H_2O$]

mol of H_3A $= \frac{1}{3} \times$ mol of NaOH

$= \frac{1}{3} \times 2.00 \times \frac{25.0}{1000} = 0.0167$ mol

$\therefore$ approx. vol of H_3A at equivalence point $= \frac{0.0167}{0.8} \times 1000 = 20.90\ cm^3$

[1]

(ii) Outline how you would carry out the proposed thermometric titration using only the materials provided.

In your plan, you should include

- brief, but specific, details of the apparatus you would use, considering the levels of precision they offer;
- measurements you would make to allow for a suitable graph to be drawn in **3(b)(iii)**, in order to determine the value of $\Delta H_n^{\ominus}$ for this reaction; and
- how you would recognise that the equivalence point had been passed.

Outline your plan as a series of numbered steps.

1. **Pipette 25.0 cm^3 of aq. NaOH into a plastic cup supported in a 250 cm^3 beaker. Record the initial temperature of aq. NaOH (using a thermometer calibrated to 0.2°C)**
2. **Fill a 50 cm^3 burette with the citric acid.**
3. **Add 5.00 cm^3 of citric acid from the burette to the plastic cup. Stir the mixture with the thermometer and record the highest temperature reached.**
4. **Add a further 5.00 cm^3 of citric acid to the plastic cup, and again record the highest temperature reached.**
5. **Repeat step 4 until the temperature recorded starts to decrease, showing that equivalence point has been passed. Then add three further 5.00 cm^3 portions of citric acid and record the steady temperature reached after each addition.**

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [4]

(iii) Sketch, on the axes provided, the graph you would expect to obtain using information in **3(b)(i)** and the measurements you planned to make in **3(b)(ii)**. Label clearly the axes. You should also indicate on your graph,

- the equivalence point, and
- the maximum temperature rise, ΔT_1.

[3]

(iv) Write an ionic equation to represent the enthalpy change of neutralisation, ΔH_n.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ …………………………………………………… [1]

(v) Given that ΔT_1 is 11.0 °C and using the information in **3(b)(i)**, determine the value of $\Delta H_n^{\ominus}$ for this reaction.

heat evolved = $mc\Delta T_1$ = (25.0 + 20.90) × 4.3 × 11.0 = 2171 J

mol of H_2O = mol of NaOH = 2.00 × $\frac{25.0}{1000}$ = 0.0500 mol

$\therefore \Delta H_n^{\ominus} = -\frac{2171}{0.0500}$ = –4340 J mol^{-1} = –43.4 kJ mol^{-1}

$\Delta H_n^{\ominus}$ =……**–43.4**……… kJ mol^{-1} [2]

[Total: 13]

4 Inorganic Analysis

You are provided with three solutions, **FA 6**, **FA 7** and **FA 8**, each containing one cation and one anion.

Identification of the anions in FA 6, FA 7 and FA 8.

One or more of the solutions contains a halide ion.

(a) From the *Qualitative Analysis Notes* on page 15, you are to select and use

(i) one reagent to precipitate any halide ion that is present,

(ii) a second reagent to confirm the identity of any halide ion present.

Since the solutions are coloured, you will need to remove traces of solution from the precipitate.

Record the tests performed, the practical procedures used and the observations made for each of the solutions.

Present this information as clearly as possible in a single table in the space below.

Test	FA 6	FA 7	FA 8
1. Add aq AgNO$_3$ to each solution. **Decant / filter to remove the coloured solution.**	**white ppt.**	**yellow ppt**	**no ppt**
2. Add aq NH$_3$ to the precipitate obtained in the above test.	**ppt dissolves to give a colourless solution**	**ppt insoluble in aq. NH$_3$**	**–**

[4]

(b) Use your observations to identify any halide ions present in the solutions, **FA 6**, **FA 7** and **FA 8**, and state which ion is present in which solution.

- **Cl^- present in FA 6, I^- present in FA 7, and no halide ions present in FA 8**

[1]

Identification of the cations in FA 6, FA 7 and FA 8.

(c) Using aqueous NaOH and aqueous NH_3, it is possible to identify two of the cations present and to draw conclusions about the nature of the remaining cation.

Carry out tests with these reagents and record details of the observations made for each of the solutions.

Test	**FA 6**	**FA 7**	**FA 8**
1. Add aqueous NaOH dropwise until no further change is seen.	**red-brown ppt.** **insoluble in excess NaOH**	**grey-green ppt** **soluble in excess NaOH giving a dark green solution**	**blue ppt turns brown with excess NaOH;** **insoluble in excess NaOH**
2. Add aqueous NH_3 dropwise until no further change is seen.	**red-brown ppt.** **insoluble in excess NH_3**	**grey-green ppt** **insoluble in excess NH_3**	**blue ppt;** **insoluble in excess NH_3**

[4]

(d) Use your observations in **4(c)** to identify two of the cations present and state which of the solutions contain those cations.

The cation contained in **FA** ...**6**...... is ......**Fe^{3+}**.......

Evidence:

FA 6 gives red-brown ppt with NaOH and with NH_3

The cation contained in **FA** ...**7**...... is ......**Cr^{3+}**.......

Evidence:

FA 7 gives grey-green ppt with NaOH and with NH_3

OR grey-green ppt with NaOH, soluble in excess to give a green solution [2]

(e) From your observations in **4(c)**, what conclusion can you draw about the general nature of the third cation? Explain your answer.

- **FA 8 contains a transition metal cation deduced from the coloured solution and ppt.** [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 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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Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

30 September 2019
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.

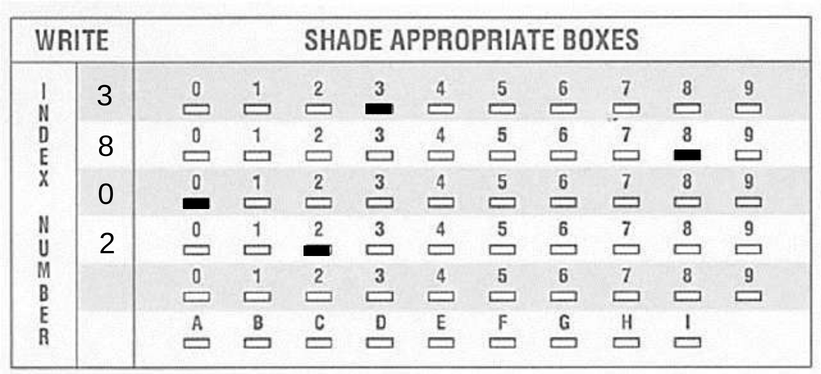
4 Any rough working should be done in this booklet.

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”.



WRITE		SHADE APPROPRIATE BOXES									
INDEX NUMBER	3	0 ☐	1 ☐	2 ☐	3 ■	4 ☐	5 ☐	6 ☐	7 ☐	8 ☐	9 ☐
	8	0 ☐	1 ☐	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐	7 ☐	8 ■	9 ☐
	0	0 ■	1 ☐	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐	7 ☐	8 ☐	9 ☐
	2	0 ☐	1 ☐	2 ■	3 ☐	4 ☐	5 ☐	6 ☐	7 ☐	8 ☐	9 ☐
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		A ☐	B ☐	C ☐	D ☐	E ☐	F ☐	G ☐	H ☐	I ☐	

This question paper consists of **16** printed pages and **no** blank pages.

1 Sodium azide, NaN_3, and potassium nitrate, KNO_3, are both present in the airbags of some cars.

When the airbag is activated, sodium azide first decomposes to give sodium and nitrogen.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

The sodium then reacts with potassium nitrate to produce more nitrogen.

$$10Na(s) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$$

The nitrogen produced in these two reactions inflates the airbag.

2.00 mol of gas is needed to inflate the airbag.

What is the amount of sodium azide needed to inflate the airbag?

A 0.625 mol

B 1.00 mol

C 1.25 mol

D 1.33 mol

2 *Use of the Data Booklet is relevant to this question*.

Sodium percarbonate, $(Na_2CO_3)_x$•$y(H_2O_2)$ is an oxidising agent in some home and laundry cleaning products.

10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate releases 48.0 cm^3 of carbon dioxide at room conditions on acidification.

An identical sample reacts with 24.0 cm^3 of 0.0500 mol dm^{-3} $KMnO_4$ before the first pink colour appears.

Given that $5H_2O_2 \equiv 2KMnO_4$, what is the ratio of $\frac{y}{x}$?

A $\frac{1}{3}$

B $\frac{2}{3}$

C $\frac{3}{2}$

D $\frac{3}{1}$

3 *Use of the Data Booklet is relevant to this question*.

A compound is made up from two elements, **Y** and **Z**. Each separate atom of **Y** and of **Z** in their ground states has exactly 2 unpaired electrons.

What could the compound be?

1 $TiCl_4$

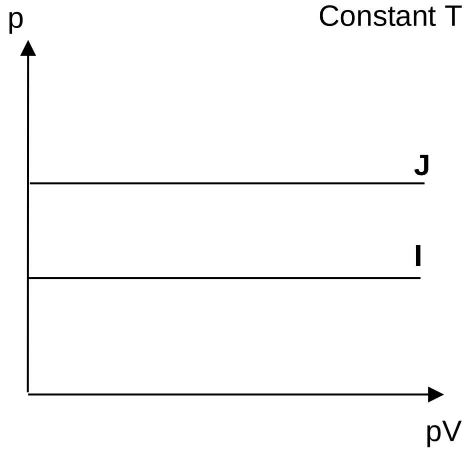
2 SiO_2

3 NiS

A	1, 2 and 3	**B**	2 and 3 only
C	1 and 3 only	**D**	2 only

4 Which graph correctly describes the behaviour of fixed masses of the ideal gases **I** and **J**, where **I** has a higher M_r than **J**?

A



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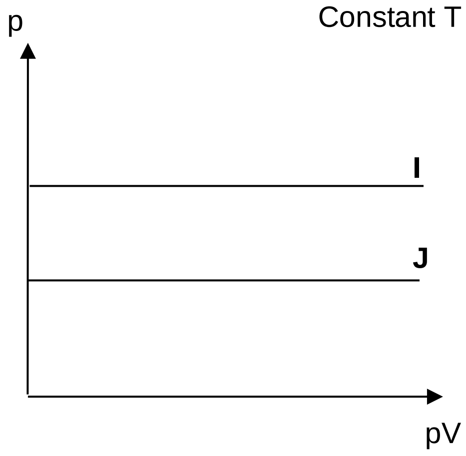

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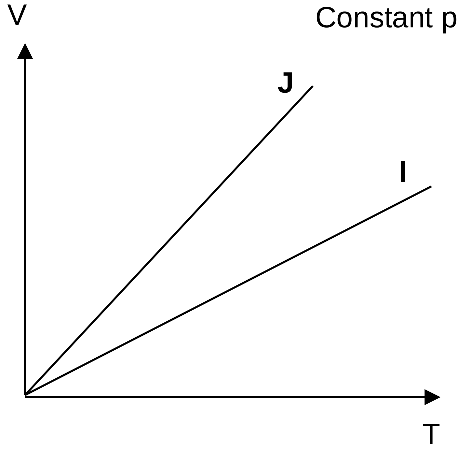

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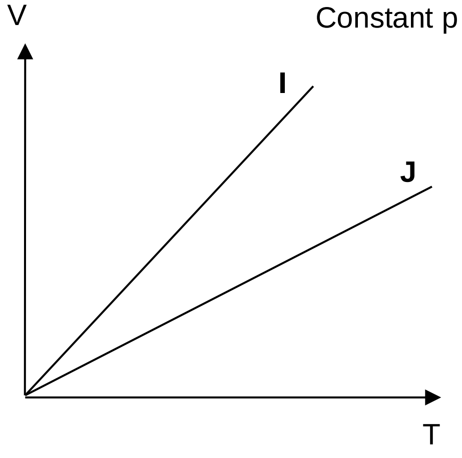


5 Which feature is present in the carbonate, ethanoate, nitrate and phenoxide ions?

A All bond angles are 120°

B Dative covalent bonds

C Delocalised electrons

D Hydrogen bonds

6 When an equilibrium is established in a reversible reaction, the standard Gibbs free energy, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, by the following equation.

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

where R is the gas constant and T is the temperature in Kelvin.

Which of the following statement is correct?

1 At constant temperature, a shift in position of equilibrium to the right results in the same value of $\Delta G^\ominus$.

2 The forward reaction is spontaneous for all values of K_c.

3 Adding a catalyst makes $\Delta G^\ominus$ more negative.

A	1, 2 and 3 only	**B**	2 and 3 only
C	1 and 3 only	**D**	1 only

7 Three equilibrium reactions are shown below. All three reactions have an equilibrium constant, K_c, that is greater than one.

$$N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$$
$$NH_3 + HBr \rightleftharpoons NH_4^+ + Br^-$$
$$N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$$

Assuming that all solutions have the same concentration, which correctly lists the three solutions in order of decreasing pH?

A	$HBr > N_2H_5^+ > NH_4^+$	**B**	$N_2H_5^+ > NH_4^+ > HBr$
C	$NH_4^+ > N_2H_5^+ > HBr$	**D**	$N_2H_5^+ > HBr > NH_4^+$

8 Which of the following resultant solutions will have the lowest pH?

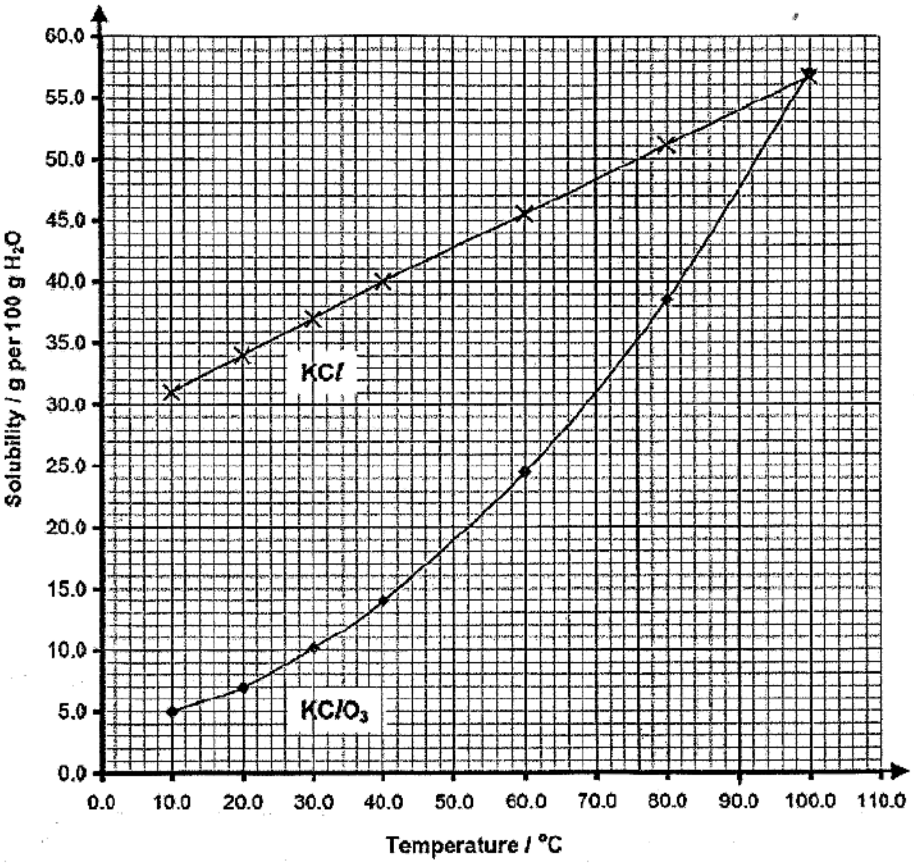
A 15 cm^3 of 0.100 mol dm^{-3} KOH added to 15 cm^3 of 0.050 mol dm^{-3} benzoic acid

B 50 cm^3 of 0.050 mol dm^{-3} KOH added to 25 cm^3 of 0.100 mol dm^{-3} benzoic acid

C 25 cm^3 of 0.100 mol dm^{-3} KOH added to 50 cm^3 of 0.100 mol dm^{-3} benzoic acid

D 5 cm^3 of 0.100 mol dm^{-3} KOH added to 50 cm^3 of 0.100 mol dm^{-3} benzoic acid

9 The graph below shows how the solubility of two salts, $KClO_3$ and KCl, varies with temperature.



10 g of $KClO_3$ and 50 g of KCl was added to 100 g of water at 90 °C.

Which statement is correct as the mixture is cooled to 10 °C?

1 The first trace of precipitate occurs at about 76 °C.

2 The aqueous solution is saturated with $KClO_3$ and KCl at 10 °C.

3 The maximum mass of KCl that can be precipitated without any trace of solid $KClO_3$ is approximately 13 g.

A	1, 2 and 3	**B**	2 and 3 only
C	1 and 2 only	**D**	3 only

10 Hydrazine, N_2H_4, used in rocket fuels can be obtained by the reaction of ammonia and hydrogen peroxide according to the following equation.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_{reaction}^{\ominus} = -241 \text{ kJ mol}^{-1}$$

Using the value of $\Delta H_{reaction}^{\ominus}$ given above and the data below, calculate the $\Delta H^{\ominus}$ (in kJ mol^{-1}) for decomposition of hydrazine into $N_2(g)$ and $H_2(g)$.

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$NH_3(g)$	–46
$H_2O_2(l)$	–188
$H_2O(l)$	–286

A +189 **B** +51

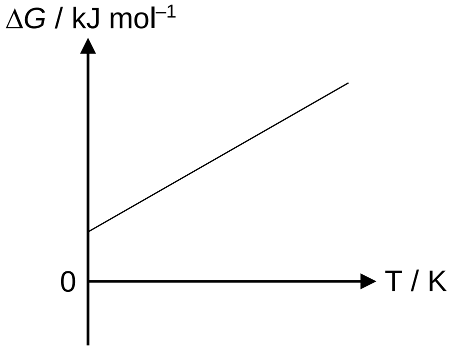
C –189 **D** –51

11 Methanol can be synthesised from carbon monoxide and hydrogen according to the equation

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Higher yield of methanol can be achieved at a lower temperature. Which graph corresponds to the forward process?

A



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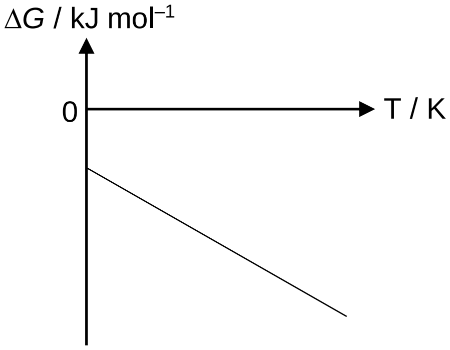

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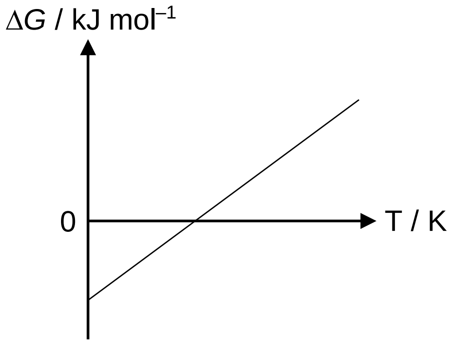

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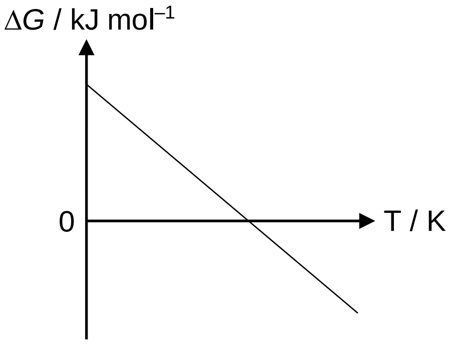


12 The table below shows the results of three experiments conducted for the following reaction.

$$\mathbf{P} + \mathbf{Q} \rightarrow \text{products}$$

experiment	[**P**] / mol dm^{-3}	[**Q**] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1	0.012	0.005	1.0×10^{-4}
2	0.024	0.010	2.0×10^{-4}
3	0.048	0.010	4.0×10^{-4}

Another three experiments were carried out at different temperatures and the results obtained are shown below.

experiment	[**P**] / mol dm^{-3}	[**Q**] / mol dm^{-3}	temperature / ^{o}C
4	0.10	0.20	40
5	0.20	0.20	30
6	0.30	0.30	20

If the rate constant doubles for each 10 ^{o}C rise in temperature, which statements regarding experiments 4 to 6 are correct?

1 rate of reaction of experiments 4 and 5 are the same.

2 rate of reaction of experiment 4 is two times faster than experiment 6.

3 rate of reaction of experiment 6 is the slowest.

A 1, 2 and 3

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

13 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table. The results of some experiments carried out with compounds of these elements are shown.

	X	**Y**	**Z**
result of reacting the oxide of the element with $HCl(aq)$	salt solution	salt solution	mixture of acids
result of adding the oxide of the element to $H_2O(l)$	no reaction	alkaline solution	acid solution
result of adding the chloride of the element to $H_2O(l)$	hydrolyses	dissolves	hydrolyses

What could be the identities of **X**, **Y** and **Z**?

	X	**Y**	**Z**
A	Al	P	S
B	Al	Na	P
C	Si	Mg	P
D	Si	Na	Al

14 The table shows the results of experiments in which the halogens, $\mathbf{K}_2$, $\mathbf{L}_2$ and $\mathbf{M}_2$ were added to separate aqueous solutions containing $\mathbf{K}^-$, $\mathbf{L}^-$ and $\mathbf{M}^-$ ions.

	$\mathbf{K}^-$ (aq)	$\mathbf{L}^-$ (aq)	$\mathbf{M}^-$ (aq)
$\mathbf{K}_2$	no reaction	$\mathbf{L}_2$ formed	no reaction
$\mathbf{L}_2$	no reaction	no reaction	no reaction
$\mathbf{M}_2$	$\mathbf{K}_2$ formed	$\mathbf{L}_2$ formed	no reaction

Which statements are correct?

1 When $\mathbf{L}_2$ reacts with thiosulfate ions, the oxidation state of sulfur increases the most compared to the reaction between $\mathbf{M}_2$ and thiosulfate ions.

2 $\mathbf{L}^-$(aq) forms a precipitate with aqueous silver nitrate that is insoluble in excess aqueous ammonia.

3 $\mathbf{K}^-$ and $\mathbf{M}^-$ solutions can be distinguished by adding hexane.

A 2 only

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

15 Which hydrocarbon, when reacted with chlorine in the presence of sunlight, will form a monochlorinated product which shows both *cis-trans* isomerism and enantiomerism?

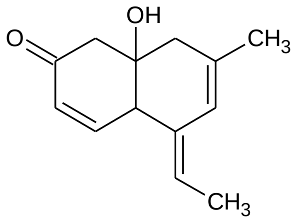
A $CH_3CH{=}CH_2$

B $(CH_3)_2C{=}CH_2$

C $CH_3CH{=}C(CH_3)_2$

D $CH_3CH{=}CHCH_2CH_3$

16 Which statement regarding compound **K** is correct?



Compound **K**

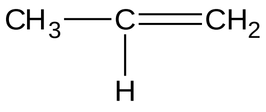
A 1 mol of **K** reacts with excess gaseous HBr to yield a major product with 7 chiral centres.

B 1 mol of **K** reacts with hot acidified $KMnO_4$ to give a dicarboxylic acid as one of the products.

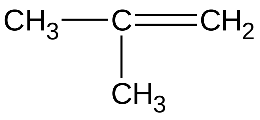
C 1 mol of **K** reacts with 4 mol of H_2 in the presence of nickel catalyst to yield a saturated compound.

D 1 mol of **K** reacts with sodium to give 24.0 dm^3 of hydrogen gas at room temperature and pressure.

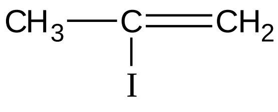
17 A comparison is made of the rate of electrophilic addition of Br_2 (in CCl_4) to the following compounds:


$CH_3{-}C(H){=}CH_2$

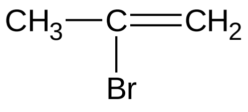
S


$CH_3{-}C(CH_3){=}CH_2$

T


$CH_3{-}C(I){=}CH_2$

U


$CH_3{-}C(Br){=}CH_2$

V

How will the reaction rate vary for each compound?

	Fastest ⟶ Slowest			
A	**T**	**S**	**U**	**V**
B	**U**	**V**	**S**	**T**
C	**T**	**S**	**V**	**U**
D	**S**	**T**	**V**	**U**

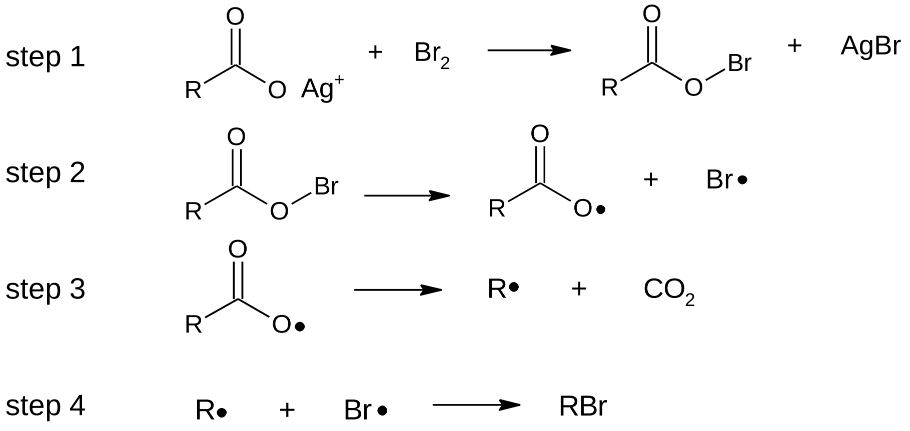
18 Consider all benzene-containing isomers with molecular formula C_9H_{10}.

How many isomers will produce benzene-1,2-dicarboxylic acid on heating with acidified manganate(VII) ions?

A 1 **B** 2

C 3 **D** 4

19 The Hunsdiecker reaction can be used to prepare alkyl bromides. Its mechanism is believed to involve the following steps.

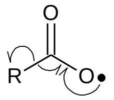


Which statement about the mechanism is correct?

1 RCO_2^- attacks the δ+ bromine atom of Br_2 in step 1.

2 Homolytic fission of O–Br bond occurs in step 2.

3 The curly arrows show the movement of electrons in step 3:

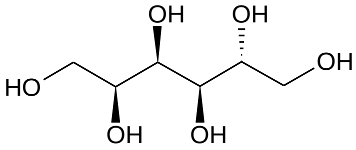


4 Heat energy is absorbed in step 4.

A 1, 2 and 3 only **B** 2 and 3 only

C 1 and 4 only **D** 1 and 2 only

20 The structure of sorbitol is as shown.



How many moles of gas is produced when one mole of sorbitol reacts with an excess of thionyl chloride, $SOCl_2$?

A 0

B 3

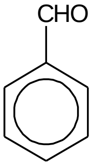
C 6

D 12

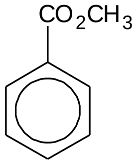
21 Compound **X** gives orange precipitate with 2,4–DNPH but does not react with Fehling's solution. When heated with alkaline aqueous iodine, **X** gives pale yellow precipitate.

What could compound **X** be?

A



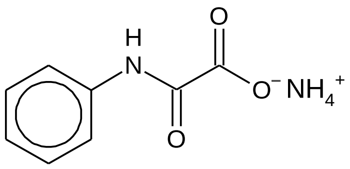
B



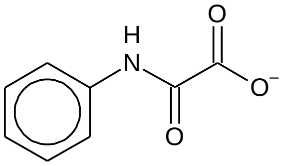
C $CH_3CH_2COCH_2CH_3$

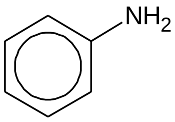
D $CH_3COCOCH_3$

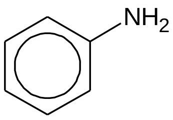
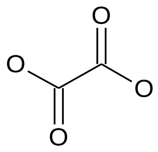
22 What are the products when ammonium N-phenyloxamate is heated with NaOH(aq)?

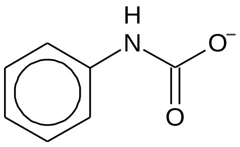


ammonium N-phenyloxamate

A  + NH_3

B  + CO_3^{2} + NH_3

C  +  + NH_3

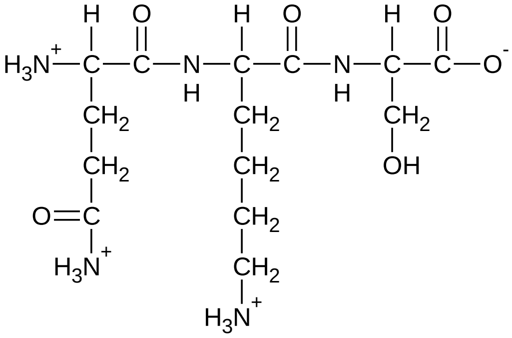
D  + CO_3^{2-} + NH_3

23 The table below shows three common amino acids in the human body.

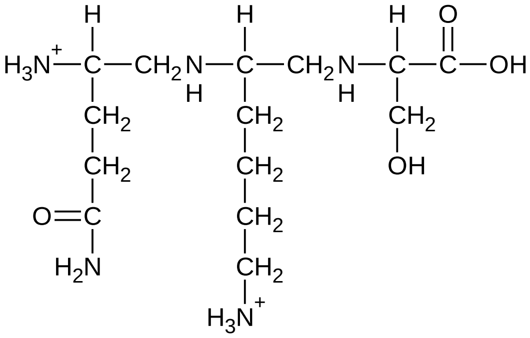
Amino acid	3–letter abbreviation	Formula of side chain (R group)
Glutamine	*gln*	$-CH_2CH_2CONH_2$
Lysine	*lys*	$-CH_2CH_2CH_2CH_2NH_2$
Serine	*ser*	$-CH_2OH$

A tripeptide is formed from the three amino acids above. What is the structure of this tripeptide when hydrochloric acid is added to it at room temperature?

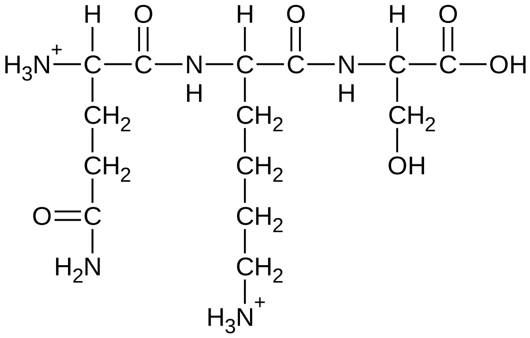
A



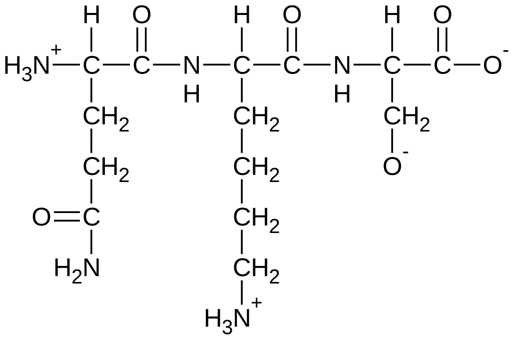
B



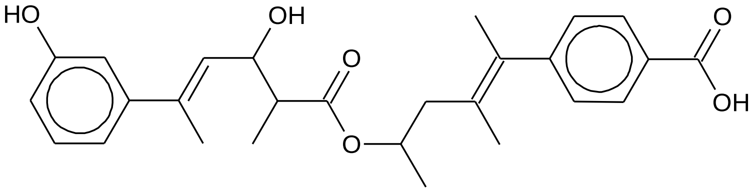
C



D



24 Which reagent and condition will **not** give an observable change with compound **Z**?



compound **Z**

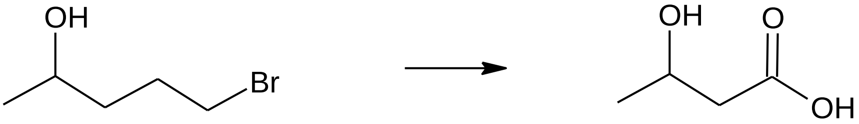
A Alkaline aqueous iodine, heat

B Anhydrous phosphorus pentachloride

C Lithium aluminium hydride in dry ether

D Cold dilute alkaline potassium manganate(VII)

25 Which sequence will achieve the conversion below?



	Step 1	Step 2	Step 3
A	NaOH(aq), heat	Hot acidified $KMnO_4$	H_2 gas, nickel catalyst, heat
B	Hot ethanolic KOH	Hot acidified $KMnO_4$	$NaBH_4$ in methanol
C	Hot acidified $KMnO_4$	KCN in ethanol, heat	H_2SO_4(aq), heat
D	Excess conc. H_2SO_4, heat	Hot acidified $KMnO_4$	Excess NaOH(aq), heat

Use of the Data Booklet is relevant to questions 26 – 29.

26 When a dilute **X**$(NO_3)_2$ solution undergoes electrolysis, the metal **X** and gas **Y** are produced at the cathode and the anode respectively.

What could be the identities of metal **X** and gas **Y**?

	X	**Y**
A	Cu	NO_2
B	Fe	NO_2
C	Mg	O_2
D	Zn	O_2

27 Zinc plating is frequently used to protect metals such as iron from corrosion.

A piece of iron was immersed into a solution of zinc nitrate and a current of 0.5 A was passed through it. How many minutes must the piece of iron be immersed in the solution to achieve an electroplated coating that weighs 0.4 g?

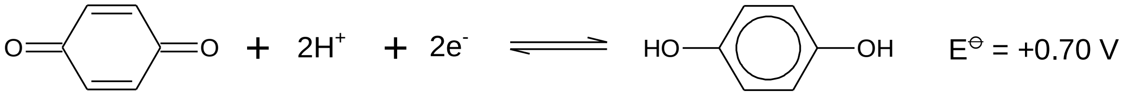
A 46.1

B 39.3

C 19.7

D 9.8

28 Quinone can be formed by oxidising quinol.



Quinone

Quinol

Which aqueous reagent will give a good yield of quinone when added to quinol?

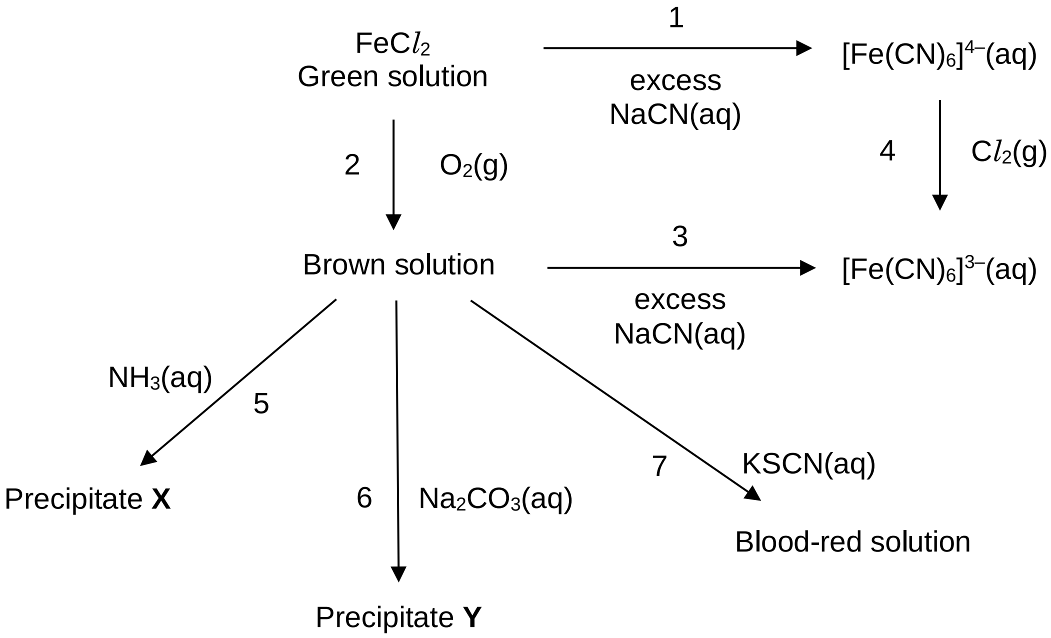
A H_2O_2 / H^+

B Br_2

C Cu^{2+}

D NaC*l*

29 The following reaction scheme shows the chemistry of some iron-containing species in aqueous solution.



Which statement is **false** regarding the reaction scheme above?

A Precipitates **X** and **Y** are different compounds.

B A ligand exchange reaction happens in step 7.

C A redox reaction happens in step 2.

D The $E^{\ominus}_{cell}$ for step 4 is +1.00 V.

30 $\mathbf{M}(H_2O)_xCl_y$ is an ionic compound which contains a metal complex cation, where ***x*** and ***y*** are integers.

When excess $AgNO_3(aq)$ was added to 1 mol of aqueous $\mathbf{M}(H_2O)_xCl_y$, 2 mol of $AgCl$ was precipitated. What is the possible identity of the complex cation?

A $[\mathbf{M}(H_2O)_6]^{3+}$

B $[\mathbf{M}(H_2O)_5Cl]^{2+}$

C $[\mathbf{M}(H_2O)_4Cl_2]^{+}$

D $[\mathbf{M}(H_2O)_2Cl_4]^{+}$

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2019
2 hours

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 Write your answers in the spaces provided on this 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.	**Section A Marks**
1	**21**
2	**14**
3	**12**
4	**13**
5	**15**
Total	**75**

This question paper consists of **21** printed pages and **1** blank page.

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

1 This question explores the chemistry of transition metal complexes.

(a) Cobalt cations readily form complexes with ligands. Some of the cobalt complexes with their absorption frequencies are shown in Table 1.1. The absorption frequency is the frequency of light absorbed for each complex, and is proportional to the energy of light absorbed.

Table 1.1

Complex	**Absorption Frequency / cm^{-1}**
$[Co(CN)_6]^{4-}$	15300
$[Co(CN)_6]^{3-}$	33500
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200
$[Co(NH_3)_6]^{3+}$	22870

(i) State the electronic configuration of the cobalt cation in $[Co(CN)_6]^{3-}$.

…………………………………………………………………………………….[1]

(ii) Using the information in Table 1.1, state the relationship between the oxidation state of the metal cation and the absorption frequency of its complex.

……………………………………………………………………………………..

…………………………………………………………………………………….[1]

(iii) Stronger field ligands generate a *d* orbital splitting pattern with a larger energy gap when bonded to transition metal cations.

Using the information in Table 1.1, rank CN^-, H_2O and NH_3 in order of increasing ligand field strength.

…………………………………………………………………………………….[1]

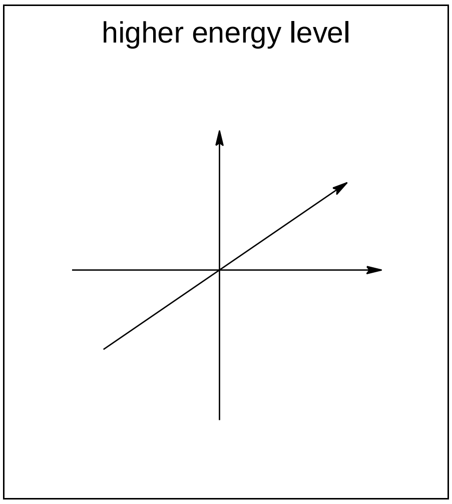
(iv) Hence, predict a value for the absorption frequency of $[Co(NH_3)_6]^{2+}$.

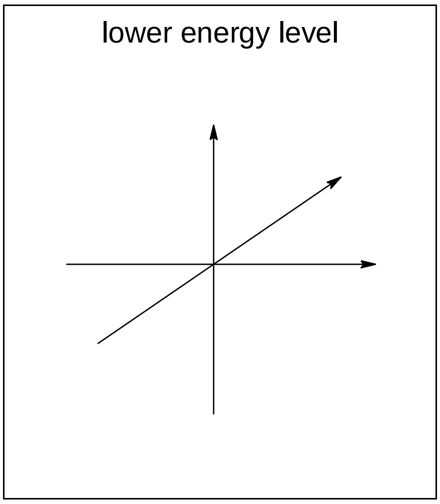
…………………………………………………………………………………….[1]

(b) In the presence of an octahedral ligand field, the 3*d* orbitals of cobalt are split into two energy levels.

(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

- a higher energy level,
- a lower energy level, in the presence of an octahedral ligand field.





[2]

(ii) Hence, explain why the 3*d* orbitals of cobalt are split into two energy levels in the presence of an octahedral ligand field.

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

……………………………………………………………………………………….[2]

(iii) In the presence of a tetrahedral ligand field, the ligands approach in between the axes.

Complete Fig 1.1 to show how the degenerate 3*d* orbitals of cobalt will split in a tetrahedral ligand field. Label all the orbitals in your diagram.

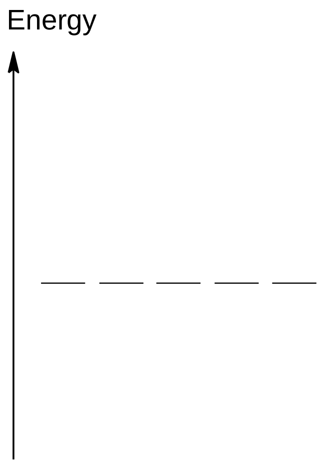


Fig 1.1

[2]

(c) Another cobalt complex, $[CoCl_6]^{3-}$ undergoes ligand exchange with CN^- ligands to form $[Co(CN)_6]^{3-}$ according to the following equilibrium.

$$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$$

The effect of pH on the concentration of $[Co(CN)_6]^{3-}$ formed is shown in the graph in Fig 1.2 .

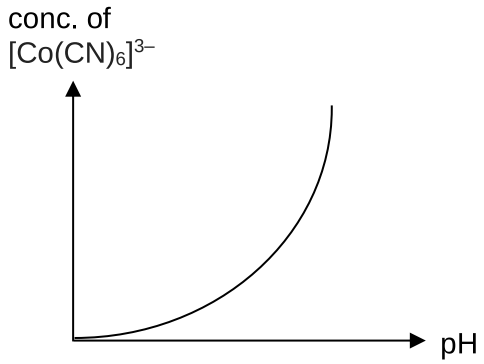


Fig 1.2

(i) Write an equation that describes the dissociation of the weak acid, HCN, in water.

…………………………………………………………………………………………..[1]

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(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph in Fig 1.2.

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

……………………………………………………………………………………….[2]

(iii) Explain why the Gibbs free energy change and enthalpy change for the forward reaction are approximately equal.

…………………………………………………………………………………………..

…………………………………………………………………………………………..

…………………………………………………………………………………………..

……………………………………………………………………………………….[1]

(iv) Hence deduce the sign of the enthalpy change of the forward reaction given that it is spontaneous.

…………………………………………………………………………………………..

……………………………………………………………………………………….[1]

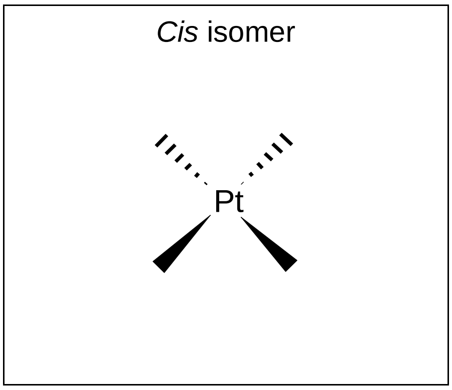
(d) Similar to organic compounds, transition metal complexes may exhibit stereoisomerism.

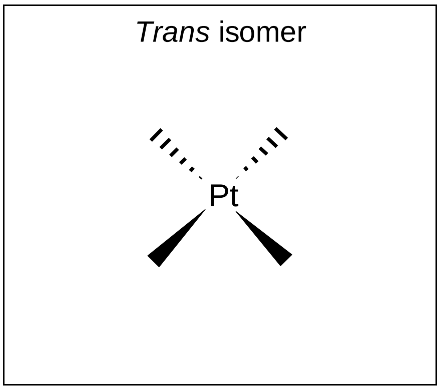
(i) For square planar complexes, *cis-trans* isomerism can be exhibited for $\mathbf{MA_2B_2}$ type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

cis and *trans* isomers are differentiated in the following way:

cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

$[Pt(Cl)_2(NH_3)_2]$ is a square planar complex. Complete the diagrams below to show the structures of its *cis* and *trans* isomers.





[1]

(ii) For any transition metal complex, enantiomerism is exhibited if it has:

- Mirror images that are non-superimposable and
- No internal plane of symmetry

Deduce if the *trans* isomer of $[Pt(Cl)_2(NH_3)_2]$ can exhibit enantiomerism.

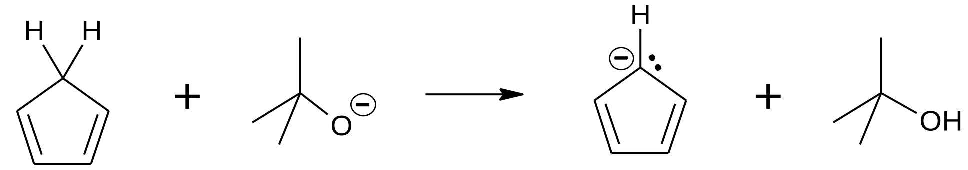
……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..[1]

(e) The cyclopentadienyl anion is a common ligand in transition metal complexes. This anion can be generated via the following reaction between tert–butoxide anion and cyclopentadiene.



Cyclopentadiene tert-butoxide cyclopentadienyl anion

An organic compound is considered aromatic if all of the following three criteria are met:

- it is a cyclic planar compound,
- it has a delocalised *π* electron system, and
- it has (4*n* + 2) *π* electrons, where *n* is an integer.

One such example is benzene.

(i) State the type of reaction that generates the cyclopentadienyl anion from cyclopentadiene.

……………………………………………………………………………………….[1]

(ii) Given that the cyclopentadienyl anion is aromatic, explain fully how it meets the three criteria stated above.

………………………………………………………………………………………..

………………………………………………………………………………………..

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………………………………………………………………………………………..

………………………………………………………………………………………..

………………………………………………………………………………………..

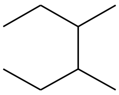
……………………………………………………………………………………….[3]

[Total: 21]

2 Halogenoalkanes are widely used commercially as they are important precursors for many organic synthesis.

(a) One method of synthesising halogenoalkanes is the free radical substitution of alkanes. For example, butane can be chlorinated in the presence of UV light.

However, this is not a preferred method of synthesising halogenoalkanes as there are multiple by–products. For example, one by–product of the monochlorination of butane is shown below.



3,4–dimethylhexane

(i) Draw the mechanism of the reaction between butane and chlorine that would result in the formation of 3,4–dimethylhexane. Show the movement of electrons by using suitable curly arrows and indicate any unpaired electron using a dot (•).

[3]

(ii) State the number of chiral centre(s) present on 3,4–dimethylhexane and the number of stereoisomers that are optically active.

Number of chiral centre(s) ……………………………….. [1]

Number of stereoisomers that are optically active …………………………..[1]

(b) One application of halogenoalkanes was the use of chlorofluorocarbons (CFCs) as refrigerants in the 20th century. However, CFCs have been replaced with hydrofluorocarbons (HFCs) due to their detrimental impact on the ozone.

CFCs produce radicals in the presence of UV light. For example, chlorodifluoromethane, $CHClF_2$, readily produces chlorine radicals in the stratosphere. These radicals speed up the depletion of the ozone layer.

HFCs, such as fluoroform, CHF_3, do not produce radicals in the presence of UV light.

With reference to the *Data Booklet*, explain why CHF_3 does not deplete the ozone layer whereas $CHClF_2$ does.

……………………………………………………………………………………………..

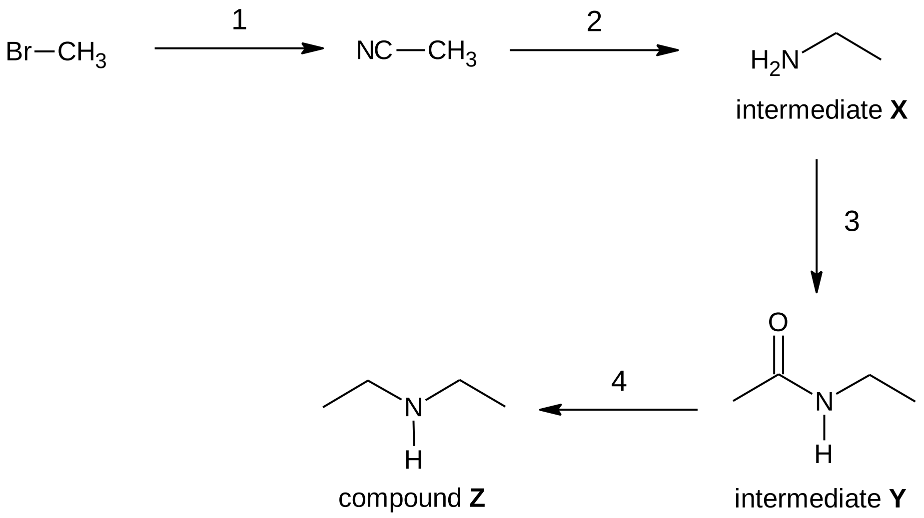
……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..[2]

(c) Halogenoalkanes also find their application as precursors in the synthesis of nitrogen–containing organic compounds. One such synthesis involving bromomethane is shown below.



(i) Draw a dot–and–cross diagram to show the bonding in CH_3CN and state the types of orbitals used to form the carbon–carbon bond in the molecule.

Types of orbitals used …………………………………………

[2]

(ii) State the type of reaction occurring in step 4 and the reagent(s) and condition(s) needed.

Type of reaction ………………………..…………………………..……. [1]

Reagent(s) and condition(s) ….……………………………………………….. [1]

(iii) Explain why ethanoic acid **cannot** be used in step 3 to form intermediate **Y**.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..[1]

(iv) Compare and explain the basicity of intermediate **X** and compound **Z**.

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……………………………………………………………………………………..

……………………………………………………………………………………..[2]

[Total: 14]

3 Brown iodine water is decolourised when warmed with ethanol in an alkaline medium. A series of 'clock' experiments were conducted to study the kinetics of this reaction. The time taken for the decolourisation of iodine in each experiment is found in Table 3.1.

Table 3.1

Expt	Volume of I_2(aq) / cm^3	Volume of ethanol / cm^3	Volume of NaOH (aq) / cm^3	Volume of deionised water / cm^3	Time taken, *t* / s
1	5	20	20	10	42
2	5	30	20	0	28
3	10	20	20	5	42

(a) **(i)** Describe another observable change that occurs as the reaction proceeds.

………………………………………………………………………………………..

……………………………………………………………………………………..[1]

(ii) Explain why the total volume of reaction mixture is kept constant.

………………………………………………………………………………………..

……………………………………………………………………………………..[1]

(iii) Given relative rate $\propto \frac{\text{volume of } I_2}{t}$, use this relationship to deduce the order of reaction with respect to [ethanol] and [iodine]. Explain your answer.

[2]

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(b) The clock method can also be used to study the comproportionation reaction between bromate(V) and bromide ions in acidic medium.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

A small, fixed amount of phenol and a few drops of litmus are used in every experiment. The time taken for the disappearance of the pink colouration is measured.

(i) Comment if the reaction is expected to occur via an elementary step.

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……………………………………………………………………………………..[1]

(ii) Using a suitable equation, explain the purpose of adding a small, fixed amount of phenol in every experiment.

…………………………………………………………………………………………..

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……………………………………………………………………………………..[2]

(c) The pH of a reaction mixture can be kept constant in a kinetics experiment using a suitable buffer. Phosphoric acid, H_3PO_4, can be used to prepare buffers of varying pH values as it has three pK_a values of 2.14, 7.20 and 12.37.

(i) State the components present in a phosphate buffer of pH 7.50.

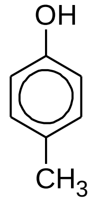
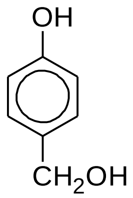
……………………………………………………………………………………..[1]

(ii) Write a suitable equation to show how the buffer system outlined in **(c)(i)** can resist change in pH when a small amount of OH^- is added.

……………………………………………………………………………………..[1]

(d) Two physical properties of two substituted phenols are shown in Table 3.2.

Table 3.2

	p–cresol	4–hydroxybenzyl alcohol
Structure		
pK_a	10.3	9.82
Boiling point / °C	202	252

Suggest a reason for the difference in each property.

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……………………………………………………………………………………………[3]

[Total: 12]

4 Methanal reacts with propene to form an organic product **A**.

(a) The mechanism for the formation of **A** is shown in Fig 4.1.

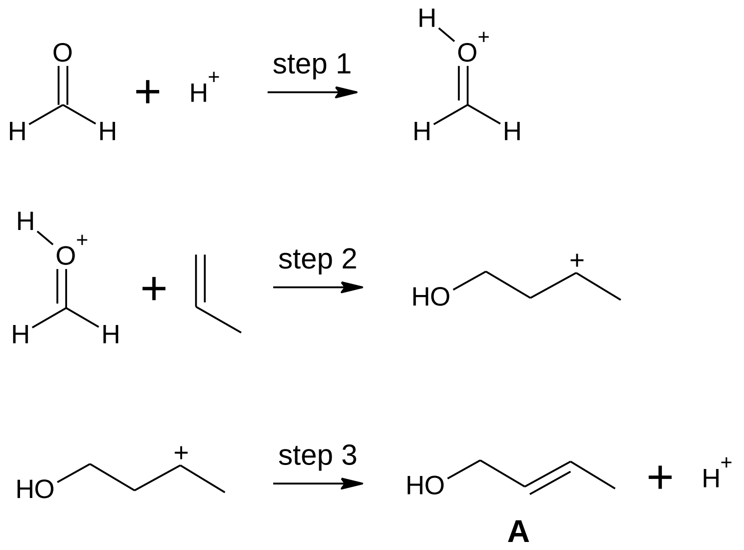

Fig. 4.1

(i) Deduce whether propene is acting as an electrophile or a nucleophile in step 2. Explain your answer.

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……………………………………………………………………………………..[1]

(ii) Complete Fig 4.2 using curly arrow(s) to show the movement of electron pair(s) for step 2.

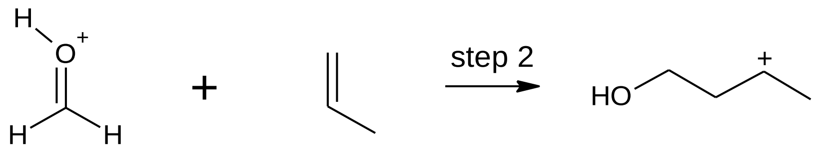

Fig. 4.2

[1]

(iii) In step 2, intermediate **B** is produced rather than **C**.

Suggest an explanation for the preferential production of intermediate **B**.

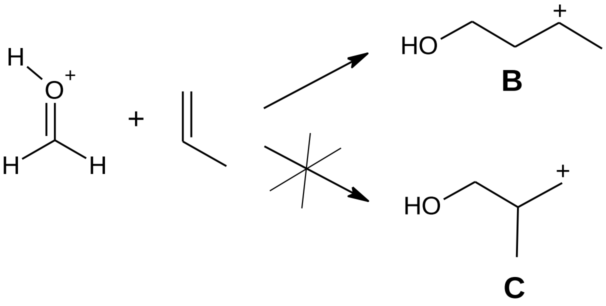

Fig. 4.3

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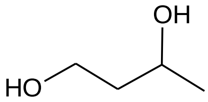
……………………………………………………………………………………………[2]

(iv) Step 3 may result in three isomeric organic products. Draw the displayed formula of the organic product which is a constitutional isomer of **A**.

[1]

(b) The reaction between methanal and propene under a different set of conditions gives molecule **D** with the following structure.



It can also be made from propene in the 4-step process shown in Fig 4.4.

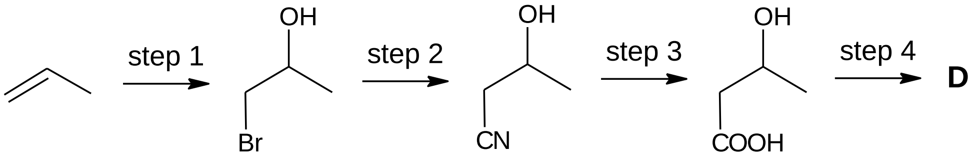


Fig. 4.4

(i) Name the product formed in step 1.

………………………………………………..……………………………..[1]

(ii) State the reagents and conditions needed for steps 2 and 3.

step 2 ……………………………………………………………………………..[1]

step 3 …………………………………………………………………...…………[1]

(iii) Step 4 is a reduction reaction. Write an equation for step 4 using [H] to represent the reducing agent.

[1]

(c) Molecule **E** has molecular formula $C_5H_{10}O_2$.

It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

(i) Suggest **two** structures of **E** that are consistent with the information provided.

[2]

(ii) The formation of **E** involves the nucleophilic attack of methanal on intermediate **B**.

Complete Fig 4.5 using curly arrow(s) to show the movement of electron pair(s) for this nucleophilic attack.

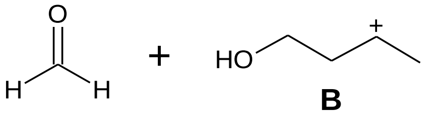


Fig. 4.5

Hence deduce the likely structure of **E** from your answer in **(c)(i)**. Explain your reasoning.

E

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..[2]

[Total: 13]

5 **(a)** **R**, **T**, **U** and **V** are consecutive elements in the third period of the Periodic Table. Among these four elements, **T** has the highest melting point and **U** has the highest first ionisation energy.

(i) Identify element **T**.

……………………………………………………………………………………………[1]

(ii) The oxides of elements **T** and **U** can be obtained when the elements are burned in excess oxygen. The oxides of **T** and **U** have melting points of 1710 °C and 340 °C respectively.

Explain briefly the difference in melting points between these oxides.

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……………………………………………………………………………………………..

……………………………………………………………………………………………[2]

(iii) Describe the reactions, if any, of the oxides of elements **R** and **V** with water. Include the approximate pH value of any resulting solution formed.

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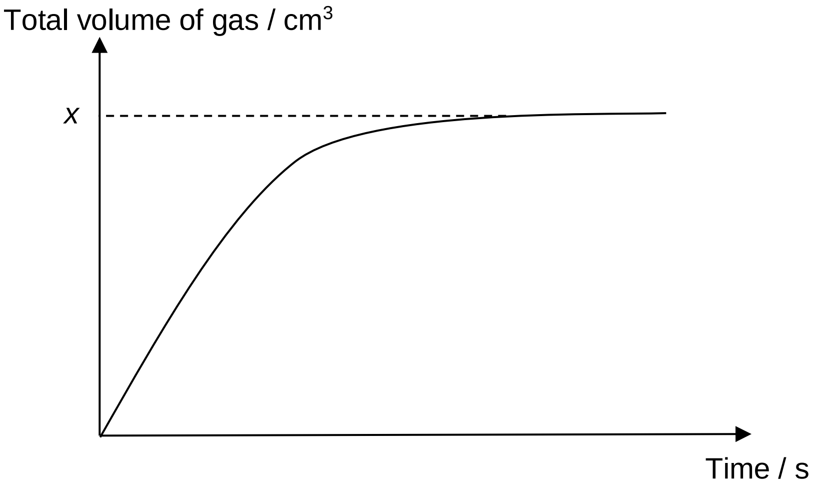
……………………………………………………………………………………………[2]

(b) Barium and magnesium form iodate(V) compounds, $Ba(IO_3)_2$ and $Mg(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Write a balanced equation, with state symbols, for the thermal decomposition of $Mg(IO_3)_2$.

…………………………………………………………………………………………………[1]

The graph below shows the total volume of gas collected over time when 0.1 mol of $Mg(IO_3)_2$ is heated.



(ii) Sketch, on the same axes above, the graph that would be obtained when 0.1 mol of $Ba(IO_3)_2$ was heated at the same temperature till no further change was observed.

[1]

(iii) Explain the shape of the graph that you have drawn for **(b)(ii)**.

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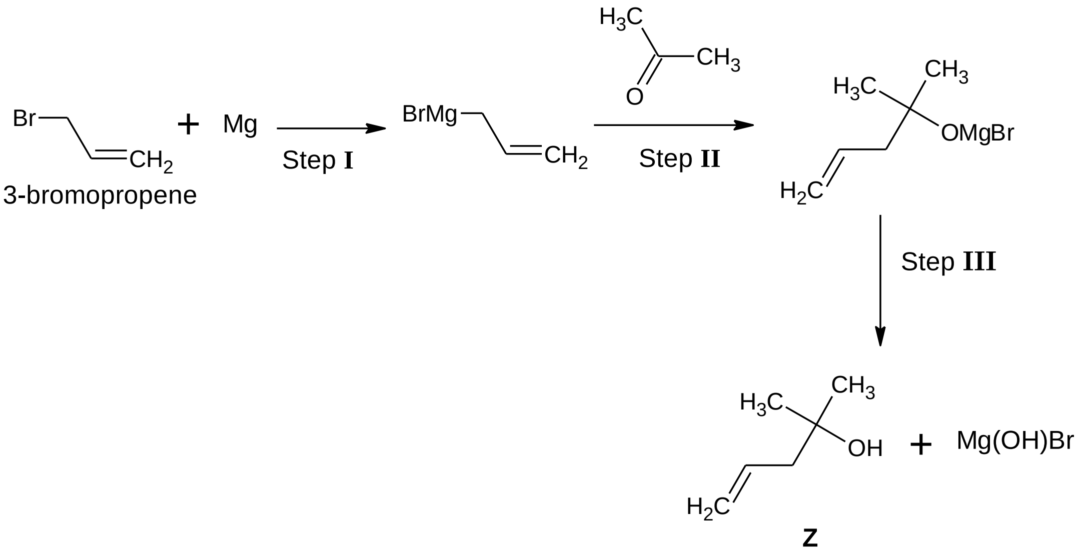
…………………………………………………………………………………………………[3]

(c) Grignard reagents, RMgX, are organo-magnesium halides derived from an alkyl halide, RX, and magnesium.

The use of a Grignard reagent in the conversion of 3-bromopropene to compound **Z** is given below.



(i) The alkyl group in RMgX behaves like an anion, R^-, and is a strong Lewis base.

Explain why propene is formed as a side product in both steps I and II if both reactions are **not** carried out under anhydrous conditions.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[1]

(ii) Suggest the type of reaction occurring in steps II and III.

Step II ……………………………………………………………………………[1]

Step III ……………………………………………………………………………[1]

(iii) A small amount of 3-bromopropene, propanone and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish 3-bromopropene from the other two compounds. State what you would observe.

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…………………………………………………………………………………………..[2]

[Total: 15]

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Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Free Response

25 September 2019
2 hours

Additional Materials: Data Booklet
Answer Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Write your answers on the separate answer booklet 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 page.
[Marks will be deducted if you fail to do so.]
6 Do not use staples, paper clips, glue or correction fluid.

Section A

7 Answer **all** questions.

Section B

8 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.

Section A

Answer **all** the questions from this section.

1 To facilitate better plant growth, there is widespread use of fertilisers and soil additives in the agricultural sector.

(a) Agricultural lime is a soil additive used to increase soil pH so as to facilitate uptake of plant nutrients such as nitrogen and phosphorous. It is usually made up of a combination of calcium carbonate and magnesium carbonate.

A manufacturer claims that a 2.00 g sample of agricultural lime contains 92 % calcium carbonate (M_r = 100.1) and 8 % magnesium carbonate (M_r = 84.3) by mass.

To verify the manufacturer's claim, the following steps were carried out:

Step 1 The solid carbonate mixture was dissolved in 250 cm^3 of 0.25 mol dm^{-3} hydrochloric acid.

Step 2 A 25 cm^3 aliquot of this resultant solution was titrated with 0.14 mol dm^{-3} potassium hydroxide.

It was found that 12.50 cm^3 of potassium hydroxide was required for complete neutralisation.

(i) Based on the manufacturer's claim of 92 % calcium carbonate and 8 % magnesium carbonate by mass, calculate the theoretical amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

(ii) Use the information above to calculate the amount of HCl that reacted with the carbonate mixture in step 1.

[2]

(iii) The manufacturer's claim is considered valid if the difference between the actual and theoretical total amount of carbonate present in the sample is less than 0.0010 mol.

Using your answers in **(a)(i)** and **(a)(ii)**, determine if the manufacturer's claim is valid.

[2]

(iv) When solid magnesium chloride is dissolved in water, it produces a slightly acidic solution of pH 6.5.

Using appropriate equation(s), explain the above observation.

[2]

(v) However, the resultant solution is neutral when solid calcium chloride is dissolved in water.

By quoting relevant values from the *Data Booklet*, explain why a solution of calcium chloride is neutral while a solution of magnesium chloride is slightly acidic.

[3]

(b) Nitrogen fertilisers are also important in enhancing the growth of plants. Almost all nitrogen fertilisers are produced from ammonia, which in turn, is manufactured in the Haber Process. This process combines nitrogen and hydrogen gas to form ammonia according to the following equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State how the percentage yield of ammonia will change with increasing pressure.

[1]

(ii) N_2 and H_2 was introduced into an enclosed vessel at 300 °C. The initial partial pressures of N_2 and H_2 were 2 atm and 3 atm respectively. After an equilibrium has been established, the total pressure in the vessel was 4.7 atm.

Calculate the value of K_p at 300 °C, stating its units.

[3]

(iii) 1 atm of N_2 was added to the equilibrium mixture in **(b)(ii)** at 300 °C and time was allowed for a new equilibrium to be established. State and explain how the K_p value at this point will compare to that in **(b)(ii).**

[1]

[Total: 15]

2 Mandelic acid, $C_6H_5CH(OH)COOH$, is a white crystalline solid that is soluble in water.

(a) Benzaldehyde is a useful starting material for the preparation of mandelic acid.

Suggest a two–step synthesis of mandelic acid from benzaldehyde, stating clearly the reagents and conditions used and the structure of the intermediate.

[3]

(b) Suggest how you would distinguish between aqueous solutions of mandelic acid and nitric acid of the same concentration by means of a **physical** method.

Explain your reasoning.

[3]

(c) **(i)** 20 cm^3 of 1.0 mol dm^{-3} mandelic acid solution was titrated with 2.0 mol dm^{-3} aqueous sodium hydroxide. Calculate the concentration of the salt, sodium mandelate, formed at equivalence point.

[1]

(ii) Hence calculate the pH of the solution at equivalence point, given pK_a of mandelic acid is 3.41.

[2]

(iii) Use your answer in **(c)(ii)** to identify a suitable indicator from Table 2.1 for the titration. Explain your choice.

Table 2.1

Indicator	pH range
Methyl red	4.2 – 6.3
Phenolphthalein	8.2 – 10.0
Titan yellow	12.0 – 13.0

[2]

(d) **(i)** To another 20 cm^3 sample of 1.0 mol dm^{-3} mandelic acid solution, excess sodium carbonate was added and the gas liberated was collected in a gas syringe at 50 °C and atmospheric pressure.

Calculate the volume of gas you would expect to obtain at the end of the reaction.

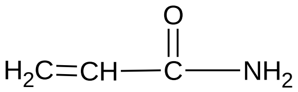
[2]

(ii) The volume of gas collected was found to be smaller than the calculated value in **(d)(i)**. Assuming that no gas escaped in the experiment, suggest **two** reasons for the discrepancy.

[2]

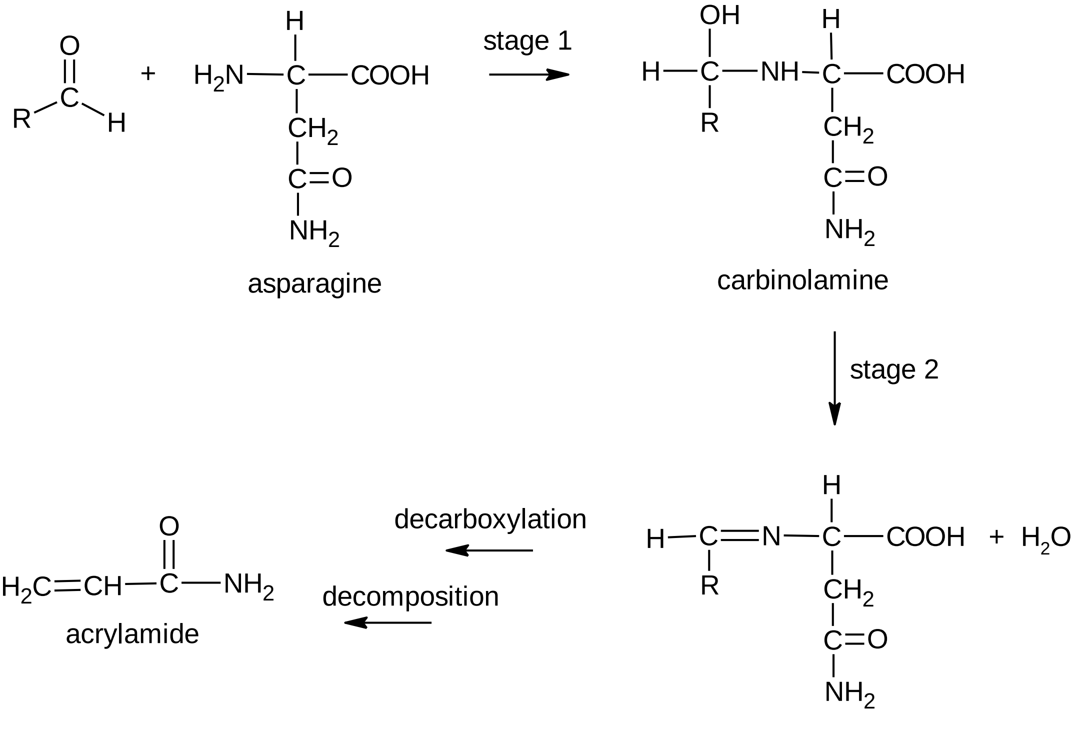
[Total: 15]

3 **(a)** High levels of acrylamide, which is harmful to human health, are produced when starchy foods are heated at high temperature.


$H_2C{=}CH{-}C({=}O){-}NH_2$

acrylamide

The formation of acrylamide begins with the reaction between an aldehyde and asparagine, $H_2NCH(CH_2CONH_2)COOH$. This process involves the formation of carbinolamine and a Schiff base.

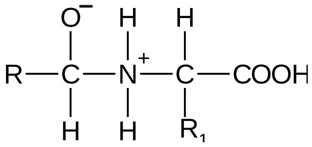


(i) State the type of reaction occurring in stages 1 and 2 respectively.

[2]

The mechanism for stage 1 is thought to involve the following three steps.

step 1 Nucleophilic attack of α–NH_2 of asparagine on carbonyl carbon atom to form the following intermediate where R_1 is –CH_2CONH_2.



step 2 The intermediate is deprotonated by a water molecule, breaking the N–H bond.

step 3 The protonated water molecule from step 2 then transfers the proton to the negatively charged oxygen to form carbinolamine.

(ii) Using the information above, draw the mechanism for stage 1 by showing relevant lone pairs of electrons, dipoles and curly arrows to represent the movement of electron pairs.

[3]

(iii) The experiment was repeated with the use of an aparaginase enzyme which hydrolyses asparagine, $H_2NCH(CH_2CONH_2)COOH$ to aspartic acid, $H_2NCH(CH_2COOH)COOH$. The level of acrylamide, $CH_2{=}CHCONH_2$ in food products is reduced by 99 %. Suggest a reason why this is so.

[1]

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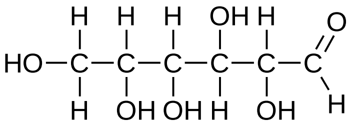
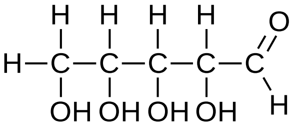
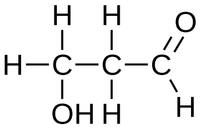
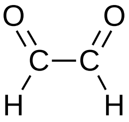
(b) Several aldehydes can be found in starchy foods. Fixed amount of each aldehyde was heated with asparagine. The mass of acrylamide formed from each aldehyde is shown in Table 3.1 below.

Table 3.1

Aldehyde	Structure	Mass of acrylamide (μg)
glucose		1454
ribose		2425
glyceraldehye		2669
glyoxal		3936

(i) In solution, glucose molecules can exist in an isomeric cyclic form. The oxygen of the hydroxyl group on carbon number 5 joins to the carbonyl carbon atom and the total number of hydroxyl groups remain unchanged. The mechanism for the formation of the isomeric cyclic form is similar to that for stage 1 in **(a)**.

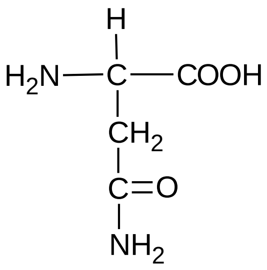
Draw the structural formula of glucose in the isomeric cyclic form.

[1]

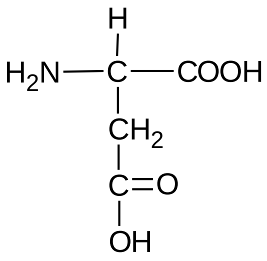
(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

[2]

(c) The structures of two amino acids, asparagine and aspartic acid, are given below.



asparagine



aspartic acid

(i) Suggest a simple chemical test to distinguish between asparagine and aspartic acid.

[2]

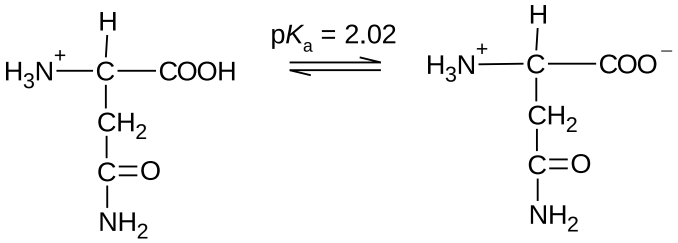
(ii) The three pK_a values associated with aspartic acid are 1.88, 3.65 and 9.60.

Suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 3
- pH 7

[2]

(iii) The following equilibrium exists in an aqueous solution of asparagine at pH 2.02.



protonated cation

zwitterion

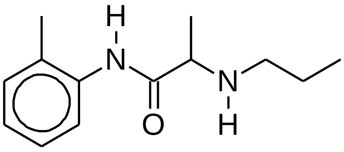
Calculate the ratio of the concentration of asparagine zwitterion to the concentration of the protonated cation when the pH of the solution is 3.10.

You may represent the cation as HA and the zwitterion as A^- in your working.

[2]

[Total: 15]

4 **(a)** Prilocaine is a local anaesthesia used in dentistry.



prilocaine

It can be synthesised by reacting propylamine, $CH_3CH_2CH_2NH_2$, with a suitable alkyl halide.

(i) Draw the structure of the alkyl halide.

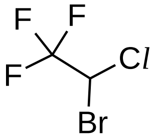
[1]

Propylamine can be formed from bromoethane in 2 steps.

(ii) Suggest the reagents and conditions needed for each step.

[2]

(b) Halothane is a general anaesthetic given by inhalation.



halothane

0.1 mol of (+)–halothane is warmed with 0.1 mol of aqueous sodium hydroxide.

(i) State which halogen atom reacts. Give a reason for your answer.

[1]

The progress of the reaction can be followed using a polarimeter as the reactant rotates plane–polarised light while the resulting mixture is optically inactive.

(ii) Draw the mechanism for the reaction between halothane and sodium hydroxide.

[2]

(iii) Considering your answer to **(b)(ii)**, suggest a reason why it is unexpected for halothane to undergo substitution via the mechanism drawn.

[1]

(c) The presence of alkyl halides can be verified by warming the sample with aqueous sodium hydroxide, followed by addition of nitric acid and lastly silver nitrate.

A student used sulfuric acid instead of nitric acid, leading to the formation of silver(I) sulfate precipitate, Ag_2SO_4.

(i) Explain how the formation of silver(I) sulfate affects the test.

[1]

(ii) Calculate the solubility of silver(I) sulfate given that its K_{sp} value is 1.2×10^{-5}.

[2]

(iii) State and explain how the solubility of silver(I) sulfate is affected by the addition of aqueous ammonia.

[1]

(d) Table 4.1 contains thermochemical information related to silver(I) sulfate.

Table 4.1

Enthalpy change of formation of silver(I) sulfate	-717 kJ mol^{-1}
Enthalpy change of formation of gaseous sulfate anions	$+126$ kJ mol^{-1}
Enthalpy change of atomisation of silver	$+284$ kJ mol^{-1}
Enthalpy change of hydration of silver cations	-473 kJ mol^{-1}
Enthalpy change of hydration of sulfate anions	-1035 kJ mol^{-1}

(i) Using relevant information from the *Data Booklet* and Table 4.1, draw an energy cycle to determine the lattice energy of silver(I) sulfate.

[3]

(ii) Using your answer to **(d)(i)** and appropriate data in Table 4.1, calculate the standard enthalpy change of solution for silver(I) sulfate.

[1]

[Total: 15]

Section B

Answer **one** question from this section.

5 **(a)** Fig 5.1 shows a sequence of reactions involving acrylic acid, the simplest unsaturated carboxylic acid.

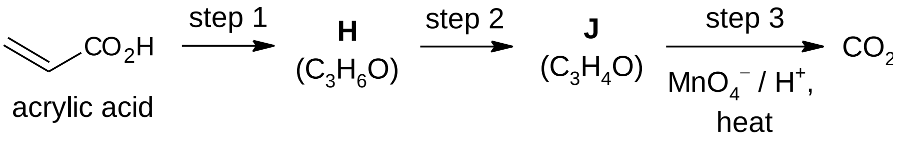


Fig. 5.1

(i) Compound **H** effervesces with sodium and compound **J** reacts with 2,4–dinitrophenylhydrazine.

Suggest structures for compounds **H** and **J**.

[2]

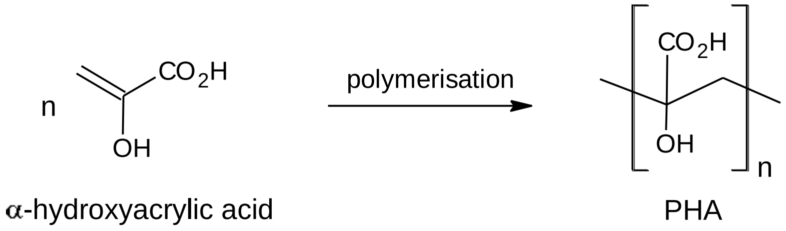
(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

[2]

(iii) Compound **G**, an isomer of acrylic acid, is neutral and does not react with Tollens' reagent. Deduce the structure of **G**.

[1]

(b) α–hydroxyacrylic acid undergoes addition polymerisation to give a polymer, PHA.



(i) Suggest and explain the relative acidities of α–hydroxyacrylic acid and acrylic acid, CH_2=$CHCO_2H$.

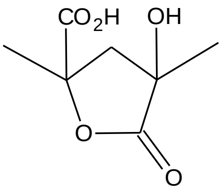
[2]

(ii) Studies suggests that PHA interacts with divalent metal cations such as calcium and magnesium under alkaline conditions.

Suggest and explain the type of interaction that is likely to exist between PHA and the metal cations in alkaline medium.

[2]

(c) PHA can form intramolecular lactone rings between –COOH and –OH groups on adjacent repeat units. Part of the structure of PHA with an intramolecular ring is shown below.



(i) State the type of reaction occurring in the formation of the lactone ring.

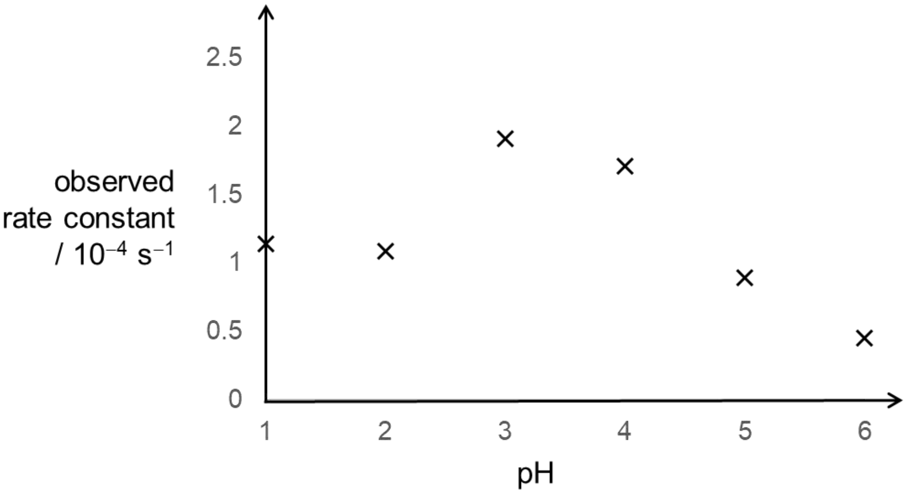
[1]

A series of experiments were carried out to investigate the rate of the lactone ring build–up of PHA as a function of pH at constant temperature.

The rate equation for the reaction is given as follows.

$$\text{rate} = k[\text{PHA}]^{m}[\text{H}^{+}]^{n}$$

The reaction was observed to follow pseudo first order kinetics with respect to PHA and the following graph of the observed rate constant against pH was obtained.



(ii) Suggest how the pseudo first order kinetics with respect to PHA was achieved experimentally.

[1]

(iii) From the graph, identify the pH range for which the value of *n*, order of reaction with respect to H^+, is zero.

Explain your reasoning.

[2]

(iv) At a certain pH that lies within the range identified in **(c)(iii)**, the observed rate constant was found to be 1.14×10^{-4} s^{-1}. Calculate the time taken for 75 % of lactone rings to be formed at this pH.

[2]

(v) Hence sketch a graph of percentage of lactone ring formation against time, assuming that the reaction goes to completion. Label clearly how the percentage of lactone changes with time.

[2]

(d) The PHA samples used in the kinetic study was prepared by dilution of the reagent solution with heavy water, D_2O.

[Deuterium, D = ^2H]

(i) Suggest, with reasoning, how the first ionisation energy of deuterium would compare with that of hydrogen.

[1]

(ii) Beams of D^+ and H^+ particles, at the same speed, were passed through an electric field.

Explain, qualitatively, how the angle and direction of deflection of the two beams would compare.

[1]

(iii) Water enriched in heavier oxygen–18 isotope, $H_2{}^{18}O$, is also commercially available.

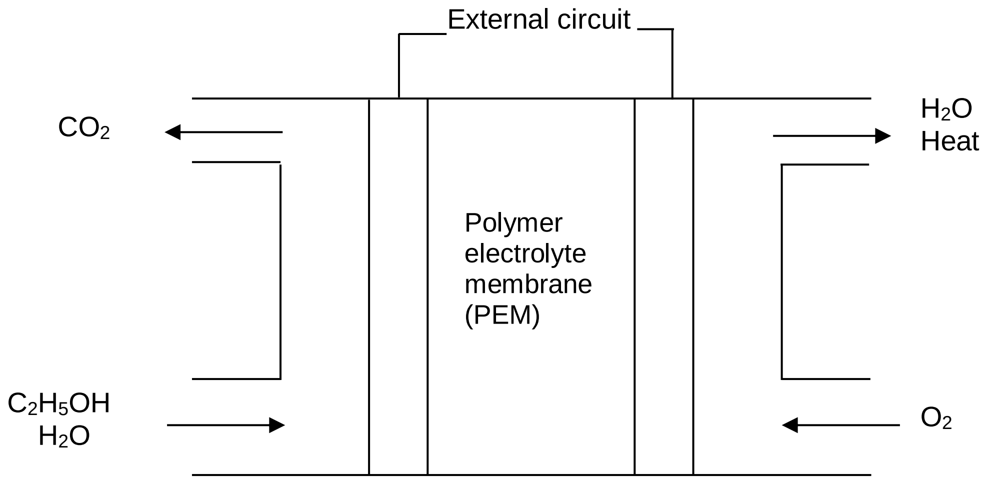
Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen–18 isotope.

[1]

[Total: 20]

6 **(a)** The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

Direct–ethanol fuel cell or DEFC is one common example of fuel cells where ethanol is fed directly into the cell to produce carbon dioxide. Hydrogen ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water, while the electrons travel through the external electrical circuit to generate electrical power.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

[2]

(ii) The cell is capable of producing an e.m.f. of +1.62 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/C_2H_5OH electrode reaction.

[1]

(iii) Pyrogallol solution is an organic compound that absorbs oxygen efficiently. Explain, qualitatively, the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

[2]

(iv) Suggest a possible advantage of using the DEFC compared to a hydrogen fuel cell.

[1]

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process is an aqueous solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolytic cell.

(i) Write the half–equation for the reaction occurring at the cathode.

[1]

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current with density of 3.5×10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[2]

(c) Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis, both for fundamental research and industrial manufacturing.

When alkaline potassium manganate(VII) is added to a primary alcohol, the purple solution first becomes dark green and then produces a brown precipitate.

(i) State the identities of the dark green solution and the brown precipitate. You may find the use of *Data Booklet* to be relevant.

[1]

When acidified potassium manganate(VII) is added to a secondary alcohol, the purple solution decolourises. Propan–2–ol reacts with acidified potassium manganate(VII) to yield propanone, according to the **unbalanced** equation as shown below.

$$CH_3{}^{a}CH(OH)CH_3 + MnO_4^- \rightarrow CH_3{}^{b}COCH_3 + Mn^{2+}$$

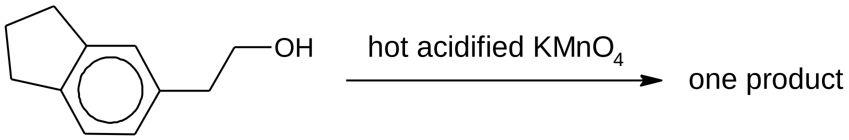
(ii) State the oxidation number of ${}^{a}C$ and ${}^{b}C$ respectively.

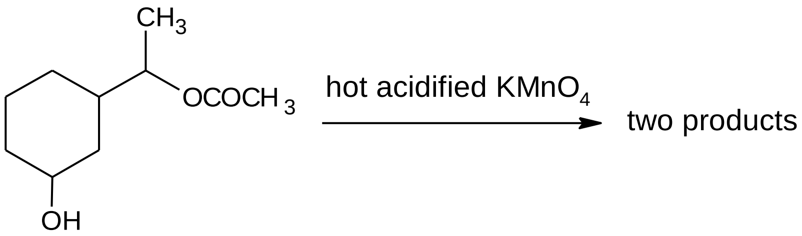
[1]

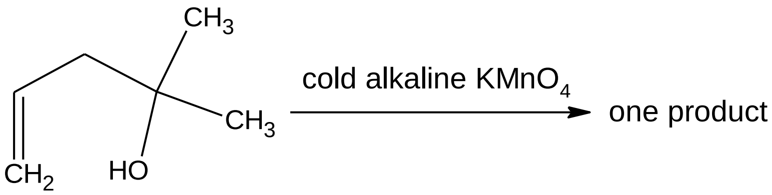
(iii) Hence, or otherwise, determine the reacting mole ratio of propan–2–ol to potassium manganate(VII).

[1]

(iv) Predict the organic products of the following reactions with $KMnO_4$(aq).

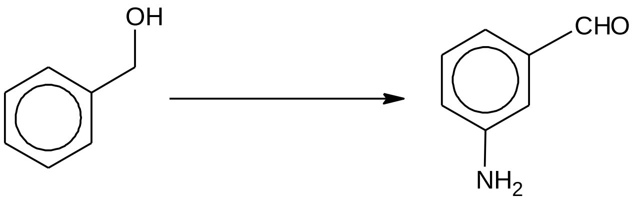






[4]

(d) Devise a synthetic pathway (in no more than 3 steps) for the following conversion.



In your answer, state the reagents and conditions required for each step as well as the structure of any intermediates formed.

[4]

[Total:20]

Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2019
Year 6

H2 CHEMISTRY

Paper 4 Practical

9729/04
27 August 2019
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 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.

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	**17**
2	**10**
3	**14**
4	**14**
Total	**55**

This question paper consists of **19** printed pages and **1** blank page.

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

1 Determination of acid concentration and enthalpy change of neutralisation using calorimetry

When an acid is added into an alkali, an exothermic reaction takes place and the temperature of the mixture increases. Maximum heat is given out when stoichiometric amounts of H^+ and OH^- are added together.

FA 1 is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HCl, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4
FA 2 is 2.00 mol dm^{-3} sodium hydroxide, NaOH

In this question, you are to follow the neutralisation of known volumes of **FA 2**, NaOH, by measuring the highest temperature obtained as different volumes of **FA 1** are added.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following.

- the value of ***y***, concentration of the acids present in **FA 1**
- the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(a) Method

1 Fill the burette with **FA 2**.
2 Support the Styrofoam cup in a 250 cm^3 glass beaker.
3 Run 20.00 cm^3 **FA 2** from the burette into the Styrofoam cup. Stir and measure the temperature of this **FA 2**.
4 Measure 20 cm^3 **FA 1** in a measuring cylinder.
5 Tip the **FA 1** in the measuring cylinder into the **FA 2** cup, stir and record the maximum temperature obtained in the reaction.
6 Rinse and carefully dry the Styrofoam cup.
7 Repeat **steps 1 to 6** three more times, each time using 20.00 cm^3 of **FA 2.** Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 1** respectively in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 1** which will allow you to investigate more precisely the volume of **FA 1** that produces the highest temperature rise when added to 20.00 cm^3 of **FA 2**.

Record your results in an appropriate format in the next page. Record all measurements of volume, temperature and temperature change, ΔT.

(i) **Experimental results**

[5]

(ii) Plot ∆***T*** (*y*–*axis*) against volume of **FA 1** (*x*–*axis*) on the grid below.
Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

[3]

(iii) Read from the graph the maximum temperature change, $\Delta \boldsymbol{T}_{\text{max}}$, and the volume, $\boldsymbol{V}_{\text{neut}}$, of **FA 1** needed to obtain this value. Record these values in the spaces provided below.

maximum temperature change, $\Delta \boldsymbol{T}_{\text{max}}$ = …………………..°C

volume of **FA 1** used at $\Delta \boldsymbol{T}_{\text{max}} = \boldsymbol{V}_{\text{neut}}$ = ………………. cm^3

[1]

(b) Use your results from **(a)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**.

concentration of hydrogen ions in **FA 1** = …………………………………

[1]

(ii) Hence, the value of ***y***.

value of ***y*** is …………………………………..

[1]

(iii) the heat change for the reaction and hence the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

[Assume that 4.18 J of energy is needed to raise the temperature of 1 g of the solution by 1 K]

[4]

(c) A student suggested using a burette rather than a measuring cylinder to measure the volume of **FA 1** to improve the precision in volume measurement. However, he was advised not to do so by his teacher.

Suggest a disadvantage of using a burette and explain how the calculated ΔH_{neut} would be affected if volume of **FA 1** had been added from a burette.

Disadvantage:

…………………………………………………………………...……………………………[1]

Explanation:

…………………………………………………………………………………………...…...…...……

…………………………………………………………………………………………...…...…...……

…………………………………………………………………………………………...…...…...……

…………………………………………………………………………………………..……………..[1]

[Total:17]

2 Determination of calcium ion concentration using complexometric titration

The calcium content of milk and tap water and the amount of calcium carbonate in various solid samples can be determined using complexometric titrations.

This method uses ethylenediaminetetraacetic acid, EDTA, which forms a complex with calcium ions in a 1:1 ratio. A blue dye called Patton–Reeder indicator is used to identify the end–point. The dye forms a pink complex with calcium ions. As this complex is less stable than the EDTA complex, the dye is displaced by EDTA as the titration proceeds. The solution turns blue at the end–point due to the uncomplexed dye.

FA 3 is a brand of milk.

In **2(a)**, you perform titrations to determine the calcium content of milk.

You are also provided with
FA 2, 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 4, 0.0170 mol dm^{-3} EDTA
Patton–Reeder indicator

As EDTA is harmful to the environment, **FA 4** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

(a) **(i)**

1. Fill the burette with **FA 4**.

2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 250 cm^3 conical flask.

3. Using appropriate measuring cylinders, add 36.0 cm^3 of deionised water then 8.0 cm^3 of **FA 2** into the conical flask. Swirl and allow the solution to stand for about 2 minutes.

4. Add half a spatula of Patton–Reeder indicator into the conical flask and swirl the mixture to dissolve the indicator. The mixture is *pink* at this point.

5. Run **FA 4** from the burette into the conical flask. The end–point is reached when the mixture *loses all trace of purple and turns blue*. As the colour change is gradual, you will find it helpful to compare against the original and / or final colour of another sample.

6. At the end of the experiment, contents of the conical flask should be disposed in the waste bottle.

7. Record your titration results, to an appropriate level of precision, in the space provided on the next page.

Titration results

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{\textbf{FA 4}}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{\textbf{FA 4}}$ = ………………. cm^3
[2]

(b) **(i)** Calculate the concentration of calcium ions present in **FA 3** using your answer in **(a)(ii)**.

concentration of calcium ions in **FA 3** = …………………………………
[1]

The nutritional label on the packaging states that this brand of milk contains 200 mg of calcium per 200 cm^3 serving.

[1 g = 1000 mg]

(ii) Use your results from **(b)(i)** to comment if your titration results supports the claim on the nutritional label.

[A_r: Ca, 40.1]

[3]

(c) Trace amounts of magnesium ions present in milk affects the accuracy of this experiment as magnesium ions also readily form a complex with EDTA.

Explain how step 3 of the procedure prevents this error.

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…………………………………………………………………………………………...…....…...….[1]

[Total: 10]

3 Investigation of some inorganic reactions

FA 5 is an aqueous solution containing two cations.

Carry out the following tests described in Table 3.1 and carefully record your observations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there are no observable change, write **no observable change**.

Table 3.1

(a)

	tests	observations
(i)	Add 1 cm depth of **FA 5** to a test–tube. Add an equal volume of aqueous sodium nitrite.	
(ii)	Add 2 cm depth of **FA 5** to a test–tube. Add 2 pieces of zinc into the test–tube. Warm the test–tube gently. Leave to stand until no further change is seen.	
While waiting, continue with the next tests		
(iii)	Add 1 cm depth of **FA 5** to a test–tube. Add **FA 2** slowly, with shaking, until no further change is seen. Filter the mixture. To 1 cm depth of the filtrate, add nitric acid dropwise until no further change is seen.	
(iv)	Add 1 cm depth of **FA 5** to a test–tube. Add aqueous ammonia slowly with shaking, until no further change is seen. Filter the mixture.	

(v)	To 1 cm depth of the filtrate from **(iv)**, add 1 cm depth of aqueous $EDTA^{4-}$ from the small vial with shaking. *The mixture at the end of this test should be disposed in the waste bottle.*	
(vi)	Add 4 cm depth of **FA 5** to a test–tube. Add 2 cm depth of aqueous sodium carbonate. The total depth of the mixture should not exceed half the test–tube. Shake well. Leave to stand for a few minutes. Filter the resultant mixture.	
(vii)	Transfer the residue from **(vi)** to a boiling tube. Heat gently then strongly until no further change is seen.	

[7]

(b) Consider your observations in Table 3.1.

(i) State the identity of the two cations present in **FA 5**.

………………… and …………………

[1]

The wavelengths and corresponding colours of visible light is shown in Figure 3.1.

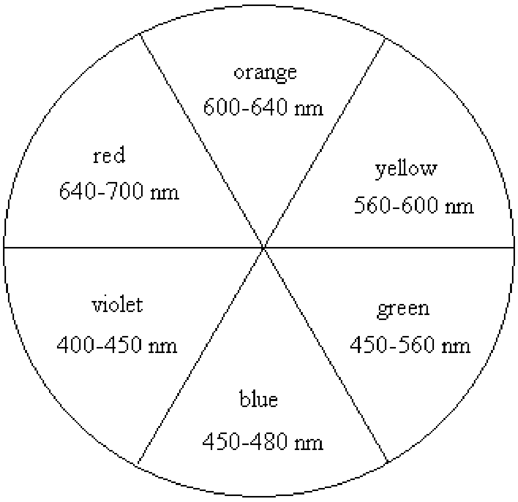

Fig. 3.1

(ii) In terms of the magnitude of d–orbital splitting, account for the colour change observed in **(a)(i)**.

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……………………………………………………………………………………………..…..... [2]

In **(a)(v)**, a ligand exchange occurs with hexadentate EDTA$^{4–}$.

(iii) Write a balanced equation for the ligand exchange reaction in **(a)(v)**.

……………………………………………………………………………………………..…..... [1]

(iv) Each donor atom on EDTA$^{4–}$ binds to the metal centre with similar strength as an ammonia molecule and a water molecule.

Using this information and your answer to **(b)(iii)**, estimate the enthalpy change for the reaction in **(a)(v)** and suggest why it occurs spontaneously.

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……………………………………………………………………………………………..…..... [2]

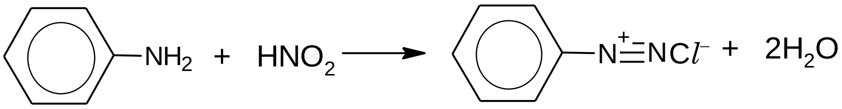
(v) Write a balanced equation for the reaction occurring in **(a)(vii)**.

……………………………………………………………………………………………………….….... [1]

[total: 14]

4 Planning

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting $NaNO_2$ with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

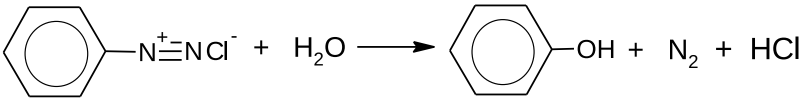
1. 3.25 cm^3 of phenylamine was placed in a 500 cm^3 volumetric flask.
2. A mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.
4. Solid $NaNO_2$ was dissolved in 30 cm^3 of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm^3 with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

(a) Suggest why $NaNO_2$ solution was added *slowly and carefully* in step 4.

………………………………………………………………………………………………..…………………

………………………………………………………………………..……………………………….[1]

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm^3 of solution **B** was raised to room temperature at constant pressure.

(b) **(i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm^3 of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm^{-3}; molar volume of gas at room temperature and pressure = 24.0 dm^3 mol^{-1}]

[3]

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40 °C.

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, V after time, t, is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final}, is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

(ii) Explain the significance of $V_{final} - V$.

……………………………………………………………………………………………..………

…………………………………………………………………………..……………………[1]

(iii) Sketch, on Fig 4.1, the graph of $V_{\text{final}} - V$ against time you would expect to obtain if the order of reaction with respect to $[C_6H_5N_2^+Cl^-]$ is one.

Fig 4.1

[2]

The volume of nitrogen produced was collected using the modified apparatus as shown in Fig. 4.2 below.

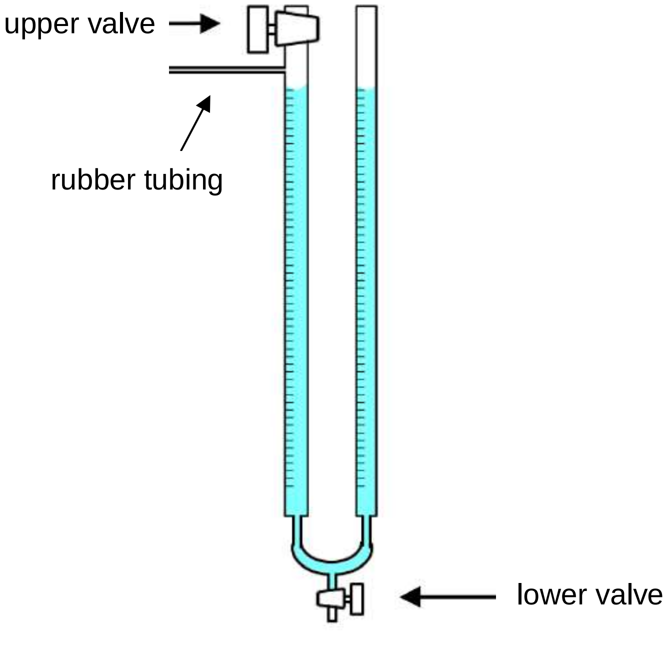


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3. The upper valve is closed once the hydrolysis of benzenediazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

(iv) Complete the diagram on Fig 4.2 to show the experimental set–up the student could have used to carry out experiment in **(b)** to measure the volume of nitrogen evolved **at 40 °C**.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

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....[5]

(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

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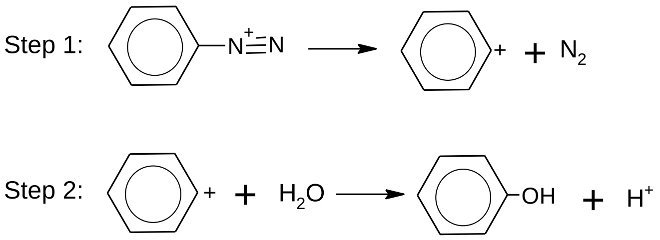
....

....[1]

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.



Deduce the role of H_2O and suggest the likely type of reaction occurring.

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....[1]

[Total:14]

2019 Y6 Prelims
H2 Chemistry 9729 Paper 1
Suggested Solutions

Answer Key

1	2	3	4	5
C	**C**	**B**	**C**	**C**

6	7	8	9	10
D	**C**	**D**	**A**	**D**

11	12	13	14	15
C	**C**	**B**	**A**	**D**

16	17	18	19	20
C	**A**	**B**	**A**	**D**

21	22	23	24	25
D	**C**	**C**	**C**	**B**

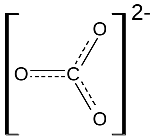
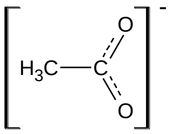
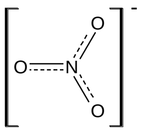
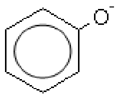
26	27	28	29	30
D	**B**	**A**	**A**	**B**

1	**C**
	From Reaction (1) $2NaN_3 \equiv 2Na \equiv 3N_2$ From Reaction (2) $10Na(s) + 2KNO_3(s) \rightarrow K_2O(s) + 5Na_2O(s) + N_2(g)$ $10Na \equiv 1\ N_2$ Combining reactions (1) and (2), $2NaN_3$ gives $3N_2$ directly, while 2Na gives 1/5 N_2 Hence, $2NaN_3$ gives a total of 16/5 N_2 $1.25NaN_3 \equiv 2N_2$

2	**C**
	Moles of sodium percarbonate = 10/1000 x 0.1 = 0.001 mol Moles of CO_2 = (48/1000) / 24 = 0.002 mol Since $(Na_2CO_3)_x{\bullet}y(H_2O_2) \equiv xCO_2$ x = 2 Moles of $KMnO_4$ = 24/1000 x 0.05 = 0.0012 mol $2KMnO_4 \equiv 5\ H_2O_2$, Moles of H_2O_2 = 5/2 x 0.00120 = 0.003 mol Since $(Na_2CO_3)_x{\bullet}y(H_2O_2) \equiv y\ H_2O_2$ y = 3 y/x = 3/2

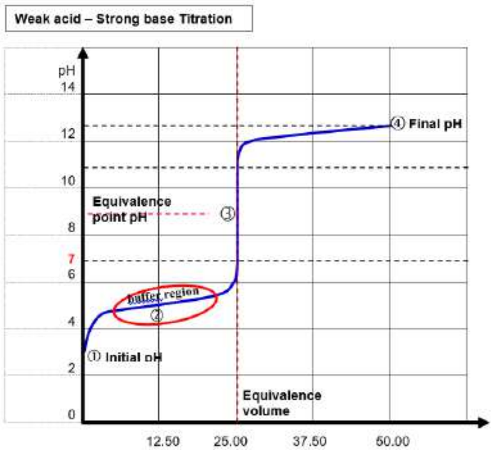
3	**B**	
	Note that elements in the same group (e.g. O and S) will have the same number of unpaired electrons in their ground state. Group 17 elements have only 1 unpaired electron. Hence, option 1 is incorrect.	
✗	**1**	Electronic configuration of Ti: $[Ar]3d^24s^2$ (2 unpaired electrons) C*l*: $[Ne]\ 3s^23p^5$ (1 unpaired electron)
✓	**2**	Electronic configuration of Si: $[Ne]\ 3s^23p^2$ (2 unpaired electrons) O: $1s^22s^22p^4$ (2 unpaired electron)
✓	**3**	Electronic configuration of Ni: $[Ar]3d^84s^2$ (2 unpaired electrons) S: $[Ne]\ 3s^23p^4$ (2 unpaired electron)

4	**C**
	$pV = nRT$ For Graphs **A** and **B**, For a fixed mass of gas at constant T, pV = constant. Since we are plotting a p against pV graph, the graph should be a vertical line instead (i.e. x = constant graph) For Graphs **C** and **D**, For a fixed mass of gas at constant p, V = (nR/p)T The graph should be y=mx graph (upward sloping straight line that passes through origin), with gradient = (nR/p) Since **I** has a higher M_r than **J**, number of moles of **I** will be smaller than **J** and hence graph of **I** should have a smaller gradient.

5	**C**
	Carbonate  Ethanoate  Nitrate  Phenoxide  In ethanoate ion, the shape with respect to the methyl carbon is tetrahedral. The common feature is the *delocalization of electrons.*

6	**D**	
✓	**1**	At constant temperature, K_c remains unchanged. Hence $\Delta G^{\ominus}$ remains unchanged.
✗	**2**	Reaction is spontaneous when $\Delta G^{\ominus} < 0$. For $0 < K_c < 1$, ln K_c is negative and hence $\Delta G^{\ominus} > 0$ (non-spontaneous)
✗	**3**	Adding a catalyst increases rate of both forward and backward reaction to the same extent, hence the position of the equilibrium remains unchanged. K_c remains unchanged and hence $\Delta G^{\ominus}$ remains unchanged.

7	C
	$N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$ Acid$_1$ Acid$_2$ $NH_3 + HBr \rightleftharpoons NH_4^+ + Br^-$ Acid$_1$ Acid$_2$ $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$ Acid$_1$ Acid$_2$ For all cases, since $K_c > 1$, strength of acid$_1$ > acid$_2$. From all 3 equations, we can deduce that Strength of acid: $HBr > N_2H_5^+ > NH_4^+$ Hence order in decreasing pH: $NH_4^+ > N_2H_5^+ > HBr$ Note: HBr is a strong acid. So the options can be narrowed down to options B and C.

8	D	
×	A	KOH (strong base) is in excess and resultant solution will have pH >7
×	B	This happens at equivalence point where KOH exactly neutralises benzoic acid. Salt hydrolysis occurs and basic salt will be formed. Resultant solution will have pH > 7.
×	C	Benzoic acid is in excess and acidic buffer will be formed. Since volume of KOH added is half the equivalence volume, this is at maximum buffer capacity. Resultant solution will have pH =pK_a.
✓	D	Benzoic acid is in excess and acidic buffer will be formed. Resultant solution will have pH < 7.  Since volume of KOH added is less than half the equivalence volume, pH will be less than that at maximum buffer capacity. Hence pH < pKa and option **D** will have the lowest pH.

9	A	
✓	1	Precipitate will start to occur when mass of solute dissolved exceed its solubility. For 10 g of KC*l*, first trace of ppt will start to appear at 30 °C. For 50 g of KC*l*O$_3$, first trace of ppt will start to appear at about 76 °C.
✓	2	At 10 °C, both solutes have exceeded its solubility and hence a saturated solution of KC*l* and KC*l*O$_3$ is formed.
✓	3	At temperatures between 30 °C and 76 °C, KC*l*O$_3$ ppt will be formed but not KC*l*. Mass of KC*l*O$_3$ ppt = 50 – 37 = 13g

10	D
	$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ $\Delta H_{reaction}^{\ominus} = -241\ kJ\ mol^{-1}$ $\Delta H_{reaction}^{\ominus} = [\Delta H_f^{\ominus}(N_2H_4(l)) + 2\Delta H_f^{\ominus}(H_2O(l))] - [2\Delta H_f^{\ominus}(NH_3(g)) + \Delta H_f^{\ominus}(H_2O_2(l))]$ $-241 = [\Delta H_f^{\ominus}(N_2H_4(l)) + 2(-286)] - [2(-46) + (-188)]$ $\Delta H_f^{\ominus}(N_2H_4(l)) = +51\ kJ\ mol^{-1}$ Decomposition of $N_2H_4(l)$ is $N_2H_4(l) \rightarrow N_2(g) + 2H_2(g)$ The reverse of formation of hydrazine, therefore, $\Delta H^{\ominus}$ for decomposition of hydrazine is **$-51\ kJ\ mol^{-1}$**

11	C
	$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ For the forward reaction, ΔS is negative as there is a decrease in the number of moles of gaseous molecules (resulting in a less disordered system). ΔH is negative as “higher yield of methanol can be achieved at a lower temperature.” That is, at lower temperature, position of equilibrium is shifted to the right, favouring an exothermic reaction. $\Delta G = \Delta H - T\Delta S$ *At* T=0 K, $\Delta G = \Delta H$ ΔG is negative. Gradient is $-\Delta S$. Since ΔS is negative, gradient is positive.

12 **C**

From the first table, comparing expt 2&3, [P] x2, rate also x2, order of reaction with respect to [P] is 1.

Comparing expt 1&2, [P] x2, [Q] x2, rate x2. Since rate α [P], two times increase in [Q] has no effect on rate. Order of reaction with respect to [Q] is 0.

Therefore, rate equation is

rate =k[P]

From the second table, if we disregard the temperatures,

$rate_4 = k(0.10)$
$rate_5 = k(0.20)$
$rate_6 = k(0.30)$

Taking temperatures into consideration, relative rates are as follows. (Using 20 °C of expt 6 as the reference)

$rate_4 = k(0.10) \times 2 \times 2 = 0.40k$
$rate_5 = k(0.20) \times 2 = 0.40k$
$rate_6 = k(0.30) \times 1$ (reference expt) = 0.30k

Hence, only statements 1 and 3 are correct.

13 **B**

Element	**X** (=A*l*)	**Y** (=Na)	**Z** (=P)
Oxide of the element	Al_2O_3	Na_2O	P_4O_{10}
Chloride of the element	$AlCl_3$	$NaCl$	PCl_5

<u>Oxides with HC*l*(aq)</u>

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

PCl_5 merely hydrolyses in aqueous solution of hydrochloric acid to give $H_3PO_4 + 5HCl$

SiO_2 is acidic and does not react with HC*l*.

<u>Oxides with water:</u>

Al_2O_3 has very exothermic lattice energy. Does not dissolve in water.

Na_2O forms NaOH in water.
$Na_2O + H_2O \rightarrow 2NaOH$

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

<u>Chlorides with water:</u>

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$Al^{3+}(aq)$ has high charge density, it undergoes partial hydrolysis in water.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

NaC*l* simply dissolves in water.

PCl_5 undergoes complete hydrolysis in water.
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

14 **A**

	K⁻ (aq)	**L**⁻ (aq)	**M**⁻ (aq)
K₂	no reaction	**L**₂ formed	no reaction
L₂	no reaction	no reaction	no reaction
M₂	**K**₂ formed	**L**₂ formed	no reaction

From the table, since **M**₂ displaces **K**₂ and **L**₂, **M**₂ is the strongest oxidising agent. If we consider the more common halogens (for convenience) – Cl_2, Br_2 and I_2, then **M**₂ is Cl_2.

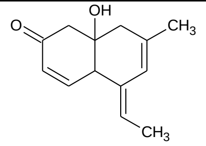
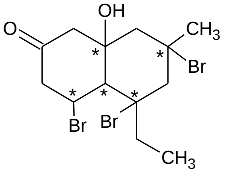
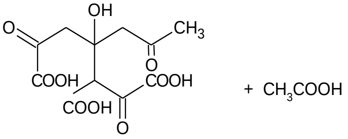
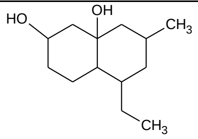
✗	1	Since **L**₂ cannot displace other halogens, **L**₂ is the weakest oxidising agent. **L**₂ is I_2. So, when **L**₂ (ie. I_2) , the weakest oxidizing agent reacts with thiosulfate ions, $S_2O_3^{2-}$, oxidation state of sulfur changes from +2 in $S_2O_3^{2-}$ to +2.5 in $S_4O_6^{2-}$ On the other hand, when **M**₂ (ie. Cl_2 reacts with $S_2O_3^{2-}$, oxidation state of sulfur changes from +2 in $S_2O_3^{2-}$ to +6 in SO_4^{2-}. Statement 1 is not correct.
✓	2	**L**⁻ is I^- which forms AgI with silver nitrate. AgI is insoluble in excess aq. ammonia.
✗	3	**K**⁻ is Br^- while **M**⁻ is Cl^-. They are halides, not halogens. Hexane can be used to distinguish between bromine and iodine but not bromide and iodide.

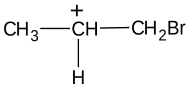
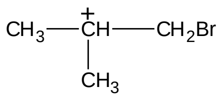
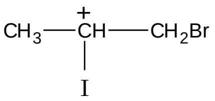
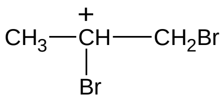
15 **D**

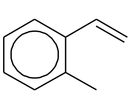
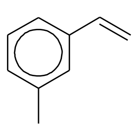
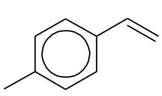
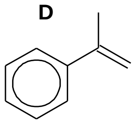
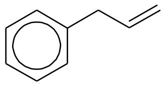
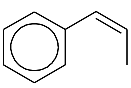
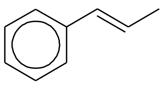
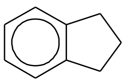
Note that all hydrogens atoms on the carbons of the C=C are unlikely to undergo free radical substitution.

In order to form a chiral carbon, the substitution must happen on a $-CH_2-$, not on a $-CH_3$.

✗	A	$CH_3CH=CH_2$ (a) (b) (c) There are three types of hydrogen atoms. Only (a) tends to undergo FRS, but it will not generate a chiral centre. The monochlorinated product will not show cis–trans isomerism or enantiomerism.
✗	B	$(CH_3)_2C=CH_2$ (a) (b) There are two types of hydrogen atoms. Only (a) tends to undergo FRS, but it will not generate a chiral centre. The monochlorinated product will not show cis–trans isomerism or enantiomerism.
✗	C	$CH_3CH=C(CH_3)_2$ (a) (b) (c) There are three types of hydrogen atoms. Only (a) and (c) tend to undergo FRS, but no substitution will generate a chiral centre. The monochlorinated product will not show enantiomerism. Cis–trans isomerism is possible if (c) is substituted.
✓	D	$CH_3CH=CHCH_2CH_3$ (a) (b) (c) (d) (e) There are five types of hydrogen atoms. Only (a), (d) and (e) tend to undergo FRS. A chiral centre is formed when (d) is substituted. All products will show cis-trans isomerism.

16	**C**	
	 Compound **K**	
✗	**A**	 The product has five chiral centres. (Need to apply Markovnikov's rule to obtain the major product)
✗	**B**	 A tribasic carboxylic acid is formed upon strong oxidation of **K**.
✓	**C**	 Alkene and ketone groups are reduced by H_2 to give the product above. 4 mol of H_2 for the three carbon-carbon double bonds and one ketone group.
✗	**D**	The –OH group in **K** reacts with Na according to: $ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$ 1 mol of **K** produces ½ mol of H_2. (= ½ (24.0) dm^3)

17	**A**
	 $\mathrm{CH_3{-}\underset{H}{\overset{+}{C}H}{-}CH_2Br}$ carbocation **S**  $\mathrm{CH_3{-}\underset{CH_3}{\overset{+}{C}H}{-}CH_2Br}$ carbocation **T**  $\mathrm{CH_3{-}\underset{I}{\overset{+}{C}H}{-}CH_2Br}$ carbocation **U**  $\mathrm{CH_3{-}\underset{Br}{\overset{+}{C}H}{-}CH_2Br}$ carbocation **V** The above corresponding carbocations are formed when electrophilic end of bromine molecule is attached to the C atom of the double bond with more H atoms (follow Markovnikov's rule). Carbocation **T** is most stable as there is an electron-donating –CH_3 substituent attached to the carbocation, dispersing the positive charge, stabilising the carbocation to the largest extent. Rate of bromination is the fastest. I and Br atoms are both electronegative. Br is more electronegative than I. Br atom therefore, destabilises the carbocation **V** to the largest extent. Rate of addition of Br_2 /CCl_4 to **V** will be the slowest as carbocation intermediate **V** is the least stable.

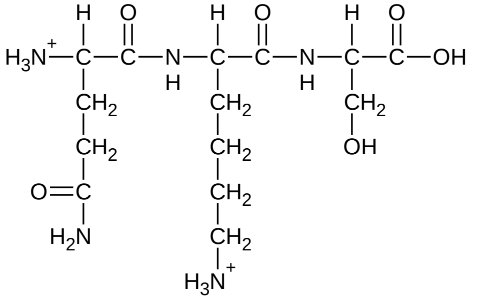
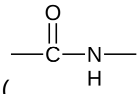
18	**B**
	There are 8 possible benzene-containing isomers. **A**  **B**  **C**  **D**  **E**  **F**  **G**  **H**  Only **A** and **H** will produce benzene-1,2-dicarboxylic acid on heating with acidified manganate(VII) ions.

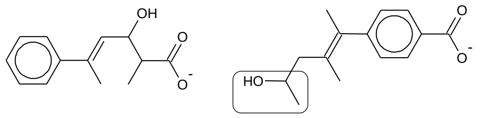
19	**A**	
✓	**1**	RCO_2^- nucleophile attacks the electrophilic δ+ bromine atom to form RCO_2Br.
✓	**2**	Homolytic fission of O–Br bond occurs to form RCOO• and Br• radicals.
✓	**3**	Correct movement of electrons showing the formation of C-O pi bond and the cleavage of R-C sigma bond.
✗	**4**	Formation of R-Br bond releases energy.

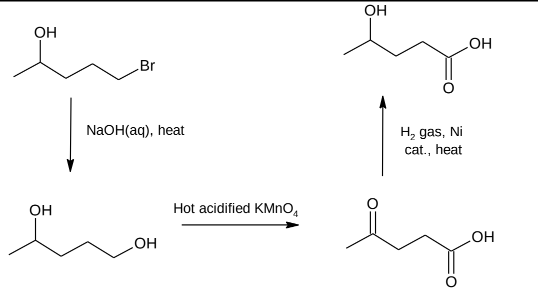
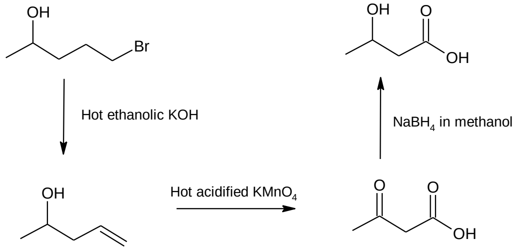
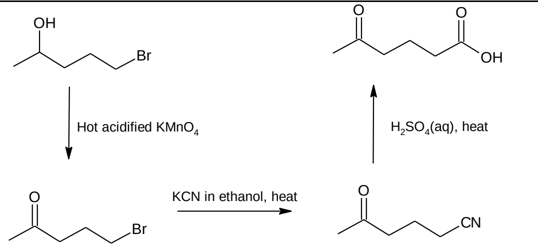
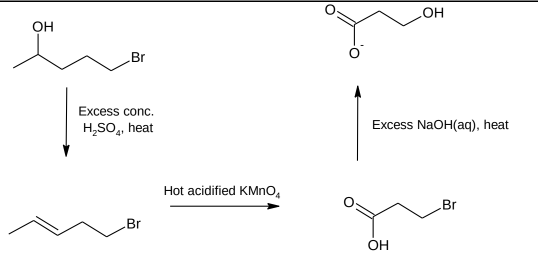
20	**D**
	$ROH + SOCl_2 \rightarrow RCl + HCl(g) + SO_2(g)$ Since 1 mol of ROH produces 2 mol of gas (HCl and SO_2), 1 mol of sorbitol has 6 mol of alcohol which will produce a total of 12 mol of gas.

21	**D**	
✗	**A**	Benzaldehyde does not give a positive iodoform test with alkaline aqueous iodine.
✗	**B**	The ester functional group does not give orange ppt with 2,4-DNPH.
✗	**C**	$CH_3CH_2COCH_2CH_3$ does not give a positive iodoform test with alkaline aqueous iodine.
✓	**D**	The ketone functional groups can give orange ppt with 2,4-DNPH and do not react with Fehling's solution. The presence of –$COCH_3$ groups give a positive iodoform test with alkaline aqueous iodine.

22	**C**
	The amide functional group is hydrolysed when heated with NaOH(aq). Ammonia gas is also liberated when NH_4^+ is heated in the presence of hydroxide ions.

23	C
	 The correct structure must have 1. Peptide bonds ( $-C(=O)-N(H)-$) between each amino acid 2. Basic groups will be protonated (i.e. all amines will be protonated) 3. Amide and alcohol groups are neutral and hence do not get protonated. 4. Carboxylic acid group is acidic and hence remains protonated.

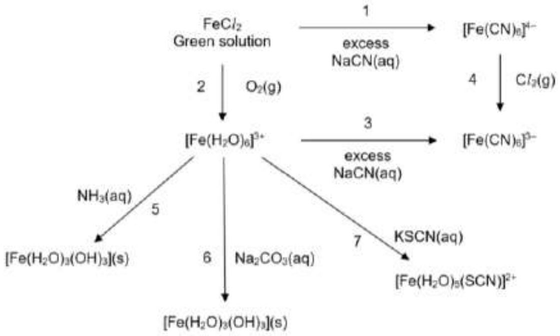
24	C	
✗	A	Ester group undergoes alkaline hydrolysis to give the following products. One of them contains the –CH(OH)CH$_3$ group which will give the yellow ppt of CHI$_3$. 
✗	B	PCl_5 reacts with alcohol and carboxylic acid groups to give white fumes of HCl.
✓	C	Ester and carboxylic acid groups are reduced to alcohols but there is no observable change.
✗	D	Mild oxidation of alkene to diol occurs. Purple KMnO$_4$ decolourises and brown ppt of MnO$_2$ is formed.

25	B	
	Please note that there is a reduction of one carbon.	
✗	A	
✓	B	
✗	C	
✗	D	

26	D
	Anode NO$_3^-$ cannot be oxidised at the anode as nitrogen is in its highest oxidation state. Hence, water must have been oxidised at the anode. $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ The gas produced at the anode is O$_2$. **Cathode** $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V For the metal to be discharged at the cathode, the $E^\ominus$ must be more positive than –0.83 V. $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76$ V Hence, Zn^{2+} is reduced at the cathode to Zn metal.

27	**B**
	Amt of Zn = 0.4 ÷ 65.4 = 0.0061162 mol $Zn^{2+} + 2e^- \rightarrow Zn$ No. of moles of e^- = 2 × 0.0061162 = 0.012232 mol Charge required = 0.012232 × 96500 = 1180.4 C Time required = 1180.4 ÷ 0.5 = 2360.9 s = **<u>39.3 min</u>** (3 s.f.)

28	**A**	
✓	**A**	$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.77$ V $E^\ominus_{cell} = +1.77 - (+0.70) = +1.07$ V Since $E^\ominus_{cell} > 0$, reaction is spontaneous.
✗	**B**	$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V $E^\ominus_{cell} = +1.07 - (+0.70) = +0.37$ V Since $E^\ominus_{cell} > 0$, reaction is spontaneous. However, aq Br_2 will undergo an electrophilic substitution with quinol (due to the presence of the phenol grp). Hence, quinone will not be produced in good yield.
✗	**C**	$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V $E^\ominus_{cell} = +0.34 - (+0.70) = -0.36$ V Since $E^\ominus_{cell} < 0$, reaction is not spontaneous.
✗	**D**	Cl^- is a reducing agent and hence will not be able to oxidise quniol to quinone.

29	**A**	
		
✓	**A**	**False** Step 5 involves the two equilibria below: $NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$ $Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3(s)$ Step 6 involves an acid-base reaction (because Fe^{3+} is an acidic cation) $2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightleftharpoons 2[Fe(H_2O)_3(OH)_3](s) + 3CO_2 + 6H_2O$
✗	**B**	**True** $[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O$
✗	**C**	**True** Fe^{2+} is oxidised to Fe^{3+} in step 2.
✗	**D**	**True** $[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^\ominus = +0.36$ V $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V $E^\ominus_{cell} = +1.36 - (+0.36) = \underline{+1.00\text{ V}}$

30	**B**
	Since 2 mol of AgC*l* is formed from 1 mol of the ionic compound, there are 2 mol of free Cl^- ions that are not ligands. Hence, the charge of the complex cation must be 2+ for the ionic compound to be uncharged. Note that the other chloride anion is a ligand. It has already formed a dative bond with the central metal cation and hence, this chloride does not form a precipitate when $AgNO_3$ is added to the ionic compound.

Name:	Answers	**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Prelims Examination 2019
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

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 Write your answers in the spaces provided on this 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.	**Section A Marks**
1	**21**
2	**14**
3	**12**
4	**13**
5	**15**
Total	**75**

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

1 This question explores the chemistry of transition metal complexes.

(a) Cobalt cations readily form complexes with ligands. Some of the cobalt complexes with their absorption frequencies are shown in Table 1.1. The absorption frequency is the frequency of light absorbed for each complex, and is proportional to the energy of light absorbed.

Table 1.1

Complex	Absorption Frequency / cm^{-1}
$[Co(CN)_6]^{4-}$	15300
$[Co(CN)_6]^{3-}$	33500
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200
$[Co(NH_3)_6]^{3+}$	22870

(i) State the electronic configuration of the cobalt cation in $[Co(CN)_6]^{3-}$.

Electronic configuration: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$**

[1]

(ii) Using the information in Table 1.1, state the relationship between the oxidation state of the metal cation and the absorption frequency of its complex.

A **higher oxidation state** of the metal cation will result in a **higher absorption frequency** of the complex.

[1]

(iii) Stronger field ligands generate a *d* orbital splitting pattern with a larger energy gap when bonded to transition metal cations.

Using the information in Table 1.1, rank CN^-, H_2O and NH_3 in order of increasing ligand field strength.

Ligand field strength: **$H_2O < NH_3 < CN^-$**

[1]

(iv) Hence, predict a value for the absorption frequency of $[Co(NH_3)_6]^{2+}$.

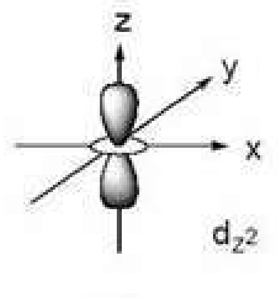
Any value between 9300 and 15300 (excluding boundaries)

[1]

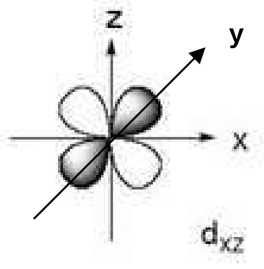
(b) In the presence of an octahedral ligand field, the 3*d* orbitals of cobalt are split into two energy levels.

(i) Using the axes below, draw the shape of a 3*d* orbital of cobalt of

- a higher energy level,
- a lower energy level, in the presence of an octahedral ligand field.



Higher energy level
(accept $d_{x^2-y^2}$)



Lower energy level
(accept d_{xy}, d_{yz})

[2]

(ii) Hence, explain why the 3*d* orbitals of cobalt are split into two energy levels in the presence of an octahedral ligand field.

The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that **are in the region of the lone pairs of the ligands**. There is **greater repulsion between these orbitals and the incoming ligands**. As a result, these orbitals are **more destabilised** and higher in energy.

The d_{xy}, d_{yz} and d_{xz} orbitals have lobes that project **between the lone pairs of the ligands**. There is **less repulsion** between these orbitals and the negative charges (lone pairs of the ligands). As a result, these orbitals are **less destabilised** and lower in energy.

[2]

(iii) In the presence of a tetrahedral ligand field, the ligands approach in between the axes.

Complete Fig 1.1 to show how the degenerate 3*d* orbitals of cobalt will split in a tetrahedral ligand field. Label all the orbitals in your diagram.

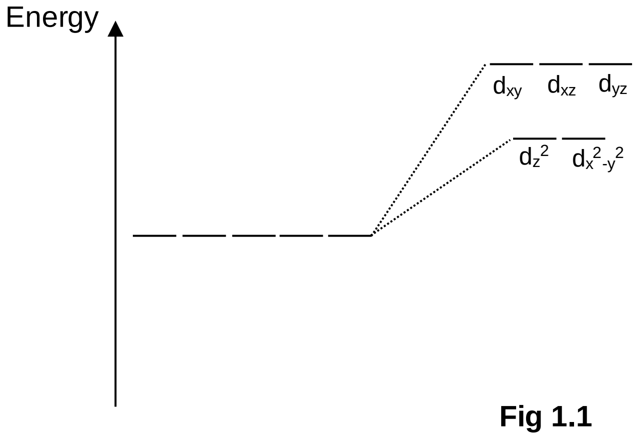


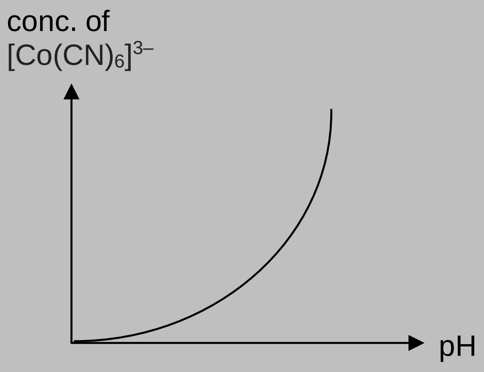
Fig 1.1

[2]

(c) Another cobalt complex, $[CoCl_6]^{3-}$ undergoes ligand exchange with CN^- ligands to form $[Co(CN)_6]^{3-}$ according to the following equilibrium.

$$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$$

The effect of pH on the concentration of $[Co(CN)_6]^{3-}$ formed is shown in the graph below.



(i) Write an equation that describes the dissociation of the weak acid, HCN, in water.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

[1]

(ii) Hence, using Le Chatelier's Principle, explain the shape of the graph above.

$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ -----(1)
$[CoCl_6]^{3-}(aq) + 6CN^-(aq) \rightleftharpoons [Co(CN)_6]^{3-}(aq) + 6Cl^-(aq)$ ------(2)

When pH increases, the **[H$^+$] decreases. This shifts the position of equilibrium (1) to the right to produce more H$^+$**. This also increases the concentration of CN^-.

The **increase in CN$^-$ causes the position of equilibrium (2) to shift to the right to decrease the concentration of CN$^-$**. This results in an **increase in concentration of $[Co(CN)_6]^{3-}$ as pH increases**.

[2]

(iii) Explain why the Gibbs free energy change and enthalpy change for the forward reaction are approximately equal.

Since **there is no change of state or number of moles of particles from reactants to products**, the **entropy change is approximately zero**. Hence, $\Delta G \approx \Delta H$.

[1]

(iv) Hence deduce the sign of the enthalpy change of the forward reaction given that it is spontaneous.

Since reaction is spontaneous, **ΔG is negative**. Hence, given $\Delta G \approx \Delta H$, **$\Delta H$ must be negative**.

[1]

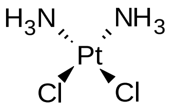
(d) Similar to organic compounds, transition metal complexes may exhibit stereoisomerism.

(i) For square planar complexes, *cis-trans* isomerism can be exhibited for $\mathbf{MA_2B_2}$ type complexes (where **M** is the metal cation, and **A** and **B** are different ligands).

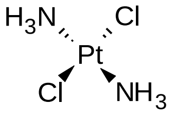
cis and *trans* isomers are differentiated in the following way:

cis:	Both **A** ligands next to one another
trans:	Both **A** ligands are separated by a **B** ligand

$[Pt(Cl)_2(NH_3)_2]$ is a square planar complex. Complete the diagrams below to show the structures of its *cis* and *trans* isomers.



Cisplatin



trans isomer

[1]

(ii) For any transition metal complex, enantiomerism is exhibited if it has:

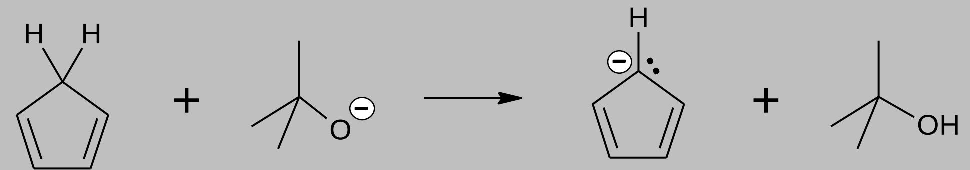
- Mirror images that are non-superimposable and
- No internal plane of symmetry

Deduce if the *trans* isomer of $[Pt(Cl)_2(NH_3)_2]$ can exhibit enantiomerism.

It **<u>cannot exhibit enantiomerism</u>** as it has an **<u>internal plane of symmetry</u>** and / or has **<u>mirror images</u>** that are **<u>superimposable</u>**.

[1]

(e) The cyclopentadienyl anion is a common ligand in transition metal complexes. This anion can be generated via the following reaction between tert–butoxide anion and cyclopentadiene.



Cyclopentadiene tert-butoxide cyclopentadienyl anion

An organic compound is considered aromatic if all of the following three criteria are met:

- it is a cyclic planar compound,
- it has a delocalised π electron system, and
- it has $(4n + 2)$ π electrons, where n is an integer.

One such example is benzene.

(i) State the type of reaction that generates the cyclopentadienyl anion from cyclopentadiene.

Acid–Base

[1]

(ii) Given that the cyclopentadienyl anion is aromatic, explain fully how it meets the three criteria stated above.

All the carbon atoms in the anion are **sp^2 hybridised and have trigonal planar geometry**. Hence, the anion is a cyclic planar anion.

The **lone pair of electrons** on the carbon is **in a *p*-orbital which is overlapping with the π bonds of the 2 C=C bonds**.

Hence, there is a delocalised π electron system with **6 π electrons**.

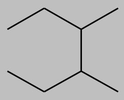
[3]

[Total: 21]

2 Halogenoalkanes are widely used commercially as they are important precursors for many organic synthesis.

(a) One method of synthesising halogenoalkanes is the free radical substitution of alkanes. For example, butane can be chlorinated in the presence of UV light.

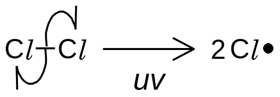
However, this is not a preferred method of synthesising halogenoalkanes as there are multiple by–products. For example, one by–product of the monochlorination of butane is shown below.



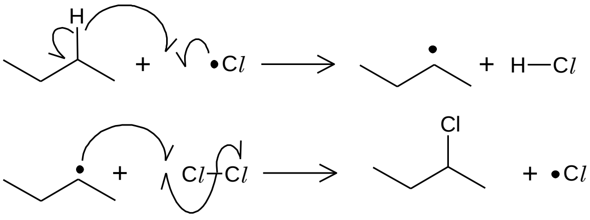
3,4–dimethylhexane

(i) Draw the mechanism of the reaction between butane and chlorine that would result in the formation of 3,4–dimethylhexane. Show the movement of electrons by using suitable curly arrows and indicate any unpaired electron using a dot (•).

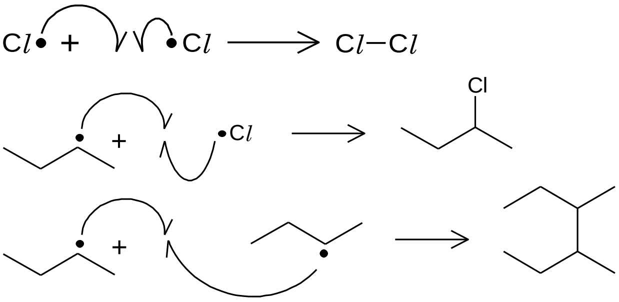
Initiation:



Propagation:



Termination:



[3]

(ii) State the number of chiral centre(s) present on 3,4–dimethylhexane and the number of stereoisomers that are optically active.

No. of chiral centres: **<u>2</u>**

No. of stereoisomers that are optically active: **<u>2</u>**

[2]

(b) One application of halogenoalkanes was the use of chlorofluorocarbons (CFCs) as refrigerants in the 20th century. However, CFCs have been replaced with hydrofluorocarbons (HFCs) due to their detrimental impact on the ozone.

CFCs produce radicals in the presence of UV light. For example, chlorodifluoromethane, $CHClF_2$, readily produces chlorine radicals in the stratosphere. These radicals speed up the depletion of the ozone layer.

HFCs, such as fluoroform, CHF_3, do not produce radicals in the presence of UV light.

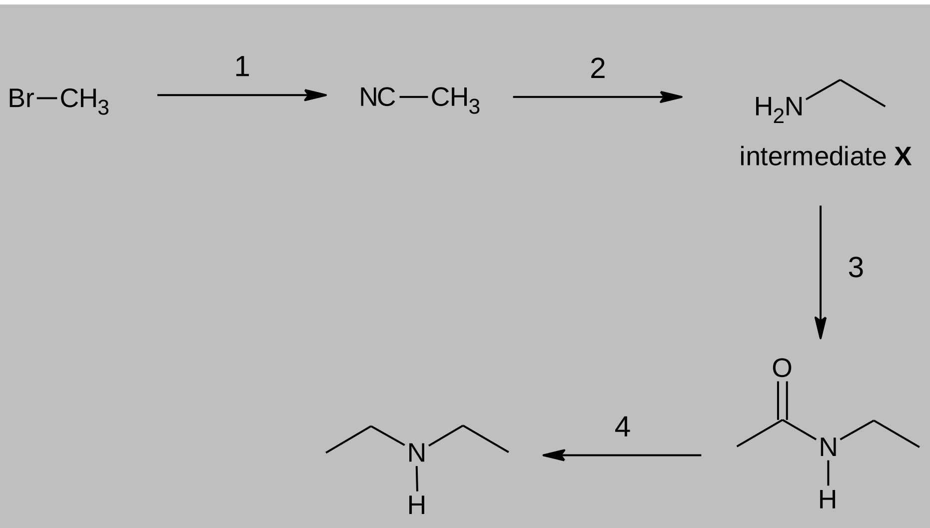
With reference to the *Data Booklet*, explain why CHF_3 does not deplete the ozone layer whereas $CHClF_2$ does.

B.E.(C–F) = 485 kJ mol^{-1}
B.E.(C–C*l*) = 340 kJ mol^{-1}

Since the bond energy of the C–F bond is higher than that of the C–C*l* bond, the **<u>C–F bond is stronger than the C–C*l* bond</u>**. Hence, the UV light **<u>does not provide sufficient energy to break the C–F bond</u>** to produce fluorine radicals.

[2]

(c) Halogenoalkanes also find their application as precursors in the synthesis of nitrogen–containing organic compounds. One such synthesis involving bromomethane is shown below.

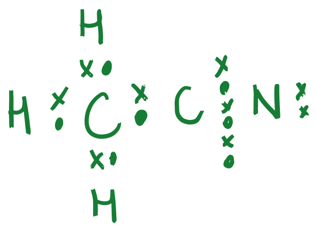


intermediate **X**

compound **Z**

intermediate **Y**

(i) Draw a dot–and–cross diagram to show the bonding in CH_3CN and state the types of orbitals used to form the carbon–carbon bond in the molecule.



Orbitals used: **2sp and 2sp^3**

[2]

(ii) State the type of reaction occurring in step 4 and the reagent(s) and condition(s) needed.

Type of reaction: **Reduction**
Reagent(s) and condition(s): **LiA*l*H$_4$ in dry ether**

[2]

(iii) Explain why ethanoic acid **cannot** be used in step 3 to form intermediate **Y**.

Ethanoic acid will undergo an **acid-base / neutralisation reaction** with the amine in intermediate **X** instead.

[1]

(iv) Compare and explain the basicity of intermediate **X** and compound **Z**.

Compound **Z is more basic than intermediate X**.

The N atom of **Z** has **2 (or more) electron-donating alkyl groups** attached to it, while that in **X** only has 1. Hence, there is a greater electron density of the N atom of Z and the **<u>lone pair of electrons on N is more available for donation</u>** to form a dative bond with H^+.

[2]

[Total: 14]

3 Brown iodine water is decolourised when warmed with ethanol in an alkaline medium. A series of 'clock' experiments were conducted to study the kinetics of this reaction. The time taken for the decolourisation of iodine in each experiment is found in Table 3.1.

Table 3.1

Expt	Volume of I_2(aq) / cm^3	Volume of ethanol / cm^3	Volume of NaOH (aq) / cm^3	Volume of deionised water / cm^3	Time taken, *t* / s
1	5	20	20	10	42
2	5	30	20	0	28
3	10	20	20	5	42

(a) **(i)** Describe another observable change that occurs as the reaction proceeds.

Yellow ppt of CHI_3 forms

[1]

(ii) Explain why the total volume of reaction mixture is kept constant.

So that the initial **concentration of each reactant** (in the reaction mixture) is **directly proportional to the volume used**.

[1]

(iii) Given relative rate $\propto \frac{\text{volume of } I_2}{t}$, use this relationship to deduce the order of reaction with respect to [ethanol] and [iodine]. Explain your answer.

Comparing experiments 1 and 2, when [iodine] is constant and [ethanol] $\times \frac{3}{2}$, time required $\times \frac{2}{3}$ OR relative rate $\times \frac{3}{2}$.
∴ first-order wrt [ethanol]

Comparing experiments 1 and 3, when [ethanol] is constant and [iodine] doubles, relative rate doubles.
∴ first-order wrt [iodine]

[2]

(b) The clock method can also be used to study the comproportionation reaction between bromate(V) and bromide ions in acidic medium.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

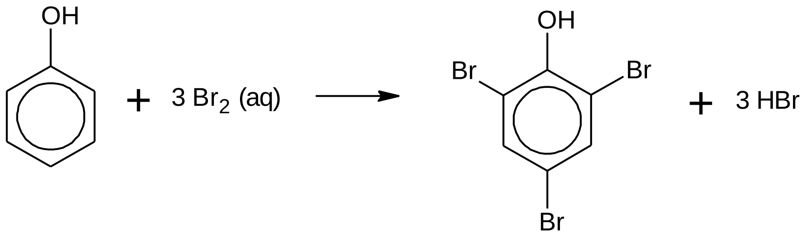
A small, fixed amount of phenol and a few drops of litmus are used in every experiment. The time taken for the disappearance of the pink colouration is measured.

(i) Comment if the reaction is expected to occur via an elementary step.

No, it is extremely **unlikely for so many (12) reactant species to collide at the appropriate geometry**.

[1]

(ii) Using a suitable equation, explain the purpose of adding a small, fixed amount of phenol in every experiment.



It ensures that the extent of reaction for every experiment is kept constant / A fixed amount of Br_2 will react with phenol before the colour change occurs.

[2]

(c) The pH of a reaction mixture can be kept constant in a kinetics experiment using a suitable buffer. Phosphoric acid, H_3PO_4, can be used to prepare buffers of varying pH values as it has three pK_a values of 2.14, 7.20 and 12.37.

(i) State the components present in a phosphate buffer of pH 7.50.

$H_2PO_4^-$ and HPO_4^{2-}

[1]

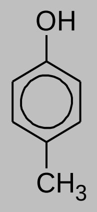
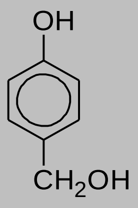
(ii) Write a suitable equation to show how the buffer system outlined in **(c)(i)** can resist change in pH when a small amount of OH^- is added.

$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$

[1]

(d) Two physical properties of two substituted phenols are shown in Table 3.2.

Table 3.2

	p–cresol	4–hydroxybenzyl alcohol
Structure		
pK_a	10.3	9.82
Boiling point / °C	202	252

Suggest a reason for the difference in each property.

- pK_a

The **electronegative O atom / the additional electron withdrawing –OH group** on 4–hydroxylbenzyl alcohol **disperses the negative charge on the phenoxide ion.**

This **stabilises the conjugate base**. Hence, 4–hydroxylbenzyl alcohol dissociates to a larger extent and is a **stronger acid** than p–cresol.

- Boiling point

4–hydroxylbenzyl alcohol forms **more extensive hydrogen bonds** with other 4–hydroxylbenzyl alcohol molecules (due to the presence of the additional –OH group). Hence, **more energy** is require to overcome these bonds in boiling.

[3]

[Total: 12]

4 Methanal reacts with propene to form an organic product **A**.

(a) The mechanism for the formation of **A** is shown in Fig 4.1.

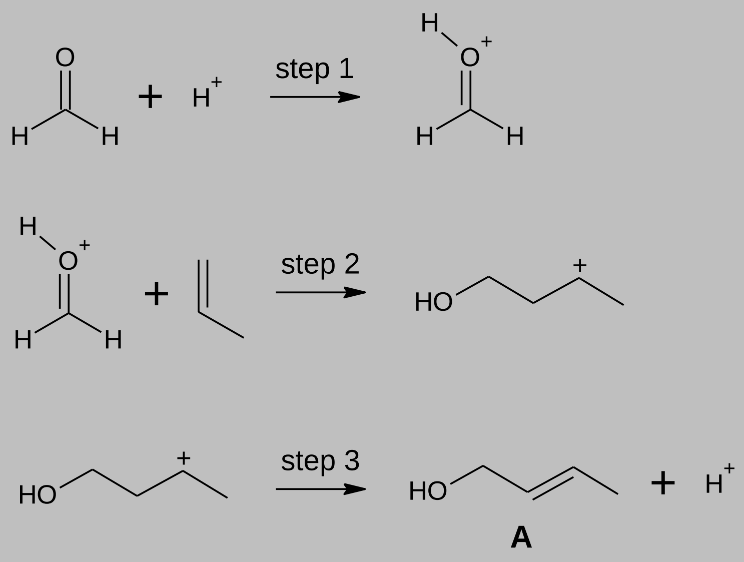


Fig. 4.1

(i) Deduce whether propene is acting as an electrophile or a nucleophile in step 2. Explain your answer.

Propene acts as a **nucleophile** because it **donates an electron pair** to the electron deficient carbon of the protonated carbonyl group.

[1]

(ii) Complete Fig 4.2 using curly arrow(s) to show the movement of electron pair(s) for step 2.

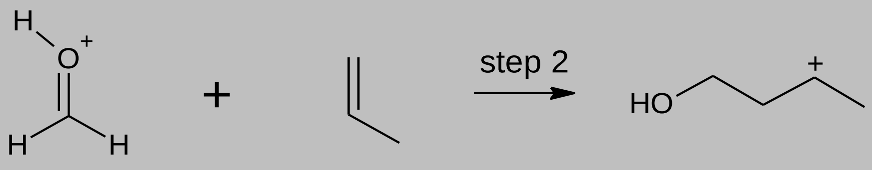
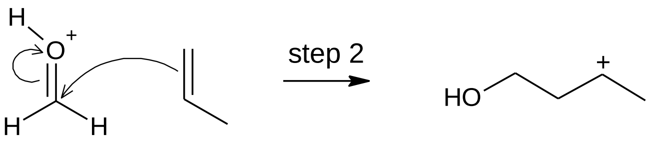


Fig. 4.2

Mechanism



[1]

(iii) In step 2, intermediate **B** is produced rather than **C**.

Suggest an explanation for the preferential production of intermediate **B**.

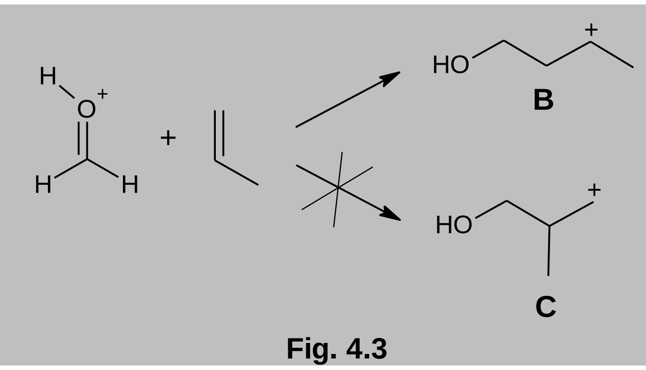
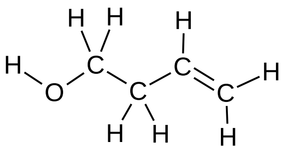


Fig. 4.3

Intermediate **B** is a **secondary carbocation** which is **more stable** than **C**, a **primary carbocation**, as there are **more electron-donating alkyl groups** to **disperse its positive charge**.

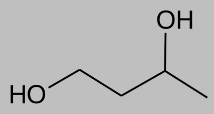
[2]

(iv) Step 3 may result in three isomeric organic products. Draw the displayed formula of the organic product which is a constitutional isomer of **A**.



[1]

(b) The reaction between methanal and propene under a different set of conditions gives molecule **D** with the following structure.



It can also be made from propene in the 4-step process shown in Fig 4.4.

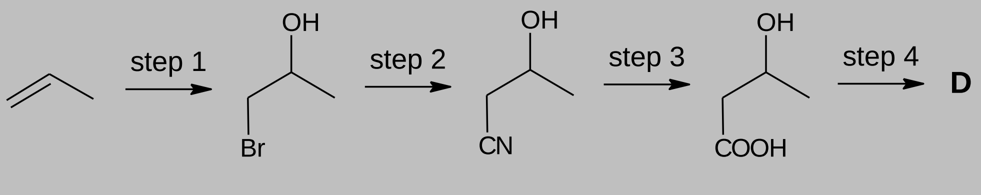


Fig. 4.4

(i) Name the product formed in step 1.

1-bromopropan-2-ol

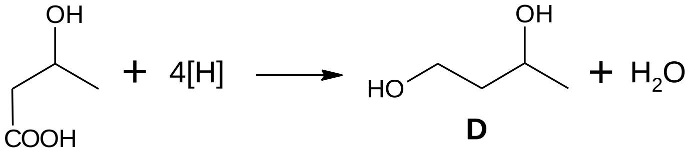
[1]

(ii) State the reagents and conditions needed for steps 2 and 3.

step 2: **KCN in ethanol, heat** under reflux step 3: **dilute HC*l*, heat** under reflux

[2]

(iii) Step 4 is a reduction reaction. Write an equation for step 4 using [H] to represent the reducing agent.

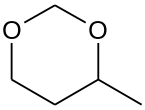


[1]

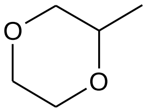
(c) Molecule **E** has molecular formula $C_5H_{10}O_2$.

It is an asymmetrical molecule comprising a 6-membered ring. It does not contain any O–O bond and has no reaction with phosphorus pentachloride.

(i) Suggest **two** structures of **E** that are consistent with the information provided.



and



[2]

(ii) The formation of **E** involves the nucleophilic attack of methanal on intermediate **B**.

Complete Fig 4.5 using curly arrow(s) to show the movement of electron pair(s) for this nucleophilic attack.

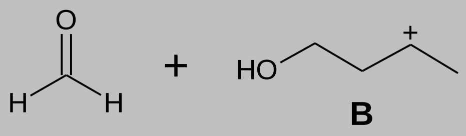
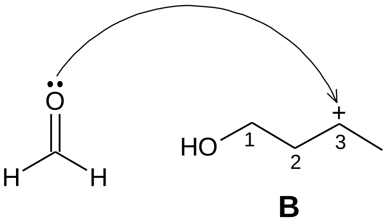
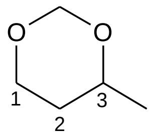


Fig. 4.5

Hence deduce the likely structure of **E** from your answer in **(c)(i)**. Explain your reasoning.



The nucleophilic attack using the lone pair of electrons on O atom of methanal on the positively charged carbon atom in intermediate **B** will result in the **two O atoms** in the product **E** being **3 carbon atoms apart**. Hence the likely structure of **E** is as follows.



[2]

[Total: 13]

5 **(a)** **R**, **T**, **U** and **V** are consecutive elements in the third period of the Periodic Table. Among these four elements, **T** has the highest melting point and **U** has the highest first ionisation energy.

(i) Identify element **T**.

Silicon

[1]

(ii) The oxides of elements **T** and **U** can be obtained when the elements are burned in excess oxygen. The oxides of **T** and **U** have melting points of 1710 °C and 340 °C respectively.

Explain briefly the difference in melting points between these oxides.

The oxide of **T** (SiO_2) has a giant molecular structure. Large amount of energy is required to break the strong and extensive covalent bonds between Si and O atoms and hence oxide of **T** has a higher melting point. [1]

The oxide of **U** (P_4O_{10}) has a simple molecular structure. Less energy is required to break the weak intermolecular forces of attraction between the molecules and hence oxide of **U** has a lower melting point.

[2]

(iii) Describe the reactions, if any, of the oxides of elements **R** and **V** with water. Include the approximate pH value of any resulting solution formed.

The oxide of **R** (Al_2O_3) is insoluble in water. Hence, the pH of the resulting solution is 7.

The oxide of **V** (SO_3) reacts readily with water to produce a strongly acidic solution of pH 2.

[2]

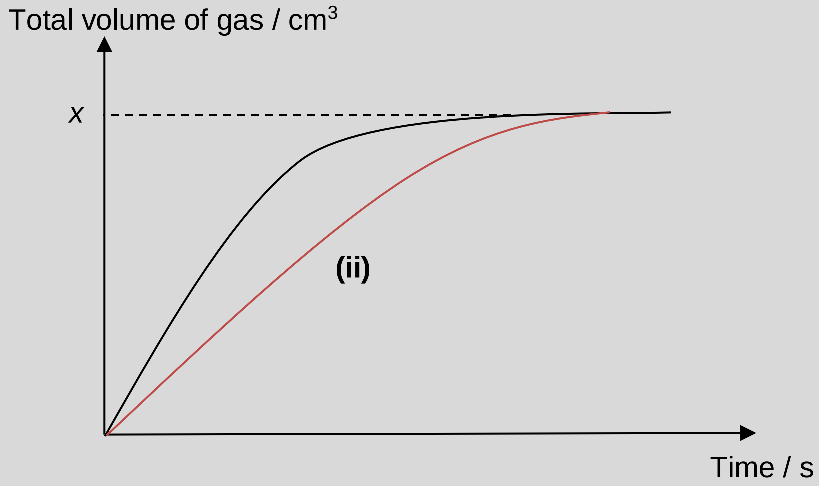
(b) Barium and magnesium form iodate(V) compounds, $Ba(IO_3)_2$ and $Mg(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Write a balanced equation, with state symbols, for the thermal decomposition of $Mg(IO_3)_2$.

$Mg(IO_3)_2(s) \rightarrow MgO(s) + I_2(g) + \frac{5}{2}O_2(g)$ [1]

[1]

The graph below shows the total volume of gas collected over time when 0.1 mol of $Mg(IO_3)_2$ is heated.



(ii) Sketch, on the same axes above, the graph that would be obtained when 0.1 mol of $Ba(IO_3)_2$ was heated at the same temperature till no further change was observed.

Gentler gradient with **same total volume**

[1]

(iii) Explain the shape of the graph that you have drawn for **(b)(ii)**.

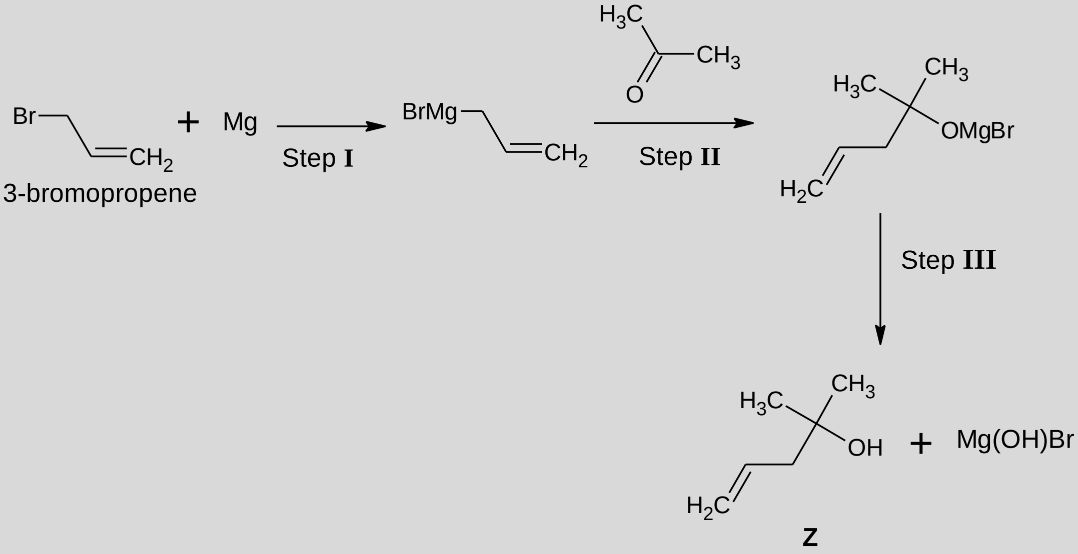
Ba^{2+} has a larger ionic radius and hence a smaller charge density. The polarising power of Ba^{2+} is smaller and the electron cloud of iodate ion is being polarised to a smaller extent. $Ba(IO_3)_2$ is hence more thermally stable and requires a longer time to decompose.

Since the initial number of moles of iodates remains the same and the number of moles of gas produced are the same, the total volume of gas collected remains unchanged for $Ba(IO_3)_2$.

[3]

(c) Grignard reagents, RMgX, are organo-magnesium halides derived from an alkyl halide, RX, and magnesium.

The use of a Grignard reagent in the conversion of 3-bromopropene to compound **Z** is given below.



(i) The alkyl group in RMgX behaves like an anion, R^-, and is a strong Lewis base.

Explain why propene is formed as a side product in both steps **I** and **II** if both reactions are **not** carried out under anhydrous conditions.

The nucleophilic carbon from $CH_2{=}CHCH_2^-$ will **accept a H^+ from water /** undergoes **acid-base reaction with water**.

[1]

(ii) Suggest the type of reaction occurring in steps **II** and **III**.

Step **II:** Nucleophilic Addition
Step **III:** Hydrolysis

[2]

(iii) A small amount of 3-bromopropene, propanone and **Z** was introduced into three separate test tubes. Describe a simple chemical test you could carry out to distinguish 3-bromopropene from the other two compounds. State what you would observe.

Add NaOH(aq) and heat, followed by excess HNO_3(aq) and then $AgNO_3$(aq).

Cream ppt is seen in the test tube containing 3-bromopropene.
No ppt seen for the other two test-tubes.

[2]

[Total: 15]

Name:	Answers	Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2019
Year 6

H2 CHEMISTRY 9729/03

Paper 3 Free Response

Additional Materials: Data Booklet
Answer Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write your answers on the separate answer booklet 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 Do not use staples, paper clips, glue or correction fluid.

Section A

7 Answer **all** questions

Section B

8 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.

Section A

1 To facilitate better plant growth, there is widespread use of fertilisers and soil additives in the agricultural sector.

(a) Agricultural lime is a soil additive used to increase soil pH so as to facilitate uptake of plant nutrients such as nitrogen and phosphorous. It is usually made up of a combination of calcium carbonate and magnesium carbonate.

A manufacturer claims that a 2.00 g sample of agricultural lime contains 92 % calcium carbonate (M_r = 100.1) and 8 % magnesium carbonate (M_r = 84.3) by mass.

To verify the manufacturer's claim, the following steps were carried out:

Step 1 The solid carbonate mixture was dissolved in 250 cm^3 of 0.25 mol dm^{-3} hydrochloric acid.

Step 2 A 25 cm^3 aliquot of this resultant solution was titrated with 0.14 mol dm^{-3} potassium hydroxide.

It was found that 12.50 cm^3 of potassium hydroxide was required for complete neutralisation.

(i) Based on the manufacturer's claim of 92% calcium carbonate and 8% magnesium carbonate by mass, calculate the amount, in moles, of each carbonate present in the sample of agricultural lime.

[1]

Mass of $CaCO_3$ present = 92 % × 2.00 g = 1.84 g
Mass of $MgCO_3$ present = 8 % × 2.00 g = 0.16 g

Moles of $CaCO_3$ present
= 1.84 g ÷ 100.1 g mol^{-1} = 0.018382 = **0.0184 mol**

Moles of $MgCO_3$ present
= 0.16 g ÷ 84.3 g mol^{-1} = 0.0018980 = **0.00190 mol**

(ii) Use the information above to calculate the amount of HCl that reacted with the carbonate mixture in Step 1.

[2]

Moles of KOH reacted with excess HCl = $\frac{12.50}{1000} \times 0.14$ = 0.00175 mol
Moles of HCl present in 25 cm^3 aliquot = 0.00175 mol

Moles of excess HCl present in 250 cm^3 solution
= 0.00175 × $\frac{250}{25}$ = **0.0175 mol**

Total moles of HCl used = $\frac{250}{1000} \times 0.25$ = 0.0625 mol

Moles of HCl reacted with carbonates = 0.0625 – 0.0175 = **0.045 mol**

(iii) The manufacturer's claim is considered valid if the difference between the actual and theoretical total amount of carbonate present in the sample is less than 0.0010 mol.

Using your answers in **(a)(i)** and **(a)(ii)**, determine if the manufacturer's claim is valid.

[2]

$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$
Total moles of carbonates present = 0.045 ÷ 2 = **<u>0.0225 mol</u>**

Total moles of carbonates based on manufacturer's claim
= 0.0184 + 0.00190 = **<u>0.0203 mol</u>**

Since the **<u>difference</u>** between the calculated moles and theoretical moles of carbonates is **<u>more than 0.0010 mol</u>**, the **<u>manufacturer's claim is false</u>**.

(iii) When solid magnesium chloride is dissolved in water, it produces a slightly acidic solution of pH 6.5.

Using appropriate equation(s), explain the above observation.

[2]

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$
$\mathbf{[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+}$ **[1]**

$MgCl_2$ dissolves in water and **<u>Mg^{2+} undergoes</u>** partial **<u>hydrolysis</u>** in water to produce H_3O^+, giving a slightly acidic solution.

(iv) However, the resultant solution is neutral when solid calcium chloride is dissolved in water.

By quoting relevant values from the *Data Booklet*, explain why a solution of calcium chloride is neutral while a solution of magnesium chloride is slightly acidic.

[3]

Cationic radius of Mg^{2+} = 0.065 mn
Cationic radius of Ca^{2+} = 0.099 mn

Since the cationic radius of Ca^{2+} is larger than that of Mg^{2+}, **<u>Ca^{2+} has a lower charge density</u>**.

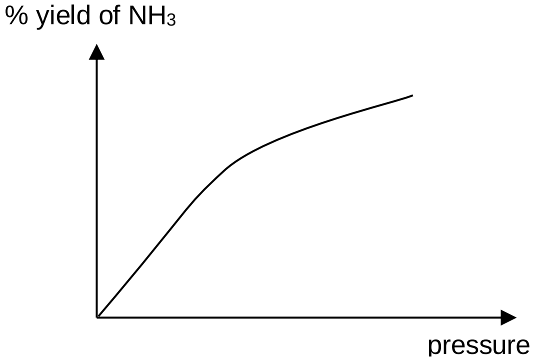
As such, it **<u>polarises the O–H bond of the water molecule to a lesser extent and no H^+ ions are produced</u>**. OR Ca^{2+} **<u>does not hydrolyse in water to produce H^+ ions</u>**. Hence, the solution is neutral.

(b) Nitrogen fertilisers are important in enhancing the growth of plants. Almost all nitrogen fertilisers are produced from ammonia, which in turn, is manufactured in the Haber Process. This process combines nitrogen and hydrogen gas to form ammonia according to the following equilibrium.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(i) State how the percentage yield of ammonia will change with increasing pressure.

[1]



<u>Percentage yield of ammonia will increase</u> with increasing pressure.

(ii) N_2 and H_2 was introduced into an enclosed vessel at 300 °C. The initial partial pressures of N_2 and H_2 were 2 atm and 3 atm respectively. After an equilibrium has been established, the total pressure in the vessel was 4.7 atm.

Calculate the value of K_p at 300 °C, stating its units.

[3]

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial partial pressure / atm	2	3		0
Change / atm	– x	– 3x		+2x
Eqm partial pressure / atm	2 – x	3 – 3x		2x

Total pressure = 4.7 atm
Hence, 2 – x + 3 – 3x + 2x = 4.7
x = **<u>0.15 atm</u>**

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Eqm partial pressure / atm	1.85	2.55		0.30

$K_p = \frac{P_{NH_3}{}^2}{P_{N_2}[H_2]^3} = \frac{(0.30)^2}{(1.85)(2.55)^3} = 0.0029339 =$ **<u>0.00293 atm^{-2}</u>**

(iii) 1 atm of N_2 was added to the equilibrium mixture in **(b)(ii)** at 300 °C and time was allowed for a new equilibrium to be established. State and explain how the K_p value at this point will compare to that in **(b)(ii).**

[1]

The K_p value will **<u>remain constant / be the same</u>** as K_p is **<u>only dependent on temperature</u>**.

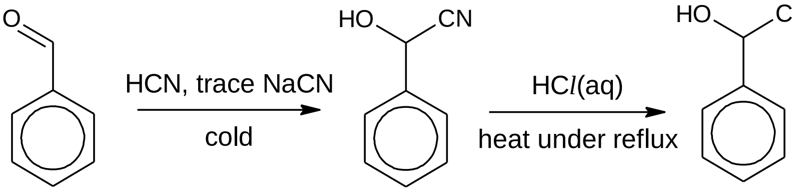
[Total: 15]

2 Mandelic acid, $C_6H_5CH(OH)COOH$, is a white crystalline solid that is soluble in water.

(a) Benzaldehyde is a useful starting material for the preparation of mandelic acid.

Suggest a two–step synthesis of mandelic acid from benzaldehyde, stating clearly the reagents and conditions used and the structure of the intermediate.

[3]



(b) Suggest how you would distinguish between aqueous solutions of mandelic acid and nitric acid of the same concentration by means of a **physical** method.

Explain your reasoning.

[3]

Measure the pH of the aqueous solutions using **pH paper / meter**. The solution of a **lower pH** is that of **nitric acid**.

Nitric acid is a **strong acid** while mandelic acid is a **weak acid**. Nitric acid **dissociates to a greater extent in water** to produce a **higher concentration of H^+** ions which results in a lower pH for its aqueous solution.

(c) **(i)** 20 cm^3 of 1.0 mol dm^{-3} mandelic acid solution was titrated with 2.0 mol dm^{-3} aqueous sodium hydroxide. Calculate the concentration of the salt, sodium mandelate, formed at equivalence point.

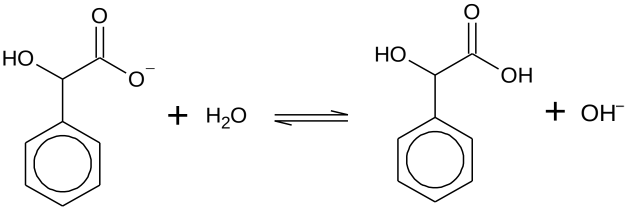
[1]

Let mandelic acid be HA.
$HA \equiv A^-$
moles of $A^- = 0.020 \times 1.0 = 0.0200$ mol
total volume at equivalence point = 20 + 10 = 30 cm^3
$[NaA] = [A^-] = 0.0200 / 0.030 =$ **0.667 mol dm^{-3}**

(ii) Hence calculate the pH of the solution at equivalence point, given pK_a of mandelic acid is 3.41.

[2]

At equivalence point, salt hydrolysis occurs:



$K_b(A^-) = 10^{-14} / 10^{-3.41} = 2.5704 \times 10^{-11}$ mol dm^{-3}

$[OH^-] = \sqrt{(2.5704 \times 10^{-11})(0.66667)} = 4.1396 \times 10^{-6}$ mol dm^{-3}
pH = 14 – pOH = 14 + lg(4.1396×10^{-6}) = **8.62**

(iii) Use your answer in **(c)(ii)** to identify a suitable indicator from Table 2.1 for the titration. Explain your choice.

Table 2.1

Indicator	pH range
Methyl red	4.2 – 6.3
Phenolphthalein	8.2 – 10.0
Titan yellow	12.0 – 13.0

[2]

Phenolphthalein

The **pH range** of phenolphthalein **lies within the region of rapid pH change** (around 8.62).

(d) **(i)** To another 20 cm^3 sample of 1.0 mol dm^{-3} mandelic acid solution, excess sodium carbonate was added and the gas liberated was collected in a gas syringe at 50 °C and atmospheric pressure.

Calculate the volume of gas you would expect to obtain at the end of the reaction.

[2]

$2HA \equiv CO_2$
moles of $CO_2 = \frac{1}{2} \times 0.0200 = 0.0100$ mol

$V = nRT / p$
$= [(0.0100)(8.31)(323)] / 101325$
$= 2.65 \times 10^{-4}\ m^3$
= **265 cm^3**

(ii) The volume of gas collected was found to be smaller than the calculated value in **(d)(i)**. Assuming that no gas escaped in the experiment, suggest **two** reasons for the discrepancy.

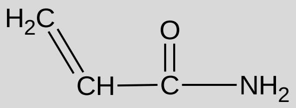
[2]

The volume of gas was measured after the **gas has cooled** (at constant pressure) from 50 °C.

The gas particles have **significant intermolecular forces of attraction** that result in them being **closer together** and hence occupy a smaller than expected volume.

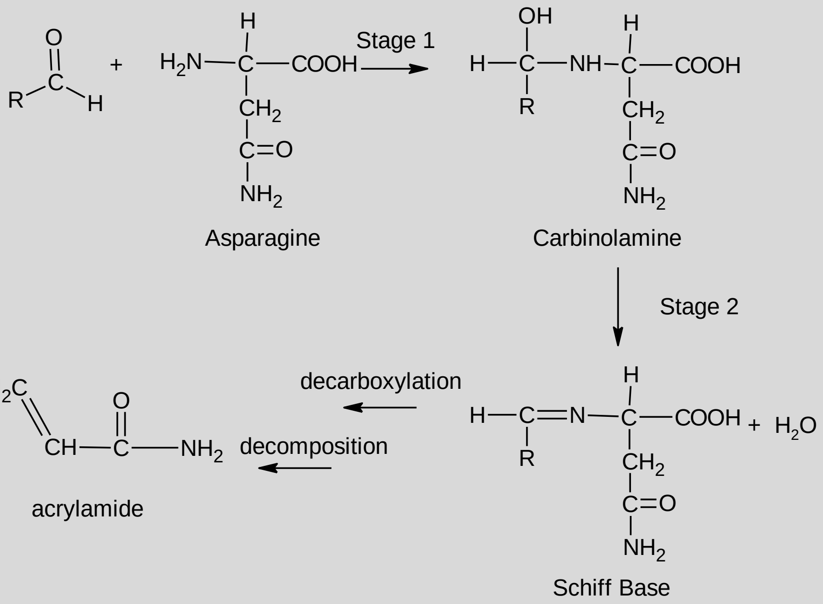
[Total: 15]

3 **(a)** High levels of acrylamide, which is harmful to human health, are produced when starchy foods are heated at high temperature.



acrylamide

The formation of acrylamide begins with the reaction between an aldehyde and asparagine, $H_2NCH(CH_2CONH_2)COOH$. This process involves the formation of carbinolamine and a Schiff Base.



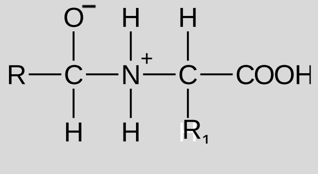
(i) State the type of reaction for stages 1 and 2 respectively.

[2]

Stage 1: Nucleophilic Addition
Stage 2: Elimination

The mechanism for stage 1 is thought to involve the following three steps.

step 1 Nucleophilic attack of α–NH_2 of asparagine on carbonyl carbon atom to form the following intermediate where R_1 is $–CH_2CONH_2$.



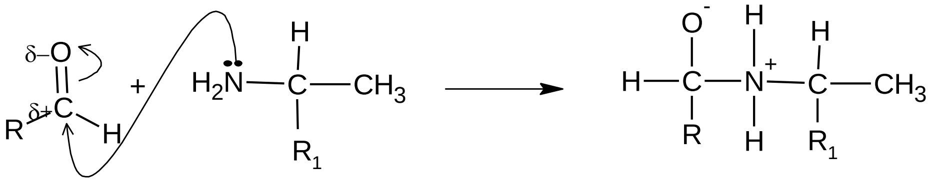
step 2 The intermediate is deprotonated by a water molecule, breaking the N–H bond.

step 3 The protonated water molecule from step 2 then transfers the proton to the negatively charged oxygen to form carbinolamine.

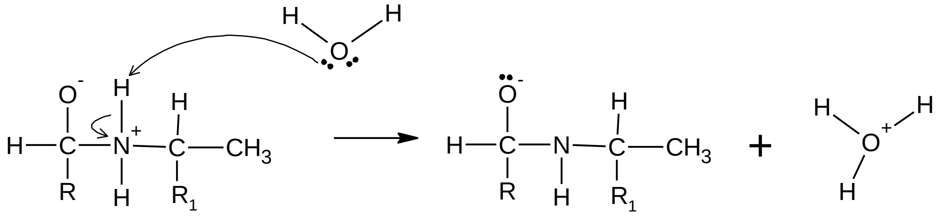
(ii) Use the information above, draw the mechanism for stage 1 by showing relevant lone pairs of electrons, dipoles and curly arrows to represent the movement of electron pairs.

[3]

Step 1: Nucleophilic addition

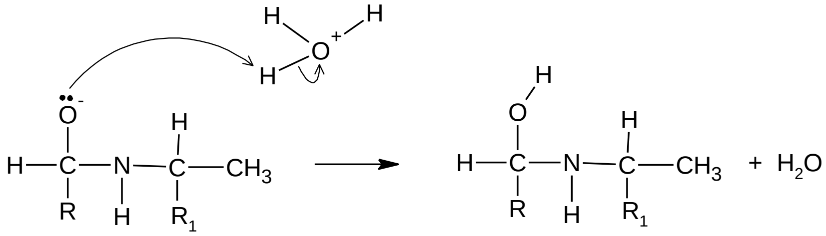


Step 2: N—H bond breaks in the presence of water solvent.



where R_1 is $—CH_2CONH_2$

Step 3: The protonated water transfers the proton to the negatively charged oxygen to form carbinolamine.



where R_1 is $—CH_2CONH_2$

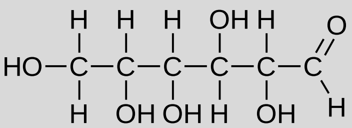
(iii) The experiment was repeated with the use of an aparaginase enzyme which hydrolyses asparagine, $H_2NCH(CH_2CONH_2)COOH$ to aspartic acid, $H_2NCH(CH_2COOH)COOH$. The level of acrylamide, $CH_2{=}CHCONH_2$ in food products is reduced by 99 %. Suggest a reason why this is so.

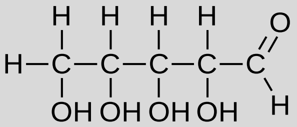
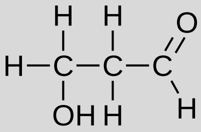
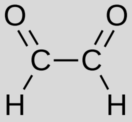
[1]

Amide group of acrylamide comes from the side chain amide group of asparagine. (During the reaction, the side chain amide group of asparagine is incorporated into acrylamide as the amide bond.) Asparaginase hydrolyses the side chain amide group of asparagine, forming aspartic acid and ammonia, and hence acrylamide is no longer produced.

(b) Several aldehydes can be found in starchy foods. Fixed amount of each aldehyde was heated with asparagine. The mass of acrylamide formed from each aldehyde is shown in Table 3.1 below.

Table 3.1

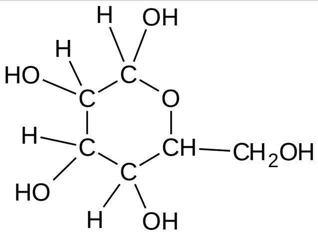
Aldehyde	Structure	Mass of acrylamide (μg)
glucose		1454

ribose		2425
glyceraldehye		2669
glyoxal		3936

(i) In solution, glucose molecules can exist in an isomeric cyclic form. The oxygen of the hydroxyl group on carbon number 5 joins to the carbonyl carbon atom and the total number of hydroxyl groups remain unchanged. The mechanism for the formation of the isomeric cyclic form is similar to that for stage 1 in **(a)**.

Draw the structural formula of glucose in the isomeric cyclic form.

[1]



(ii) Using the data in Table 3.1, state the relationship between the mass of acrylamide formed and the length of carbon chain of the aldehydes. Suggest a reason for it.

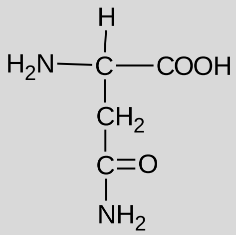
[2]

Higher mass of acrylamide obtained when shorter carbon chain is reacted.

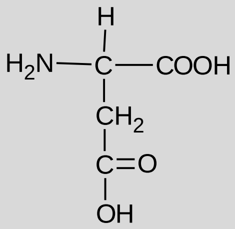
Aldehydes with shorter carbon chain are more reactive.
Possible reasons:

- Carbonyl carbon of shorter carbon chain sugar is more electrophilic, more susceptible to nucleophilic attack from α–NH_2 of asparagine;
- Carbonyl carbon of shorter carbon chain is less sterically hindered for nucleophilic attack from α–NH_2 of asparagine;
- Long carbon chain such as ribose or glucose able to form cyclic (hemiacetal) structure, therefore lower the proportion of carbonyl group for nucleophilic attack.

(c) The structures of two amino acids, asparagine and aspartic acid are given below.



asparagine



aspartic acid

(i) Suggest a simple chemical test to distinguish between asparagine and aspartic acid.

[2]

Heat both with dilute NaOH in water bath.

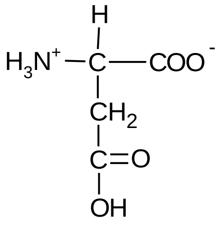
Asparagine give off ammonia which turns moist red litmus paper blue but aspartic acid does not give off ammonia gas.

(ii) The three pKa values associated with aspartic acid are 1.88, 3.65 and 9.60.

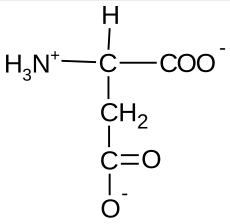
Suggest the major species present in solutions of aspartic acid with the following pH values.

- pH 3
- pH 7

[2]

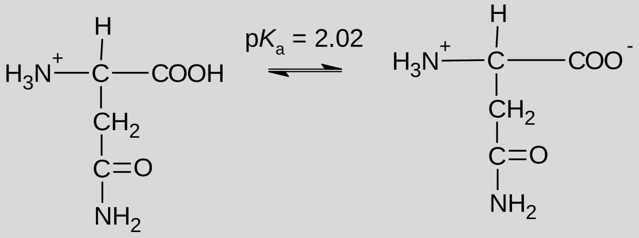


pH 3



pH 7

(iii) The following equilibrium exists in an aqueous solution of asparagine at pH 2.02.



protonated cation

zwitterion

Calculate the ratio of the concentration of asparagine zwitterion to the concentration of the protonated cation when the pH of the solution is 3.10.

You may represent the cation as HA and the zwitterion as A^- in your working. [2]

At pH 2.02 = pK_a, the equilibrium exists. The concentration of protonated cation and zwitterion would be the same. At pH 3.10, the equilibrium position is shifted to the right, concentration of zwitterion is expected to be larger than concentration of the protonated cation.

Use pH of solution = $pK_a + \log_{10}\dfrac{[A^-]}{[HA]}$

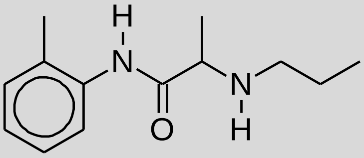
$$3.10 = 2.02 + \log_{10}\frac{[A^-]}{[HA]}$$

$$\log_{10}\frac{[A^-]}{[HA]} = 1.08$$

$$\frac{[A^-]}{[HA]} = 10^{1.08} = 12.02 = \underline{\mathbf{12.0}}$$

[Total: 15]

4 **(a)** Prilocaine is a local anaesthesia used in dentistry.

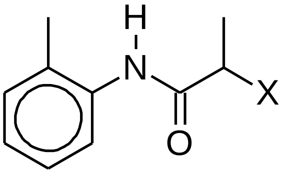


prilocaine

It can be synthesised by reacting propylamine, $CH_3CH_2CH_2NH_2$, with a suitable alkyl halide.

(i) Draw the structure of the alkyl halide.

[1]



X = C*l*, Br or I

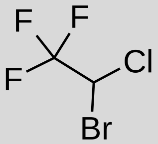
Propylamine can be formed from bromoethane in 2 steps.

(ii) Suggest the reagents and conditions needed for each step.

[2]

Step 1: ethanolic KCN, heat under reflux
Step 2: H_2 with Ni catalyst, heat OR $LiAlH_4$ in dry ether

(b) Halothane is a general anaesthetic given by inhalation.



halothane

0.1 mol of (+)–halothane is warmed with 0.1 mol of aqueous sodium hydroxide.

(i) State which halogen atom reacts. Give a reason for your answer.

[1]

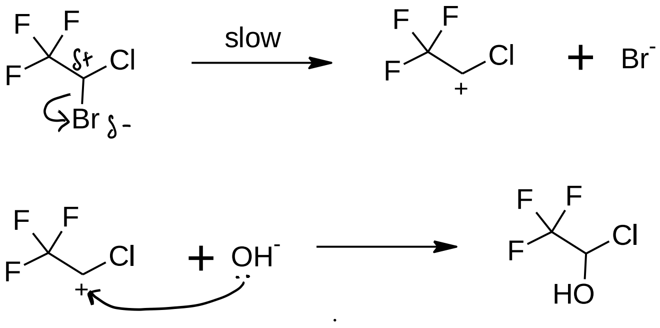
Bromine as the C–Br bond is the weakest C–X bond present.

The progress of the reaction can be followed using a polarimeter as the reactant rotates plane–polarised light while the resulting mixture is optically inactive.

(ii) Draw the mechanism for the reaction between halothane and sodium hydroxide.

[2]

Unimolecular nucleophilic substitution (S_N1)



(iii) Considering your answer to **(b)(ii)**, suggest a reason why it is unexpected for halothane to undergo substitution via the mechanism drawn. [1]

The presence of multiple **electronegative atoms** / **electron–withdrawing groups** **intensify the positive charge** on the carbocation intermediate, destabilising it.

(c) The presence of alkyl halides can be verified by warming the sample with aqueous sodium hydroxide, followed by addition of nitric acid and lastly silver nitrate.

A student used sulfuric acid instead of nitric acid, leading to the formation of silver(I) sulfate precipitate, Ag_2SO_4.

(i) Explain how the formation of silver(I) sulfate affects the test. [1]

A ppt will be observed whether an alkylhalide was present / It gives a false positive result / cannot distinguish between white silver(I) sulfate and white silver chloride ppt

(ii) Calculate the solubility of silver(I) sulfate given that its K_{sp} value is 1.2×10^{-5}. [2]

Ag_2SO_4 (s) —— 2 Ag^+ (aq) + SO_4^{2-} (aq)

$K_{sp} = [Ag^+]^2[SO_4^{2-}]$
$1.2 \times 10^{-5} = (2s)^2(s) = 4s^3$
s = **0.0144** mol dm^{-3}

(iii) State and explain how the solubility of silver(I) sulfate is affected by the addition of aqueous ammonia. [1]

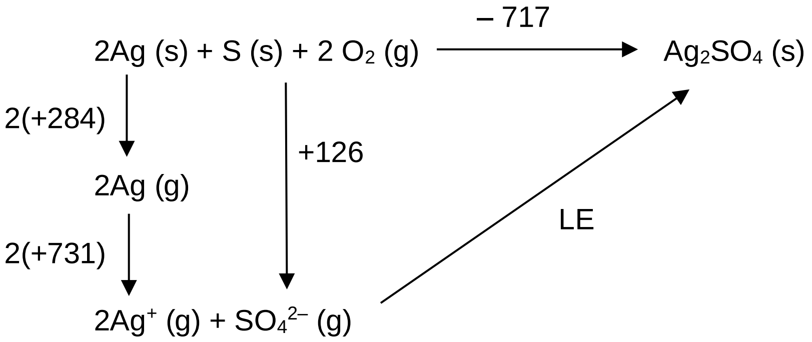
Solubility increases / silver(I) sulfate **ppt dissolves** due to **formation of soluble** $[Ag(NH_3)_2]^+$ **complex**.

(d) Table 4.1 contains thermochemical information related to silver(I) sulfate.

Table 4.1

Enthalpy change of formation of silver(I) sulfate	–717 kJ mol^{-1}
Enthalpy change of formation of gaseous sulfate anions	+126 kJ mol^{-1}
Enthalpy change of atomisation of silver	+284 kJ mol^{-1}
Enthalpy change of hydration of silver cations	–473 kJ mol^{-1}
Enthalpy change of hydration of sulfate anions	–1035 kJ mol^{-1}

(i) Using relevant information from the *Data Booklet* and Table 4.1, draw an energy cycle to determine the lattice energy of silver(I) sulfate. [3]



By Hess' Law,
LE = –126 – 2(731) – 2(284) – 717 = **<u>– 2873</u>** kJ mol^{-1}

(ii) Using your answer to **(d)(i)** and appropriate data in Table 4.1, calculate the standard enthalpy change of solution for silver(I) sulfate. [1]

$$\Delta H^{\ominus}_{sol} = \sum \Delta H^{\ominus}_{hyd} - LE = 2(-473) - 1035 + 2873 = \underline{\mathbf{+892}} \text{ kJ mol}^{-1}$$

[Total: 15]

Section B

*Answer **one** question from this section*

5 (a) Fig 5.1 shows a sequence of reactions involving acrylic acid, the simplest unsaturated carboxylic acid.

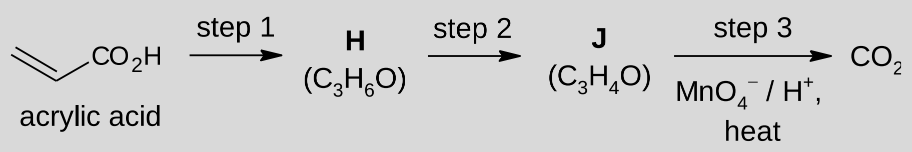
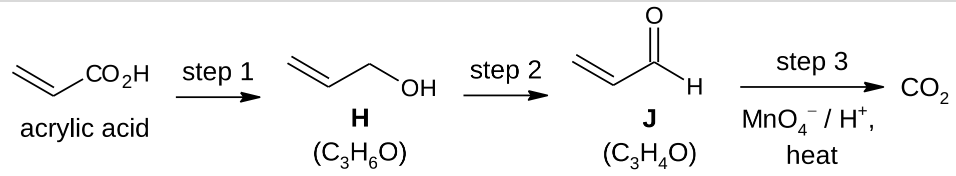


Fig. 5.1

(i) Compound **H** effervesces with sodium and compound **J** reacts with 2,4-dinitrophenylhydrazine.

Suggest structures for compounds **H** and **J**.

[2]



(ii) Suggest reagents and conditions for steps 1 and 2 in Fig. 5.1.

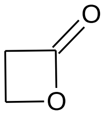
[2]

Step 1: $LiAlH_4$ in dry ether

Step 2: $K_2Cr_2O_7$ in dilute/aqueous H_2SO_4, heat with immediate distillation

(iii) Compound **G**, an isomer of acrylic acid, is neutral and does not react with Tollens' reagent. Deduce the structure of **G**.

[1]



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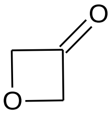

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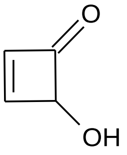

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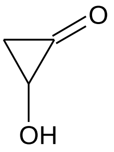

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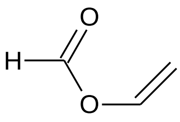

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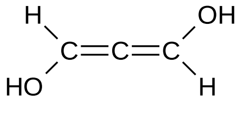

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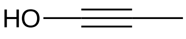
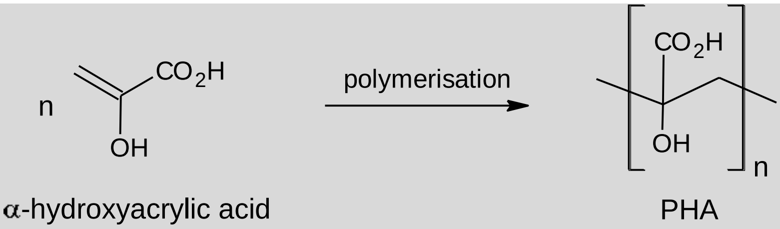


(b) α-hydroxyacrylic acid undergoes addition polymerisation to give a polymer, PHA.



(i) Suggest and explain the relative acidities of α-hydroxyacrylic acid and acrylic acid, $CH_2{=}CHCO_2H$.

[2]

α-hydroxyacrylic acid is **more acidic** than acrylic acid.

The presence of the **electron-withdrawing –OH group** in the conjugate base of α-hydroxyacrylic acid **disperses the negative charge** on the COO^- group, making the conjugate base **more stable** √ than that of acrylic acid.

(ii) Studies suggests that PHA interacts with divalent metal cations such as calcium and magnesium under alkaline conditions.

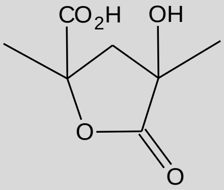
Suggest and explain the type of interaction that is likely to exist between PHA and the metal cations in alkaline medium.

[2]

Ionic interactions.

Under alkaline conditions, the carboxylic acid groups in PHA are deprotonated/neutralised. The **negatively charged carboxylate** (COO^-) groups can form **electrostatic forces of attraction** with the positively charged **metal cations**.

(c) PHA can form intramolecular lactone rings between –COOH and –OH groups on adjacent repeat units. Part of the structure of PHA with an intramolecular ring is shown below.



(i) State the type of reaction occurring in the formation of the lactone ring.

[1]

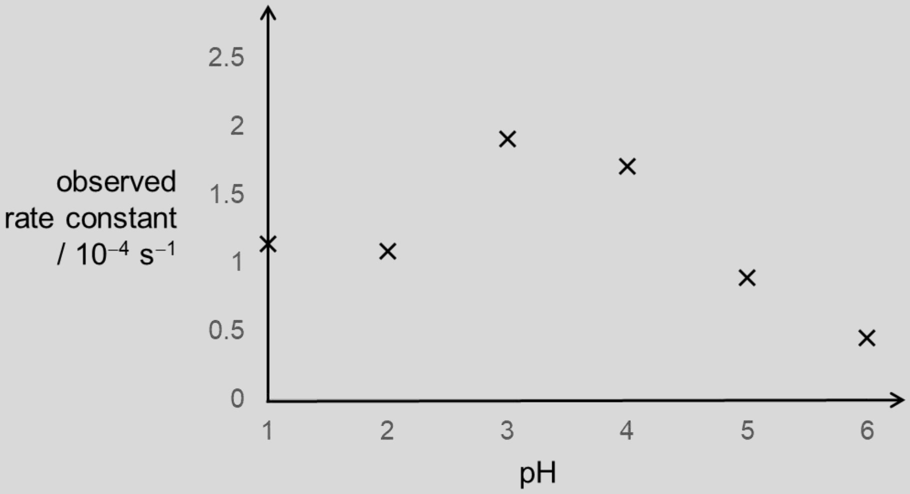
Condensation

A series of experiments were carried out to investigate the rate of the lactone ring build-up of PHA as a function of pH at constant temperature.

The rate equation for the reaction is given as follows.

$$\text{rate} = k[\text{PHA}]^m[\text{H}^+]^n$$

The reaction was observed to follow pseudo first order kinetics with respect to PHA and the following graph of the observed rate constant against pH was obtained.



(ii) Suggest how the pseudo first order kinetics with respect to PHA was achieved experimentally.

[1]

The **<u>acid</u>** (to provide H^+ ions) was used in **<u>large excess</u>** as compared to PHA.

(iii) From the graph, identify the pH range for which the value of ***n***, order of reaction with respect to H^+, is zero.

Explain your reasoning.

[2]

<u>pH 1 to pH 2</u>

Since reaction follows pseudo first order kinetics with respect to PHA,
rate = k'[PHA] where $k' = k[H^+]^n$

From pH 1 to pH 2, the **<u>observed rate constant</u>**, k', was **<u>relatively constant</u>**, suggesting that the **<u>rate was independent of $[H^+]$</u>**.

(iv) At a certain pH that lies within the range identified in **(c)(iii)**, the observed rate constant was found to be 1.14×10^{-4} s^{-1}. Calculate the time taken for 75% of lactone rings to be formed at this pH.

[2]

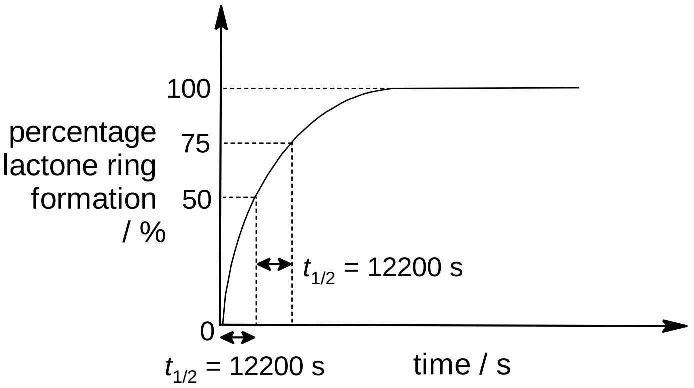
$$t_{\frac{1}{2}} = \frac{\ln 2}{k'} = \frac{\ln 2}{0.000114} = 6080.2 \text{ s}$$

Since $\frac{25}{100} = \left(\frac{1}{2}\right)^n$, number of half-lives passed, n = 2

Time taken = 6080.2 × 2 = **<u>12200 s</u>**

(v) Hence sketch a graph of percentage lactone ring formation against time, assuming that the reaction goes to completion. Label clearly how the percentage of lactone changes with time.

[2]



(d) The PHA samples used in the kinetic study was prepared by dilution of the reagent solution with heavy water, D_2O.

[Deuterium, D = ^2H]

(i) Suggest, with reasoning, how the first ionisation energy of deuterium would compare with that of hydrogen.

[1]

The first ionisation energy of deuterium would be **similar to / the same** as that of hydrogen.

Deuterium and hydrogen have the **same number of protons** and the additional neutron present in the nucleus of deuterium is uncharged. Hence the **effective nuclear charge/ electrostatic attraction between the valence electron and nucleus** is **similar / the same** for deuterium and hydrogen.

(ii) Beams of D^+ and H^+ particles, at the same speed, were passed through an electric field.
Explain, qualitatively, how the angle and direction of deflection of the two beams would compare.

[1]

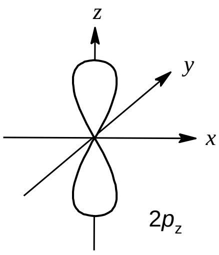
Since angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$, the D^+ particles (which are of the same charge but twice as heavy than H^+ particles) will be **deflected in the same direction but by half the angle** of that of H^+ particles.

(iii) Water enriched in heavier oxygen-18 isotope, $H_2{}^{18}O$, is also commercially available.

Draw the orbital from which the electron is removed in the **third** ionisation energy of an oxygen-18 isotope.

[1]

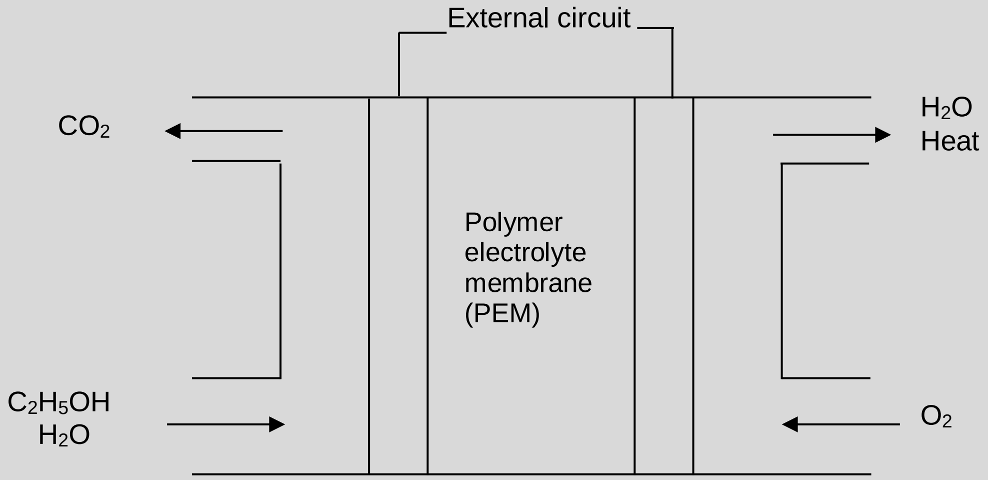
^{18}O: $1s^2 2s^2 2p^4$ and a 2*p* electron is removed in the 3rd ionisation energy.



[Total: 20]

6 **(a)** The direct oxidation of alcohols in a fuel cell represents potentially the most efficient method of obtaining useful energy from a renewable fuel.

Direct–ethanol fuel cell or DEFC is one common example of fuel cells where ethanol is fed directly into the cell to produce carbon dioxide. Hydrogen ions travel through the polymer electrolyte membrane (PEM) to the electrode to react with oxygen to produce water, while the electrons travel through the external electrical circuit to generate electrical power.



(i) Write the ion–electron half–equations for the reactions which take place at the electrodes of the DEFC, and hence an overall equation for the cell reaction.

[2]

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Anode: $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

Overall equation: $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) The cell is capable of producing an e.m.f of +1.62 V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the CO_2/C_2H_5OH electrode reaction.

[1]

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$
$+1.62 = +1.23 - E^\ominus_{anode}$
$E^\ominus_{anode} = +1.23 - 1.62$
$= -0.39V$

(iii) Pyrogallol solution is an organic compound that absorbs oxygen efficiently. Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

[2]

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$
When a small amount of pyrogallol solution is added, it decreases the partial pressure of O_2 / [O_2]. Hence **equilibrium** above will **shift to the left to increase partial pressure of** O_2 / [O_2]**.**

$\boldsymbol{E^\ominus_{cathode}}$ will be **more negative/less positive** and hence **overall $\boldsymbol{E_{cell}}$ value** will be **more negative/less positive**.

(iv) Suggest a possible advantage of using the DEFC compared to a hydrogen fuel cell.

[1]

The cost of transportation will be lower as ethanol is in the liquid state. /
It is safer to transport ethanol as it is less explosive than hydrogen / ethanol takes up less space than hydrogen.

(b) One method for the construction of the fuel cell involves electroplating a layer of platinum onto the surface of the PEM. The electrolyte used for this process is a solution of $[Pt(NH_3)_4]^{2+}$ and the PEM is the cathode in the electrolytic cell.

(i) Write the half–equation for the reaction occurring at the cathode.

[1]

$[Pt(NH_3)_4]^{2+} + 2e^- \rightarrow Pt + 4NH_3$

(ii) Calculate the mass of platinum deposited onto a PEM with surface area of 25 cm^2 if a current of 3.5×10^{-3} A cm^{-2} was passed through the circuit for 75 minutes.

[2]

$Q = It$
$= (3.5 \times 10^{-3})(25)(75 \times 60)$
$= 393.75$ C

Number of moles of electrons = 393.75 / 96500
= 0.00408 mol

Number of moles of platinum deposited = 0.00204 mol

Mass of platinum = $2.04 \times 10^{-3} \times 195.1$ = **0.398 g**

(c) Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis, both for fundamental research and industrial manufacturing.

When alkaline potassium manganate(VII) is added to a primary alcohol, the purple solution first becomes dark green and then produces a brown precipitate.

(i) State the identities of the dark green solution and the brown precipitate. You may find the use of *Data Booklet* to be relevant.

[1]

Dark green solution : MnO_4^{2-}
Brown ppt : MnO_2

When acidified potassium manganate(VII) is added to a secondary alcohol, the purple solution decolourises. Propan–2–ol reacts with acidified potassium manganate(VII) to yield propanone, according to the **unbalanced** equation as shown below.

$$CH_3{}^{a}CH(OH)CH_3 + MnO_4^{-} \rightarrow CH_3{}^{b}COCH_3 + Mn^{2+}$$

(ii) State the oxidation number of ^{a}C and ^{b}C respectively.

[1]

^{a}C – 0
^{b}C – +2

(iii) Hence, or otherwise, determine the reacting mole ratio of propan–2–ol to potassium manganate(VII).

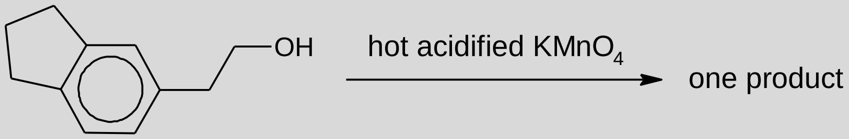
[1]

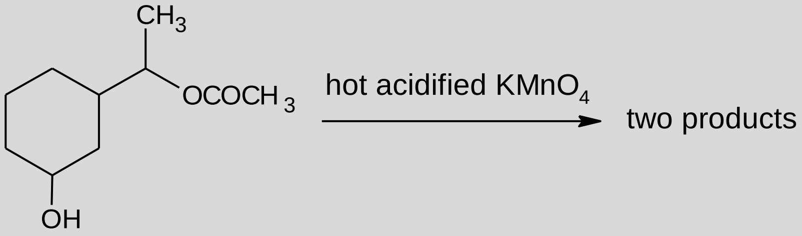
Since oxidation number of reacting carbon increases from 0 in propan-2-ol to +2 in propanone, there is a loss of 2 electrons per mole of propan-2-ol.

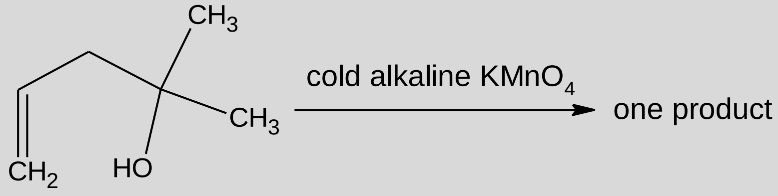
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
There is a gain of 5 electrons per mole of MnO_4^-

Since electrons lost = electrons gained in the reaction,
Reacting mole ratio of $CH_3CH(OH)CH_3 : MnO_4^- = 5 : 2$

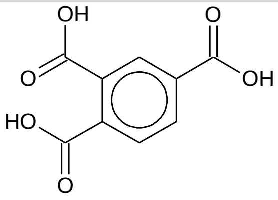
(iv) Predict the organic products of the following reactions with $KMnO_4$(aq).

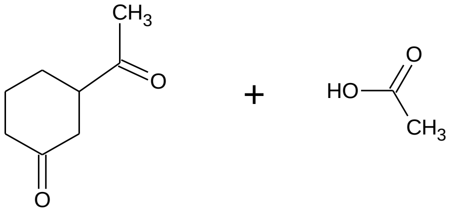


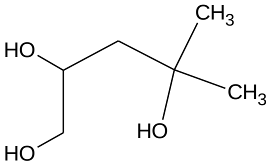




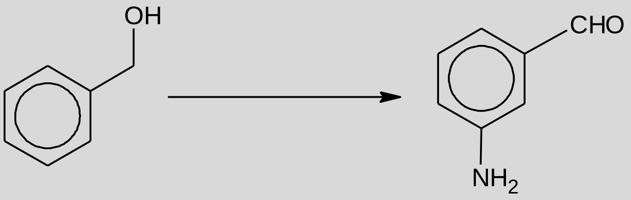
[4]





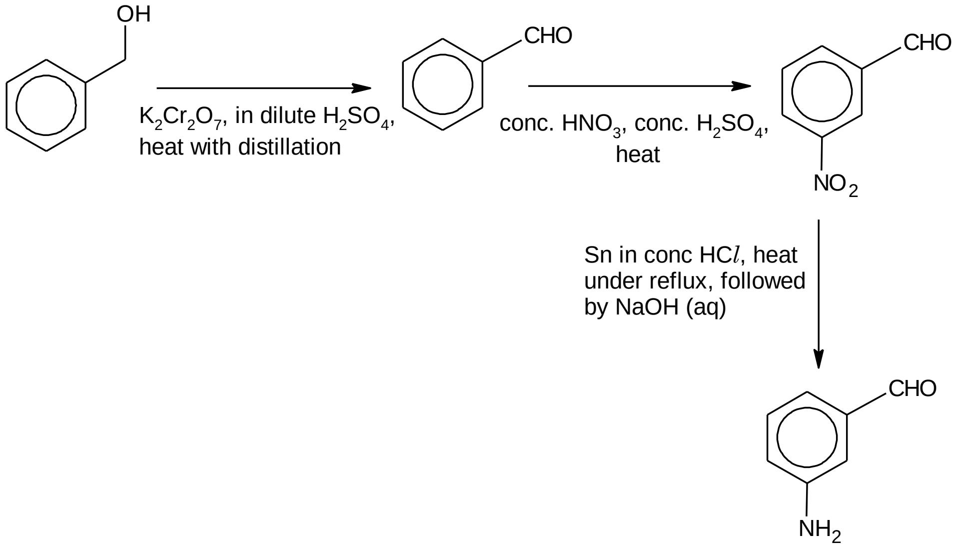


(d) Devise a synthetic pathway (in no more than 3 steps) for the following conversion.



In your answer, state the reagents and conditions required for each step as well as the structure of any intermediates formed.

[4]



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Name:		**Index Number:**		**Class:**	

DUNMAN HIGH SCHOOL
Preliminary Examinations 2019
Year 6

H2 CHEMISTRY

9729/04

Paper 4 Practical

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 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.

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	**17**
2	**10**
3	**14**
4	**14**
Total	**55**

[Turn over

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

1 Determination of acid concentration and enthalpy change of neutralisation using calorimetry

When an acid is added into an alkali, an exothermic reaction takes place and the temperature of the mixture increases. Maximum heat is given out when stoichiometric amounts of H^+ and OH^- are added together.

FA 1 is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HCl, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4
FA 2 is 2.00 mol dm^{-3} sodium hydroxide, NaOH

In this question, you are to follow the neutralisation of known volumes of **FA 2**, NaOH, by measuring the highest temperature obtained as different volumes of **FA 1** are added.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following.

- the value of ***y***, concentration of the acids present in **FA 1**
- the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(a) Method

1 Fill the burette with **FA 2**.
2 Support the Styrofoam cup in a 250 cm^3 glass beaker.
3 Run 20.00 cm^3 **FA 2** from the burette into the Styrofoam cup. Stir and measure the temperature of this **FA 2**.
4 Measure 20 cm^3 **FA 1** in a measuring cylinder.
5 Tip the **FA 1** in the measuring cylinder into the **FA 2** cup, stir and record the maximum temperature obtained in the reaction.
6 Rinse and carefully dry the Styrofoam cup.
7 Repeat **steps 1 to 6** three more times, each time using 20.00 cm^3 of **FA 2.** Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 1** respectively in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 1** which will allow you to investigate more precisely the volume of **FA 1** that produces the highest temperature rise when added to 20.00 cm^3 of **FA 2**.

Record your results in an appropriate format in the next page. Record all measurements of volume, temperature and temperature change, ΔT.

(i) **Experimental results**

Expt No.	Vol of **FA 1**/ cm^3	Vol of **FA 2**/ cm^3	Temperature of **FA 2**/ °C OR initial temperature/ °C	Maximum Temperature / °C	∆*T* / °C
1	20.0	20.00			
2	30.0	20.00			
3	40.0	20.00			
4	50.0	20.00			
5	**35**.0	**20.00**			
6	**25**.0	**20.00**			

[5]

(ii) Plot ∆***T*** (*y*–*axis*) against volume of **FA 1** (*x*–*axis*) on the grid below.
Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

[3]

(iii) Read from the graph the maximum temperature change, $\Delta \boldsymbol{T}_{max}$, and the volume, $\boldsymbol{V}_{neut}$, of **FA 1** needed to obtain this value. Record these values in the spaces provided below.

maximum temperature change, $\Delta \boldsymbol{T}_{max}$ = ……10.0…………°C

volume of **FA 1** used at $\Delta \boldsymbol{T}_{max} = \boldsymbol{V}_{neut}$ = ……34.0………….. cm^3

[1]

(b) Use your results from **(a)(iii)** to calculate:

(i) the concentration, in mol dm^{-3}, of the hydrogen ions in **FA 1**.

Moles of OH^- used = $2.0 \times (\frac{20.00}{1000}) = 0.0400$ mol

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Total moles of H^+ in **FA 1** required for neutralisation = 0.0400 mol

Total concentration of H^+ in **FA 1** = $\frac{0.0400}{0.0340} = 1.1764 = 1.18$ mol dm^{-3}

concentration of hydrogen ions in **FA 1** = ………**<u>1.18 mol dm^{-3}</u>** ……………

[1]

(ii) Hence, the value of ***y***.

Since **FA 1** is an aqueous solution prepared by mixing *equal volumes* of ***y*** mol dm^{-3} hydrochloric acid, HCl, and ***y*** mol dm^{-3} sulfuric acid, H_2SO_4;

mol ratio of H^+ from H_2SO_4 : H^+ from HCl
2 : 1

concentration of HCl in **FA 1** = $\frac{1}{3} \times (1.1764) = 0.392$ mol dm^{-3}

Since ***equal volumes*** of both acids were mixed to obtain **FA 1**

Concentration of $HCl(aq)$ before dilution = ***y*** = ***2*** x 0.392 = 0.784 mol dm^{-3}

value of ***y*** is …**<u>0.784</u>** …………………..

[1]

(iii) the heat change for the reaction and hence the enthalpy change of neutralisation, ΔH_{neut}, for the reaction

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

[Assume that 4.18 J of energy is needed to raise the temperature of 1 g of the solution by 1 K]

Heat released = $mc\Delta T_{max}$ = (20.00 + 34.0)(4.18)(10.0)
= 2257.2 J

$\Delta H_{neut} = -\frac{2257.2}{0.0400} = -56430$ J mol^{-1} = -56.4 kJ mol^{-1}

[4]

(c) A student suggested using a burette rather than a measuring cylinder to measure the volume of **FA 1** to improve the precision in volume measurement. However, he was advised not to do so by his teacher.

Suggest a disadvantage of using a burette and explain how the calculated ΔH_{neut} would be affected if volume of **FA 1** had been added from a burette.

Disadvantage
Takes **longer** to add **FA 1** into **FA 2**.

Impact on ΔH_{neut}
Since addition of **FA 1** from a burette is a slow process, heat is lost during the slow process. Heat loss reduces $\Delta \boldsymbol{T}_{\text{max}}$ and would result in a lower value for the heat change and so a lower numerical / less exothermic value for ΔH_{neut}.

[2]
[Total:17]

2 Determination of calcium ion concentration using complexometric titration

The calcium content of milk and tap water and the amount of calcium carbonate in various solid samples can be determined using complexometric titrations.

This method uses ethylenediaminetetraacetic acid, EDTA, which forms a complex with calcium ions in a 1:1 ratio. A blue dye called Patton–Reeder indicator is used to identify the end–point. The dye forms a pink complex with calcium ions. As this complex is less stable than the EDTA complex, the dye is displaced by EDTA as the titration proceeds. The solution turns blue at the end–point due to the uncomplexed dye.

FA 3 is a brand of milk.

In **2(a)**, you perform titrations to determine the calcium content of milk.

You are also provided with
FA 2, 2.00 mol dm^{-3} sodium hydroxide, NaOH
FA 4, 0.0170 mol dm^{-3} EDTA
Patton–Reeder indicator

As EDTA is harmful to the environment, **FA 4** should be disposed in the waste bottle. You should also wear gloves throughout the experiment.

(a) **(i)** 1. Fill the burette with **FA 4**.

2. Use a pipette to transfer 10.0 cm^3 of **FA 3** into a 250 cm^3 conical flask.

3. Using appropriate measuring cylinders, add 36.0 cm^3 of deionised water then 8.0 cm^3 of **FA 2** into the conical flask. Swirl and allow the solution to stand for about 2 minutes.

4. Add half a spatula of Patton–Reeder indicator into the conical flask and swirl the mixture to dissolve the indicator. The mixture is *pink* at this point.

5. Run **FA 4** from the burette into the conical flask. The end–point is reached when the mixture *loses all trace of purple and turns blue*. As the colour change is gradual, you will find it helpful to compare against the original and / or final colour of another sample.

6. At the end of the experiment, contents of the conical flask should be disposed in the waste bottle.

7. Record your titration results, to an appropriate level of precision, in the space provided.

Titration results

	1	2
Final burette reading / cm^3	14.70	29.50
Initial burette reading / cm^3	0.00	14.70
Volume of **FA 4** used / cm^3	14.70	14.80

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{\textbf{FA 4}}$, to be used in your calculations. Show clearly how you obtained this volume.

$$V_{FA\,4} = \frac{14.70 + 14.80}{2} = 14.75\ cm^3$$

[2]

(b) **(i)** Calculate the concentration of calcium ions present in **FA 3** using your answer in **(a)(ii)**.

$Ca^{2+} \equiv EDTA$

$\frac{10.00}{1000} \times [Ca^{2+}] = \frac{14.75}{1000} \times 0.0170$

$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$

[1]

The nutritional label on the packaging states that this brand of milk contains 200 mg of calcium per 200 cm^3 serving.

[1 g = 1000 mg]

(ii) Use your results from **(b)(i)** to comment if your titration results supports the claim on the nutritional label.

[A_r: Ca, 40.1]

$[Ca^{2+}] = 0.0251\ mol\ dm^{-3}$

$no. of\ moles\ of\ Ca^{2+}\ in\ 200\ cm^3 = 0.0251 \times \frac{200}{1000} = 5.025 \times 10^{-3}\ mol$

$mass\ of\ Ca^{2+}\ in\ 200\ cm^3 = 5.025 \times 10^{-3} \times 40.1 = 0.2015\ g = 201.5\ mg$

Yes, since the titration results is very close to the value in the nutritional label.

[3]

(c) Trace amounts of magnesium ions present in milk affects the accuracy of this experiment as magnesium ions also readily form a complex with EDTA.

Explain how step 3 of the procedure prevents this error.

Mg^{2+} is removed as $Mg(OH)_2$ ppt.

[1]

[Total: 10]

3 Investigation of some inorganic reactions

FA 5 is an aqueous solution containing two cations.

Carry out the following tests described in Table 3.1 and carefully record your observations.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there are no observable change, write **no observable change**.

Table 3.1

	tests	observations
(a) **(i)**	Add 1 cm depth of **FA 5** to a test–tube. Add an equal volume of aqueous sodium nitrite.	**Blue** solution turns **green**
(ii)	Add 2 cm depth of **FA 5** to a test–tube. Add 2 pieces of zinc into the test–tube. Warm the test–tube gently. Leave to stand until no further change is seen.	**Effervescence** is observed. Colourless gas evolved **extinguishes a lighted splint with a ‘pop’ sound**. √Gas is **H_2**. Blue solution **decolourises**. **Reddish–brown solid** is deposited on zinc
While waiting, continue with the next tests		
(iii)	Add 1 cm depth of **FA 5** to a test–tube. Add **FA 2** slowly, with shaking, until no further change is seen. Filter the mixture. To 1 cm depth of the filtrate, add nitric acid dropwise until no further change is seen.	A **blue ppt** forms, and is **insoluble in excess** NaOH. A **white ppt** forms, and is **soluble in excess** NaOH to form a colourless solution. Residue is a blue solid. **Filtrate is a colourless solution**. **white ppt** reforms, and is **soluble in excess** acid
(iv)	Add 1 cm depth of **FA 5** to a test–tube. Add aqueous ammonia slowly with shaking, until no further change is seen. Filter the mixture.	A **blue ppt** forms, dissolving in excess ammonia to form a **deep blue solution**. A **white ppt** forms, and is **insoluble in excess** ammonia. Residue is a white solid. Filtrate is a deep blue solution.
(v)	To 1 cm depth of the filtrate from **(iv)**, add 1 cm depth of aqueous EDTA^{4-} from the small vial with shaking. *The mixture at the end of this test should be disposed in the waste bottle.*	deep blue solution turns (lighter) **blue**.

(vi)	Add 4 cm depth of **FA 5** to a test–tube. Add 2 cm depth of aqueous sodium carbonate. The total depth of the mixture should not exceed half the test–tube. Shake well. Leave to stand for a few minutes. Filter the resultant mixture.	A **pale blue ppt** forms. Blue solution decolourises. **Effervescence** is observed. Colourless gas evolved forms **white ppt with limewater**. Gas is **CO_2**. Residue is pale blue. Filtrate is a colourless solution
(vii)	Transfer the residue from **(vi)** to a boiling tube. Heat gently then strongly until no further change is observed.	Pale blue solid turns **white** and **pale green**. A mixture of white and **black** solid remain. water droplets form on the side of the test tube. Colourless gas evolved forms white ppt with limewater. Gas is CO_2.

[7]

(b) Consider your observations in Table 3.1.

(i) State the identity of the two cations present in **FA 5**.

Cu^{2+} and Al^{3+}

[1]

The wavelengths and corresponding colours of visible light is shown in Figure 3.1.

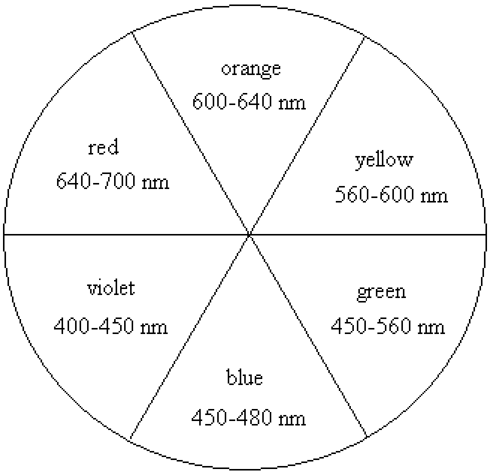


Fig. 3.1

(ii) In terms of the magnitude of d–orbital splitting, account for the colour change observed in **(a)(i)**.

Upon addition of nitrite ligand, a green mixture of the yellow nitrite complex and the original blue $[Cu(H_2O)_6]^{2+}$ complex is obtained. The colour of light absorbed changes from **orange** (600-640nm) to **violet** (400-450nm). Since the light absorbed is of a **shorter wavelength**, nitrite is a stronger field ligand that results in a **larger** magnitude of d–orbital splitting.

OR

The blue $[Cu(H_2O)_6]^{2+}$ complex **absorbs orange light** (600-640nm) while the green nitrite complex **absorbs red light** (640-700nm). Since the **light absorbed is of a longer wavelength**, the magnitude of d–orbital splitting caused by ligand in complex is **smaller**.

[2]

In **(a)(v)**, a ligand exchange occurs with hexadentate $EDTA^{4-}$.

(iii) Write a balanced equation for the ligand exchange reaction in **(a)(v)**.

[1]

$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq) + 2H_2O(l)$

(iv) Each donor atom on $EDTA^{4-}$ binds to the metal centre with similar strength as an ammonia molecule and a water molecule.

Using this information and your answer to **(b)(iii)**, estimate the enthalpy change for the reaction in **(a)(v)** and suggest why it occurs spontaneously.

As each donor atom on $EDTA^{4-}$ binds to the Cu^{2+} centre with similar strength as an ammonia molecule and a water molecule, the strength of bonds broken is similar to the strength of bonds formed. Hence **$\Delta H \approx 0$**.

There is **an increase of aqueous species** (**$\Delta n > 0$**), hence **$\Delta S > 0$**. The **disorder** of the system **increases**. Since $\Delta G = \Delta H - T\Delta S$, **$\Delta G < 0$** and the reaction is spontaneous.

[2]

(v) Write a balanced equation for the reaction occurring in **(a)(vii)**.

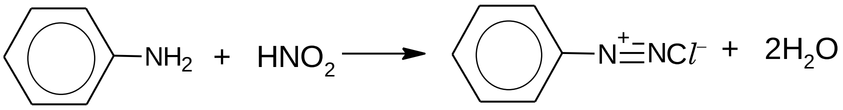
$CuCO_3 \rightarrow CuO + CO_2$ OR $Cu(OH)_2 \rightarrow CuO + H_2O$

[1]

[total: 14]

4 Planning

When an aromatic amine is treated with nitrous acid, a reaction occurs in which *diazonium salt* is formed. This process is known as **diazotisation**. The equation below shows the reaction between phenylamine and nitrous acid to form benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.



Benzenediazonium chloride, $C_6H_5N_2^+Cl^-$, is not stable at temperature above 5 °C.

Nitrous acid is a highly toxic gas. Therefore, it is generally prepared during the reaction itself by reacting $NaNO_2$ with a mineral acid.

A student followed the steps below to prepare benzenediazonium chloride.

1. 3.25 cm^3 of phenylamine was placed in a 500 cm^3 volumetric flask.
2. A mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water was added into the flask containing phenylamine to dissolve it.
3. The solution mixture was stirred and cooled to 1°C.

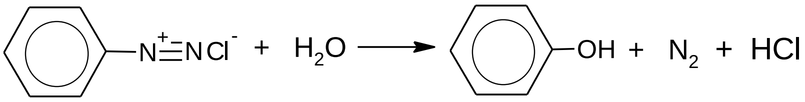
4. Solid $NaNO_2$ was dissolved in 30 cm^3 of water, then *slowly and carefully* added to the solution mixture, with stirring.
5. The resultant solution was made up to 500 cm^3 with water, mixed well and kept cool below 5 °C. This resultant benzenediazonium chloride solution prepared is labelled solution **B**.

(a) Suggest why $NaNO_2$ solution was added *slowly and carefully* in step 4.

[1]

Diazotisation is an exothermic reaction / To prevent temperature from going above 5 °C.

When the temperature is above 5 °C, benzenediazonium chloride hydrolyses to give phenol, nitrogen gas and hydrochloric acid.



The temperature of a portion of 25.0 cm^3 of solution **B** was raised to room temperature at constant pressure.

(b) **(i)** Calculate the theoretical maximum volume of N_2 produced when 25.0 cm^3 of solution **B** is hydrolysed at room temperature and pressure.

[M_r of phenylamine = 93.0; density of phenylamine = 1.02 g cm^{-3}; molar volume of gas at room temperature and pressure = 24.0 dm^3 mol^{-1}]

[3]

Mass of phenylamine used = 1.02 x 3.25 = 3.315 g

Moles of phenylamine used = $\frac{3.315}{93.0}$ = 0.0356 mol

Moles of benzenediazonium chloride prepared in 500 cm^3 = 0.0356 mol

Moles of benzenediazonium chloride prepared in 25 cm^3 portion = $\frac{25}{500}$ x 0.0356 = 0.00178 mol

Moles of N_2 produced = 0.00178 mol

Volume of N_2 produced at r.t.p. = 0.00178 x 24.0 dm^3 = 0.0428 dm^3 = **42.8 cm^3**

Another 25.0 cm^3 portion of solution **B** was transferred to a boiling tube and the hydrolysis of benzenediazonium chloride was carried out at 40 °C.

The progress of the reaction can be monitored by measuring the volume of nitrogen gas produced over time. The volume of gas produced, V after time, t, is proportional to the concentration of benzenediazonium chloride that has been hydrolysed. The final volume of gas produced, V_{final}, is proportional to the original concentration of benzenediazonium chloride.

The order of reaction can be determined from these results.

(ii) Explain the significance of $V_{final} - V$.

[1]

$V_{final} - V$ is proportional to the concentration of benzenediazonium chloride yet to be hydrolysed

(iii) Sketch, on Fig 4.1, the graph of $V_{final} - V$ against time you would expect to obtain if the order of reaction with respect to $[C_6H_5N_2^+Cl^-]$ is one.

[2]

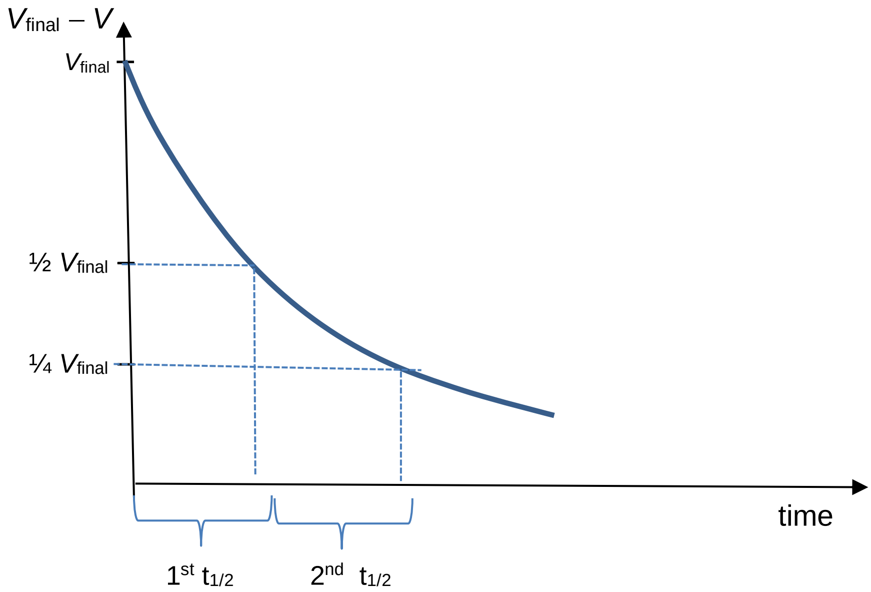


Fig 4.1

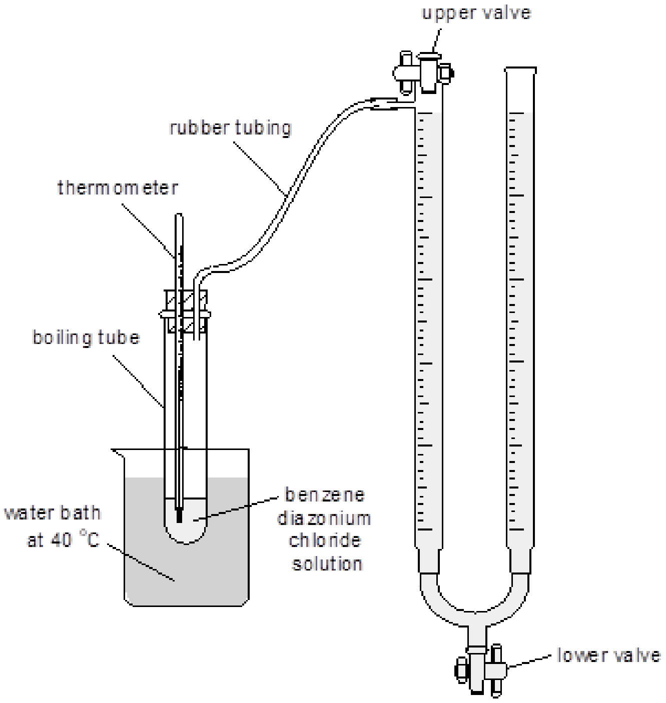


Fig. 4.2

At the start, the lower valve is closed and the upper valve is opened. The two burettes are filled with water and both levelled to 0.00 cm^3. The upper valve is closed once the hydrolysis of benzenediazonium chloride begins. As gas is collected during the experiment, the water level in both burettes will differ slightly. The lower valve is opened and closed carefully from time to time to ensure that the water levels in the two burettes are the same.

(iv) Complete the diagram on Fig 4.2 to show the experimental set–up the student could have used to carry out experiment in **(b)** to measure the volume of nitrogen evolved **at 40 °C**.

Outline the steps involved in carrying out the experiment. You may omit the step to prepare the burettes above for gas collection before the reaction begins.

Your steps should include

- the apparatus you would use
- the reactants and conditions that you would use
- the measurements you would take.

[5]

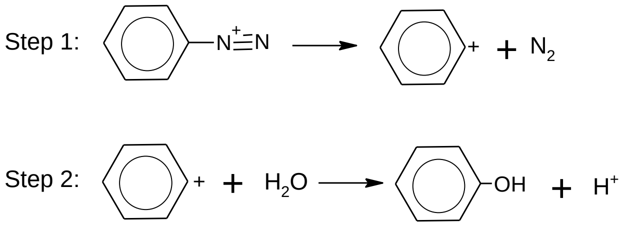
1. **Pipette 25.0 cm^3** of solution **B** in a test–tube. (Place a magnetic stirrer in it.)
2. Stoppered the solution **B** tightly and place it in a **thermostatically-controlled water bath set at 40 °C**.
3. Allow some time (10 minutes?) for the solution **B** to reach **thermal equilibrium**.
4. After 10 min, close the upper valve/stopper the test–tube and **start** the stopwatch.
   (The nitrogen gas evolved will push the water level in the left burette down and the right burette up.)
5. Open the lower valve to drain excess water so that the water level in both burettes are the same.
6. At **every** two minutes **interval** for 30 min, read and record the volume of gas evolved.
7. Continue the volume measurement until **three constant readings** are obtained.

(v) Why is there a need to ensure that the water level in both burettes are the same during the experiment?

[1]

So that gas is collected at constant / atmospheric pressure.

(c) Benzenediazonium chloride hydrolyses in water according to the following steps.



Deduce the role of H_2O and suggest the likely type of reaction occurring.

[1]

H_2O acts as nucleophile. Type of reaction is (nucleophilic) substitution or S_N1.

[Total:14]

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**18S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 September 2019

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

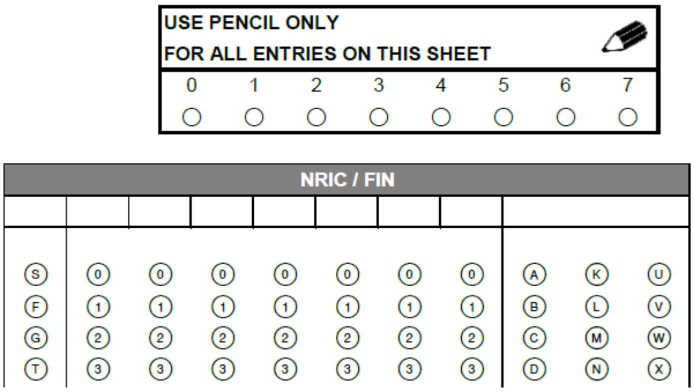
READ THESE INSTRUCTIONS FIRST

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**



USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET

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 **12** printed pages.

1 Which statement about relative atomic mass is correct?

A It is the average of the masses of all the isotopes of that element.

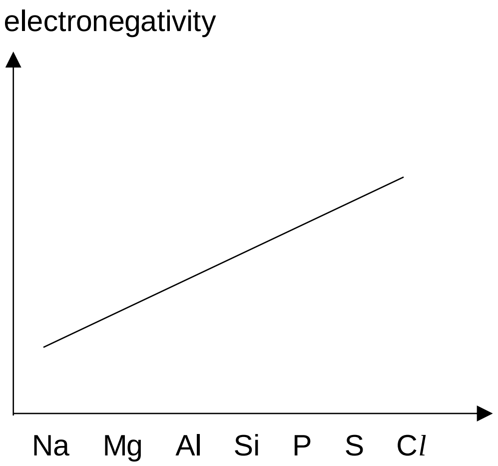
B It is the sum of the relative masses of the neutrons and protons in each atom.

C It is the ratio of the average mass of one atom of an element to the mass of one ^{1}H atom.

D It is the ratio of the mass of one mole of atoms of an element to one-twelfth the mass of one mole of ^{12}C atoms.

2 Which of the graphs correctly represent the trends in some properties of the Period 3 elements?

1



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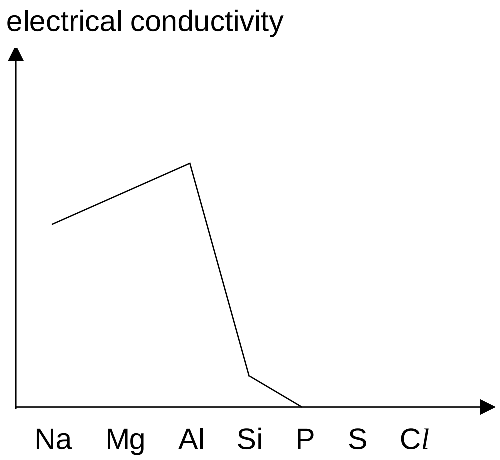

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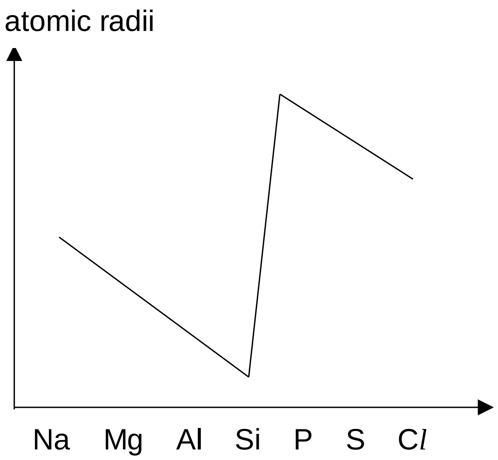

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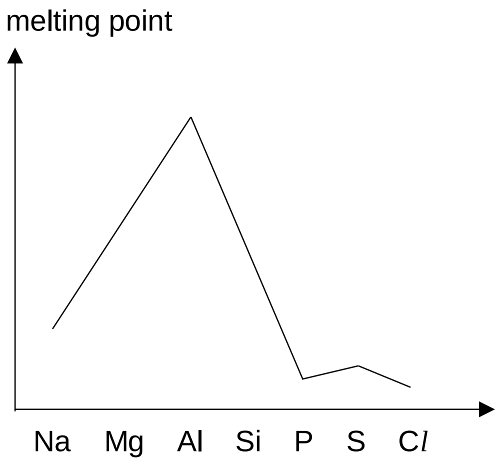


A 1 and 2 **B** 2 and 3 **C** 3 and 4 **D** 1, 2 and 4

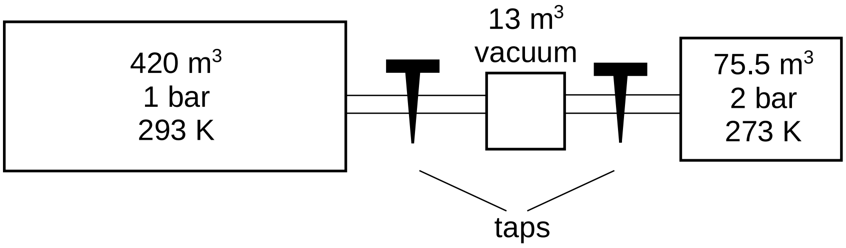
3 Which of the following correctly describes the structure and bonding present in the solid lattice of the substances given?

	substance	structure	bonding
A	ice	giant covalent	covalent bonding + hydrogen bonding
B	iodine	simple covalent	covalent bonding + permanent dipoles
C	aluminium chloride	giant ionic	ionic bonding + permanent dipoles
D	graphite	giant covalent	covalent bonding + dispersion forces

4 In which of the following pairs is the bond angle in the first species smaller than that in the second species?

A	NH_4^+	XeF_4
B	NF_3	NH_3
C	NO_2^+	SO_2
D	BCl_3	PCl_3

5 A container with a volume of 420 m^3 with an internal pressure of 1 bar at 293 K was joined to two containers as shown below. One of them has a volume of 13 m^3 with a vacuum within, while the other has a volume of 75.5 m^3 with an internal pressure of 2 bar and a temperature of 273 K.



What is the final pressure, in bar, in the combined containers when the taps were opened and the temperature allowed to equilibrate to 298 K?

A 0.84 **B** 1.12 **C** 1.16 **D** 1.19

6 *Use of the Data Booklet is relevant to this question*

Sodium percarbonate, $(Na_2CO_3)_x{\bullet}y(H_2O_2)$, is an oxidising agent in some home and laundry cleaning products.

10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate releases 45.4 cm^3 of carbon dioxide at s.t.p. on acidification.

An identical sample, on titration with 0.05 mol dm^{-3} $KMnO_4$, requires 24.0 cm^3 before the first pink colour appears. $KMnO_4$ reacts with H_2O_2 in the mole ratio 2 : 5.

What is the ratio $\frac{y}{x}$?

A $\frac{1}{3}$ **B** $\frac{2}{3}$ **C** $\frac{3}{2}$ **D** $\frac{3}{1}$

7 Which statement correctly explains why the change in Gibbs' free energy of the reaction below is relatively constant when the temperature changes?

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

A ΔS is almost zero for all temperatures in which the reactants and products are gases.

B The equilibrium constant is not affected by a temperature change.

C ΔH and ΔS do not change with temperature, hence ΔG remains constant.

D The equilibrium position will shift in such a way to offset the changes in temperature.

8 The conversion of diamond into graphite is an exothermic reaction.

$$C(diamond) \rightarrow C(graphite) \qquad \Delta H < 0 \quad \Delta G < 0$$

Which statements are correct?

1 The magnitude of the enthalpy change of atomisation of graphite is greater than that for diamond.

2 The magnitude of the enthalpy change of combustion of graphite is greater than that for diamond.

3 The bond energy of the C–C bonds in graphite is greater than that for diamond.

4 The conversion of diamond to graphite does not take place readily due to the high activation energy.

A 1 and 2 **B** 1, 3 and 4 **C** 2, 3 and 4 **D** 1, 2, 3 and 4

9 Thorium-234 undergoes radioactive decay to form protactinium-234 by emitting a beta particle. This radioactive decay is a first order reaction with a half-life of 24.1 hours.

A rock sample contains a 2 : 3 molar proportion of thorium-234 to protactinium-234. How many hours has the radioactive decay taken place if the sample was initially protactinium-234 free?

A 14.1 **B** 24.1 **C** 31.9 **D** 60.3

10 Which suggested mechanism is consistent with the experimentally determined rate equation?

	rate equation	suggested mechanism	
1	rate = k[NO]^2[H_2]	$2NO + H_2 \rightarrow N_2O + H_2O$ $N_2O + H_2 \rightarrow N_2 + H_2O$	slow fast
2	rate = k[O_2][N_2O_2]	$2NO \rightarrow N_2O_2$ $N_2O_2 + O_2 \rightarrow 2NO_2$	fast slow
3	rate = k[O_3][C*l*]	C*l* + $O_3 \rightarrow$ OC*l* + O_2 OC*l* + $O_3 \rightarrow 2O_2$ + C*l*	slow fast

A 1 and 2 **B** 1 and 3 **C** 2 and 3 **D** 1, 2 and 3

11 The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

When 0.50 mol of SO_2 and 1.00 mol of O_2 were reacted together in a container of volume 0.5 dm^3, 0.30 mol of SO_3 was present in the equilibrium mixture.

What is the numerical value of the equilibrium constant, K_c, for the equilibrium reaction below?

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

A 0.66 **B** 1.15 **C** 1.32 **D** 1.63

12 Which statement about the effect of adding a catalyst to a reversible reaction is correct?

A It increases the yield of product in the reaction.

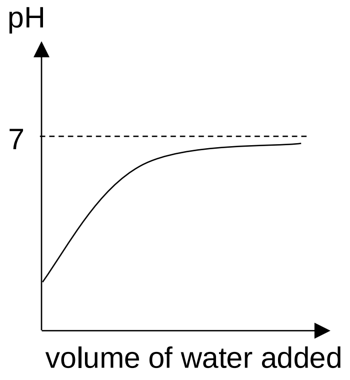
B It increases the rate constant for the forward reaction.

C It increases the equilibrium constant of the forward reaction.

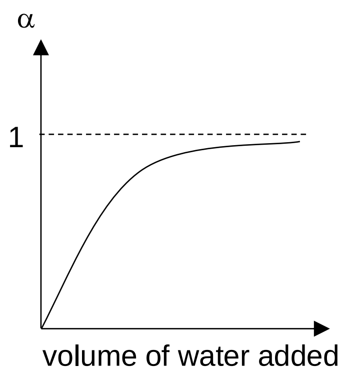
D It increases the activation energy of the reverse reaction.

13 Which graphs correctly show how the values of pH, α (degree of dissociation) and K_a for a weak acid vary with dilution at constant temperature?

1



2



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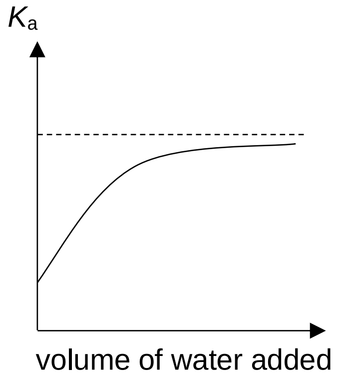


A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

14 Aluminium objects are surface treated by means of anodisation to increase the thickness of the corrosion resistant oxide layer.

Which factor will affect the mass of the oxide coating in the anodisation process?

A size of the current

B size of the cathode

C concentration of electrolyte

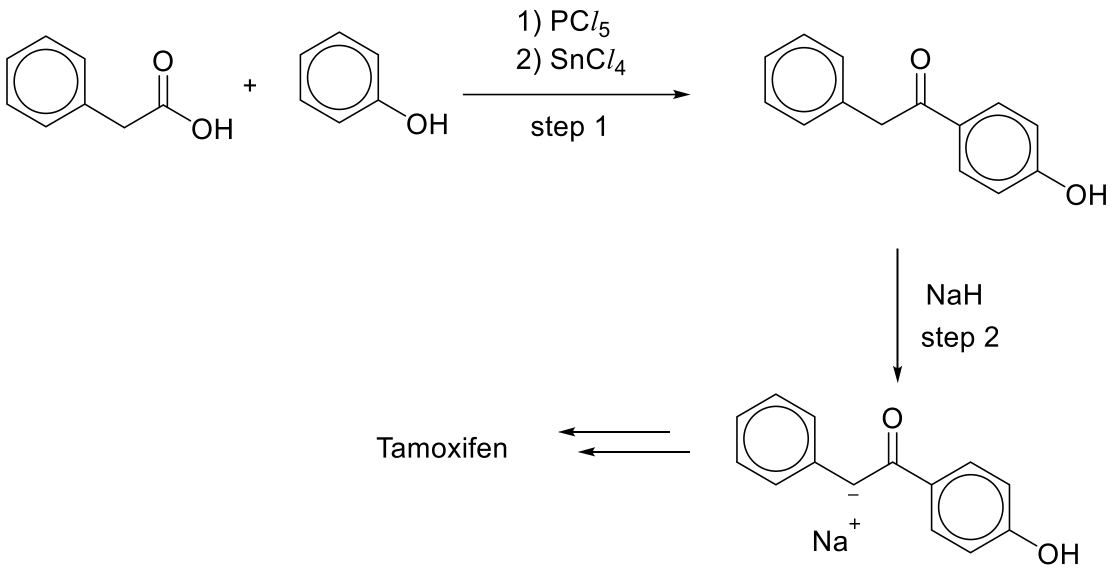
D surface area of the aluminium object

15 Compound V has the molecular formula $C_6H_{14}O$. V has an aliphatic carbon skeleton that is branched and contains a secondary alcohol functional group.

How many constitutional isomers fit this description of V?

A 2 **B** 3 **C** 4 **D** 5

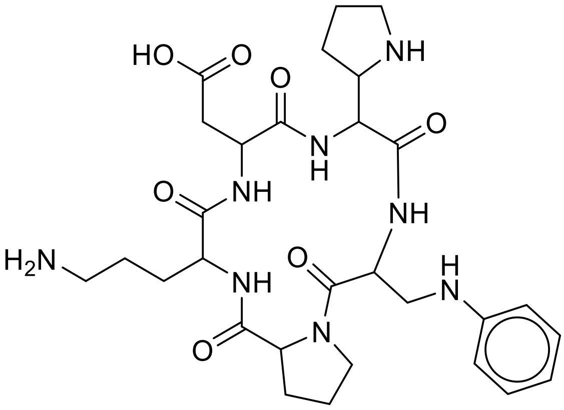
16 Tamoxifen is an important drug used in the prevention of breast cancer. The first two steps in the synthesis of Tamoxifen is shown below.



Which of the following correctly describes the type of reaction in each step in the above synthetic pathway?

	step 1	step 2
A	nucleophilic addition	acid-base
B	condensation	elimination
C	electrophilic substitution	elimination
D	electrophilic substitution	acid-base

17 Compound W is a cyclic oligopeptide.

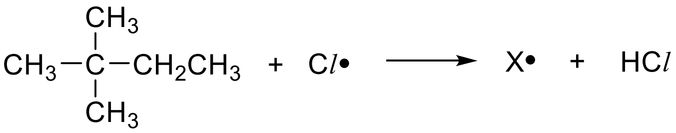


W

How many amide linkages exist in compound W?

A 5 **B** 6 **C** 7 **D** 8

18 When heated with chlorine, 2,2-dimethylbutane undergoes free radical substitution. In a propagation step, the free radical X• is formed by the loss of one hydrogen atom.

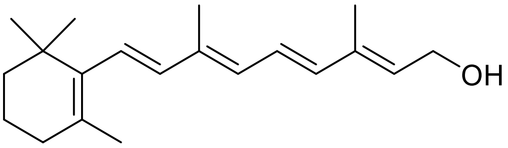


$$CH_3-C(CH_3)_2-CH_2CH_3 + Cl\bullet \longrightarrow X\bullet + HCl$$

How many different forms of X• are theoretically possible?

A 2 **B** 3 **C** 4 **D** 5

19 When retinol reacts completely with cold alkaline $KMnO_4$, it forms product Y. How many stereoisomers do retinol and Y have?



retinol

	retinol	Y
A	2^4	2^8
B	2^5	2^8
C	2^4	2^{10}
D	2^5	2^{10}

20 Which compounds may be a possible product of the reaction of $C_6H_5OCOCHBrCH_3$ with sodium hydroxide under different conditions?

1 $C_6H_5CO_2Na$

2 $CH_3CH(OH)CO_2Na$

3 $C_6H_5OCOCH=CH_2$

A 3 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

21 3-methylbutan-2-ol is treated with alkaline aqueous iodine. The mixture of products is then acidified.

Which compound is present in the final mixture of the products?

A propanoic acid

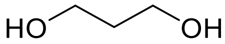
B butanoic acid

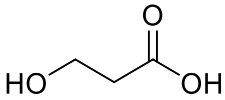
C 3-methylbutanoic acid

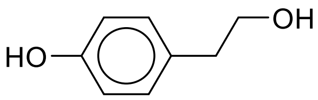
D 2-methylpropanoic acid

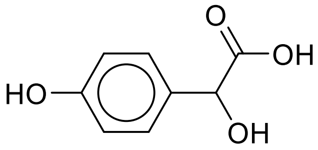
22 1 mol of compound Z reacts with sodium hydroxide to produce 2 mol of water.

Which compound could Z be?

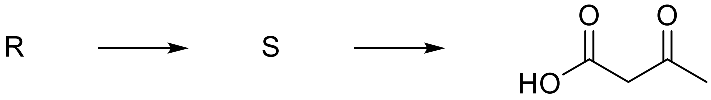
A 

B 

C 

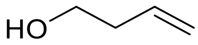
D 

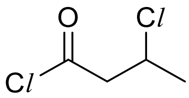
23 Acetoacetic acid can be synthesised in a two-step process starting from R.

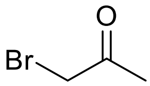


acetoacetic acid

What could be the structure of R?

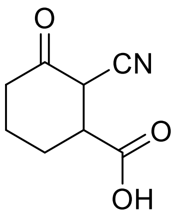
1 

2 

3 

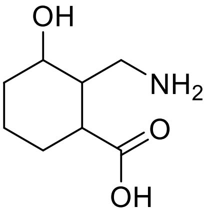
A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

24 Which is the correct product formed when P undergoes reduction using excess hydrogen gas and nickel as catalyst?

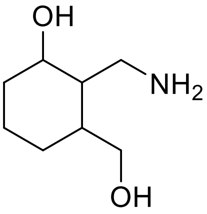


P

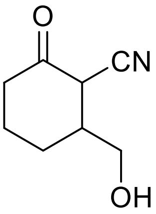
A



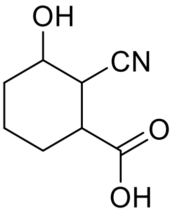
B



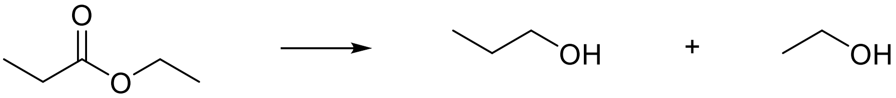
C



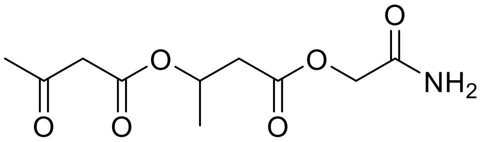
D



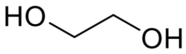
25 Esters can be reduced by LiA*l*H_4 in dry ether to give two alcohols as shown below.



What are the possible products formed when the following compound is reacted with LiA*l*H_4 in dry ether?



1



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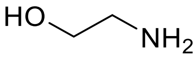

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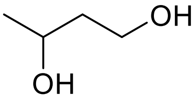
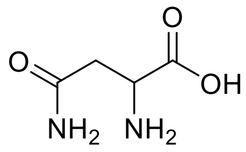


A 3 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

26 Asparagine is required for the development and function of the brain.



asparagine

Which statements about its structure are correct?

1 Asparagine exists in aqueous solution as a zwitterion.

2 The side chain ($-CH_2CONH_2$) of asparagine is neutral.

3 When hot dilute H_2SO_4 is added to asparagine, a gas which turns damp red litmus paper blue is evolved.

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

27 What is the correct order of the pH of the resulting solutions when the oxides below are added to water?

	lowest pH	→	→	highest pH
A	SO_3	SiO_2	MgO	Na_2O
B	Na_2O	MgO	SiO_2	SO_3
C	MgO	SiO_2	SO_3	Na_2O
D	SO_3	Na_2O	MgO	SiO_2

28 The electrical conductivities of two compounds, T and U, are shown in the table below.

	T	U
conductivity of the compound in the liquid state	good	does not conduct
conductivity of the mixture obtained by adding the compound to water	good	good

What could compounds T and U be?

	T	U
A	Al_2O_3	$SiCl_4$
B	NaF	Al_2O_3
C	NaF	$SiCl_4$
D	$SiCl_4$	Al_2O_3

29 *Use of the Data Booklet is relevant to this question.*

$Na_4Fe(CN)_6$ can be oxidised to $Na_3Fe(CN)_6$.

Which reagent can be used to carry out this oxidation?

A $SO_2(g)$

B $NO_2(g)$

C $Cu^{2+}(aq)$

D $I_2(aq)$

30 The rate of reaction between iodide and peroxodisulfate(VI) ions is increased by the presence of small concentrations of $Fe^{2+}(aq)$.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

Which property of iron allows it to act as a homogeneous catalyst?

A high charge density

B partially filled d subshell

C variable oxidation states

D ability to form complex ions

END OF PAPER

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**18S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

18 September 2019

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.

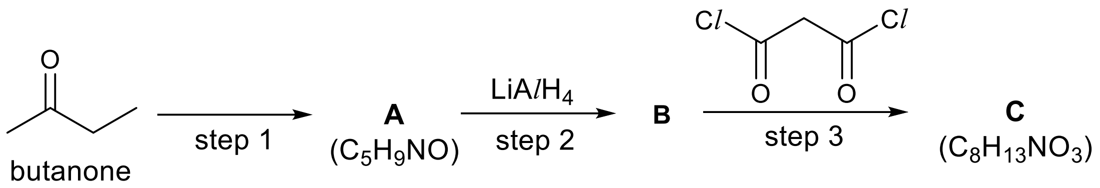
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 17**
2	**/ 13**
3	**/ 22**
4	**/ 23**
s.f.	
units	
Total	**/ 75**

Calculator Model:

This document consists of **16** printed pages.

1 **(a)** Butanone can be converted to compound **C** via the following series of reactions.



(i) Suggest the reagents and conditions for step 1.

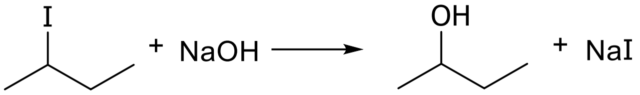
.... [1]

(ii) In the boxes below, draw the structures of compounds **A**, **B** and **C**.

A	**B**
C	

[3]

(b) 2-iodobutane is converted to its corresponding alcohol by heating with aqueous sodium hydroxide.



$\Delta H < 0$

The rate equation is:

$$\text{rate} = k[\text{2-iodobutane}][\text{NaOH}]$$

(i) Describe the mechanism of this reaction. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(ii) Draw a fully labelled reaction pathway diagram for the reaction between 2-iodobutane and sodium hydroxide.

[2]

(c) Describe and explain how the volatilities of the halogens vary from chlorine to iodine.

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…………………………………………………………………………………………………… [2]

(d) Some hydrogen halides are unstable to heat.

(i) Write an equation for the reaction undergone on heating a hydrogen halide.

………………………………………………………………………………………... [1]

(ii) Describe and explain how the thermal stabilities of the hydrogen halides (HC*l*, HBr and HI) vary down the group.

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……………………………………………………………………………………… [2]

(e) When sodium thiosulfate, $Na_2S_2O_3$, is reacted with bromine, $NaHSO_4$ is formed. However, when $Na_2S_2O_3$ reacts with iodine, $Na_2S_4O_6$ is formed instead.

Use the following data, and data from the *Data Booklet*, to suggest an explanation for this difference.

$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$ $E^\ominus = +0.09\text{ V}$
$4SO_2 + 4H^+ + 6e^- \rightleftharpoons S_4O_6^{2-} + 2H_2O$ $E^\ominus = +0.51\text{ V}$
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$ $E^\ominus = +0.17\text{ V}$

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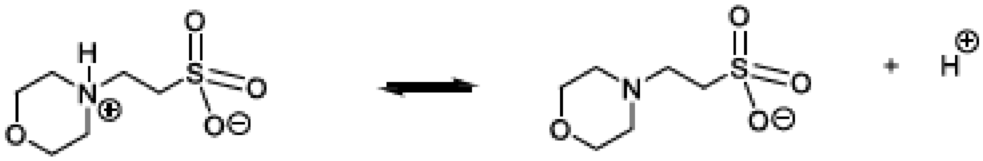
……………………………………………………………………………………… [3]

[Total: 17]

2 (a) 4-Morpholineethanesulfonic acid (MES) is commonly used to prepare buffer solutions. In aqueous solution, MES exists as a dipolar ion which dissociates to give H^+ ions:



4-Morpholineethanesulfonic acid
(MES)

FA 1 is a buffer solution prepared from MES with a pH of 5.5. The ratio of MES and its conjugate base is 4:1.

(i) Determine the pK_a of MES.

[1]

(ii) State the mole ratio of MES to its conjugate base if the pH = pK_a of MES.

[1]

A student titrated 10.0 cm^3 of **FA 1** with aqueous sodium hydroxide, and found that 20.0 cm^3 of aqueous NaOH was required for complete neutralisation.

(iii) What volume of aqueous NaOH should be added to 10.0 cm^3 of **FA 1** such that the pH of the resulting solution becomes equal to pK_a of MES?

[2]

(iv) Write an equation to show why the pH at equivalence point is more than 7.

[1]

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(v) The pH of the solution at equivalence point is 9.4. Suggest a suitable indicator for the titration of **FA 1** with aqueous NaOH, giving a reason for your choice.

Indicators	**Working range**
Congo red	3.0 – 5.0
Cresolphthalein	8.2 – 9.8
Indigo carmine	11.4 – 13.0

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………[2]

(b) Zymase, an enzyme that occurs naturally in yeasts, catalyses the fermentation of sugar into ethanol and carbon dioxide.

sugar → ethanol + carbon dioxide

Fig. 2.1 shows the results of an investigation of the initial rate of fermentation of sugar by zymase. In the experiments, the initial concentration of sugar was varied but that of zymase was kept constant.

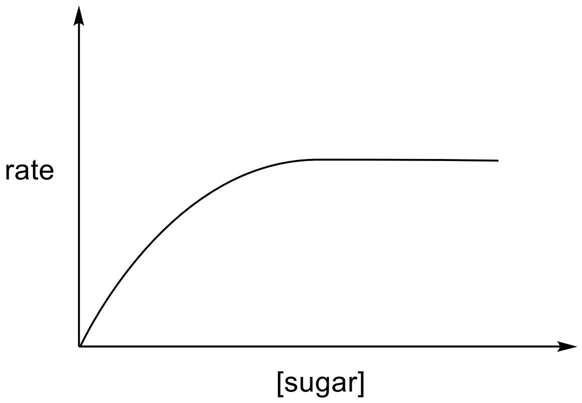

Fig. 2.1

(i) Explain fully the shape of the graph.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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…………………………………………………………………………………………………[2]

(ii) Sketch on Fig. 2.1 the shape of the line you would expect when the amount of zymase added was increased. [1]

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(iii) Three other experiments were carried out to measure the initial rates of fermentation at different concentrations of sugar and zymase. The results are shown in Table 2.2.

Table 2.2

Experiment	[sugar] /mol dm^{-3}	[zymase] /mol dm^{-3}	Relative initial rate
1	0.20	0.10	1
2	0.40	0.10	2
3	0.10	0.20	1

Deduce the orders of reaction with respect to sugar and zymase, showing how you arrive at your answers.

[3]

[Total:13]

3 This question is about alkynes, which are hydrocarbons that contain a carbon-carbon triple bond.

(a) In the past, ethyne gas, C_2H_2, was prepared from calcium carbide, CaC_2. Calcium carbide is a crystalline solid with a melting point of approximately 2160 °C.

(i) Draw the dot-and-cross diagram of CaC_2.

[1]

(ii) When excess water with a drop of universal indicator is added to some calcium carbide, ethyne is produced and the solution changes from green before the reaction, to blue after the reaction is complete.

Write an equation, with state symbols, for this reaction.

……………………………………………………………………………………………….[1]

(b) **(i)** Draw the structure of ethyne, showing correct geometry, and clearly indicate the bond angle in your drawing. State the type of hybridisation of the carbon atoms in ethyne.

Type of hybridisation of carbon: ……………………………….. [2]

(ii) Ethyne gas approaches ideal behavior at room temperature and pressure. Identify, and explain, **two** characteristics of ethyne that enable it to exhibit ideal gas behaviour.

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……………………………………………………………………………………………………

……………………………………………………………………………………………….[2]

(c) When completely combusted, ethyne reacts with oxygen according to the following equation:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$

A fixed-volume flask containing a mixture of ethyne and oxygen is connected to a manometer.

The manometer consists of a U-tube containing some liquid mercury, which is exposed to atmospheric pressure at one end. Initially, the mercury levels on both arms are at the same height, as shown in Fig. 3.1 below.

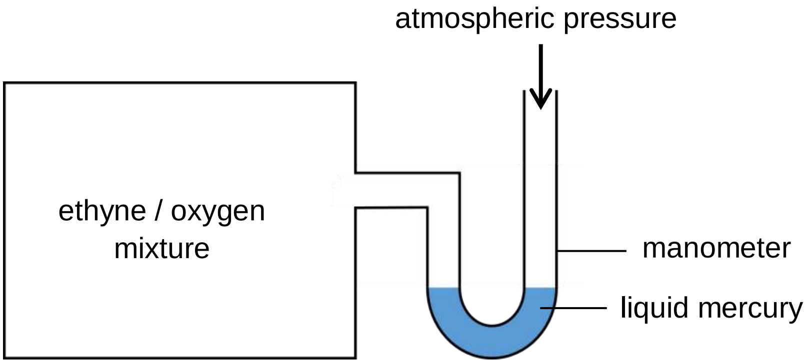

Fig 3.1

When the mixture in the flask was combusted, the final mercury levels in the manometer showed a difference in height of 65 mm. All measurements were made at room temperature and pressure. [“mm Hg” is a unit of pressure, where 760 mm Hg = 1 atm]

The initial partial pressures of ethyne and oxygen are x and y mm Hg respectively. After the combustion, the partial pressure of ethyne changed by p mm Hg.

(i) Express the total initial pressure in the flask in terms of x and y and state its value in mm Hg.

[1]

(ii) Express the total pressure after the combustion in terms of x, y, and p;

[1]

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(iii) Hence, show that the difference in height of 65 mm in the mercury levels is due to a **decrease** in pressure inside the flask.

[1]

(iv) Determine the value of *p* to 1 decimal place.

[1]

(v) Hence, calculate

(I) the partial pressure, in mm Hg, of carbon dioxide formed after the combustion;

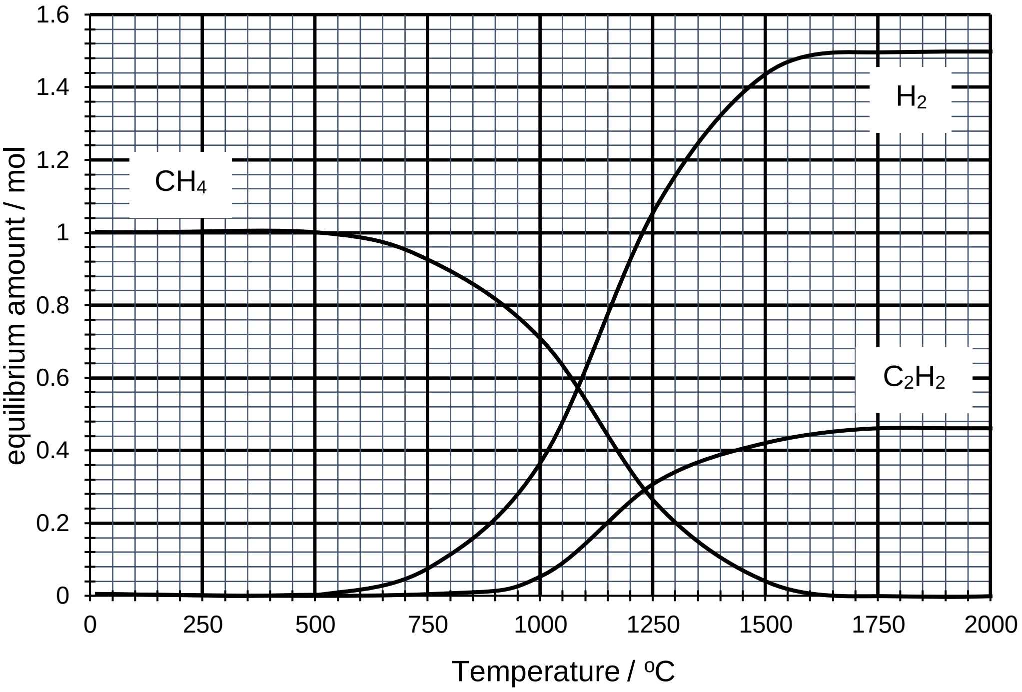
(II) the values of *x* and *y*, assuming all the oxygen was used up during the combustion, and only carbon dioxide and water were produced in the process.

[2]

(d) In more recent years, ethyne has been largely manufactured from methane. One such conversion only employs heat, and produces ethyne according to the following equilibrium:

$$2CH_4(g) \ll C_2H_2(g) + 3H_2(g) \text{ - - - - - - - - - - - - - - (1)}$$

Equilibrium compositions during the conversion of methane to ethyne in a 0.100 m^3 vessel may be predicted using the simulated data below.



(i) Assuming the gases behave ideally in the range of temperatures shown in the graph, use the simulated data to calculate the pressure of hydrogen gas in the vessel at 1250 °C.

[2]

(ii) Show that, for equilibrium (1) at 1250 °C,

$$K_p = \frac{(n_{H_2})^3(n_{C_2H_2})}{(n_{CH_4})^2} \times \left(\frac{RT}{V}\right)^2$$

where
R is the molar gas constant
T is the temperature in the vessel
V is the volume of the vessel

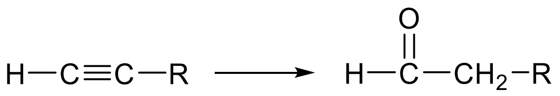
and hence, calculate K_p, showing its units.

[3]

(iii) State how the value of K_p for equilibrium (1) would change when the temperature is changed from 1250 °C to 1000 °C.

....[1]

(e) Terminal alkynes can undergo hydroboration-oxidation reactions, as shown below.



$$H{-}C{\equiv}C{-}R \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}R$$

R: alkyl or H

(i) Draw and name the product formed when propyne, C_3H_4, undergoes hydroboration-oxidation.

name of product: ....[2]

(ii) Describe a simple chemical test to distinguish propyne from the product you have drawn in **(e)(i)**. You may assume that propyne reacts similarly to propene.

....

....

....

....[2]

[Total: 22]

4 Aromatic compounds like benzene tend to undergo electrophilic substitution reactions.

(a) Explain why aromatic compounds are reactive towards electrophiles but not nucleophiles.

....

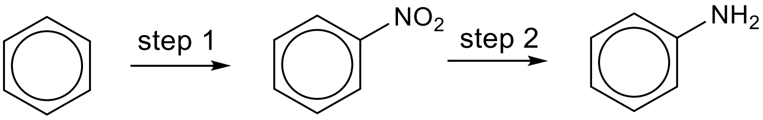
.... [1]

(b) Explain why aromatic compounds tend to undergo substitution reactions instead of addition reactions.

....

.... [1]

(c) Benzene is a starting material for the synthesis of phenylamine.



(i) State the reagents and conditions for steps 1 and 2.

step 1: ....

step 2: ....[2]

(ii) Phenylamine reacts readily with excess aqueous bromine to give a white solid **X**. Identify **X** and write a balanced equation for the reaction that occurs.

[2]

(iii) Suggest the order of reactivity of benzene, nitrobenzene and phenylamine with liquid bromine. Explain your answer.

....

....

....

....[2]

(iv) Draw the structure of the monobrominated organic product formed when nitrobenzene reacts with liquid bromine.

[1]

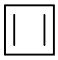
In 1931, the German chemist Erich Hückel formulated a theory to help determine if a species would be considered aromatic. This rule became known as Hückel's rule.

An aromatic species must satisfy all the following criteria:

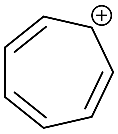
1. It must be cyclic.
2. Every atom in the ring must have a p orbital.
3. Each p orbital must overlap the p orbitals from either side in a continuous fashion to form a closed loop, which means the structure has to be planar for effective overlap.
4. The cyclic system must contain (4n+2) delocalised π electrons, where n is 0 or a positive integer (1, 2, 3 etc.)

For example, benzene is aromatic because it satisfies all the four criteria, with 6 delocalised π electrons (n = 1).

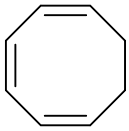
(d) Consider the following species.



D



E



F

Which species are **not** aromatic? Explain your answer briefly.

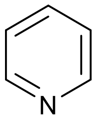
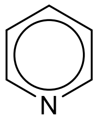
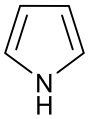
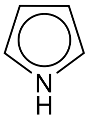
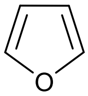
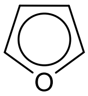
……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………[2]

Table 4.1 shows information on three aromatic compounds which obey Hückel's rule.

Table 4.1

compound	hypothetical structure of compound	actual structure of compound	pK_b	resonance energy/ kJ mol^{-1}	boiling point/ ^oC
pyridine			8.6	134	115
pyrrole			13.6	100	129
furan				80	31

The hypothetical structures of the compounds in Table 4.1 assume that there is no delocalisation of π electrons in the rings. However, in reality, delocalisation of π electrons gives rise to the extra stability of the aromatic compounds. The resonance energy is defined as the energy difference between the actual structure and hypothetical structure of each compound.

(e) **(i)** All the carbon and nitrogen atoms in pyrrole are sp^2 hybridised.

Draw the arrangement of all the hybridised and unhybridised orbitals of the nitrogen atom in pyrrole. Label the orbitals clearly.

[2]

(ii) Pyrrole has six electrons in the delocalised π electron cloud.

How many electrons does the nitrogen atom in pyrrole contribute to the delocalised π electron cloud? You may find it useful to consider the hypothetical structure of pyrrole.

……………………………………………………………………………………………[1]

(iii) The nitrogen atom in pyrrole has a lone pair of electrons. Suggest the orbital in which the lone pair resides.

……………………………………………………………………………………………[1]

(iv) Hence, using your answers in **(e)(ii)** and **(e)(iii)**, suggest why the pK_b of pyrrole is so high.

……………………………………………………………………………………………

……………………………………………………………………………………………[1]

(f) **(i)** Furan can behave differently from benzene in its reactions. Under certain conditions, furan undergoes electrophilic addition instead of electrophilic substitution. Based on your answer in **(b)**, explain this phenomenon, using relevant data from Table 4.1.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

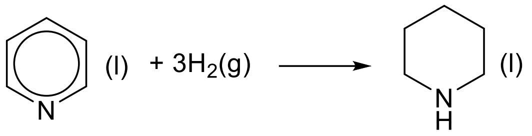
(ii) Furan can form hydrogen bonds when added to ethanol. Draw a diagram to show how hydrogen bonding occurs between one molecule of furan and one molecule of ethanol and explain how this interaction arises.

……………………………………………………………………………………………

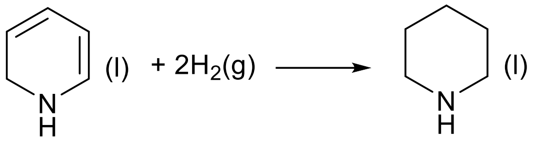
……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(g) The enthalpy changes of hydrogenation of pyridine and compound **E** can be represented by the equations below:



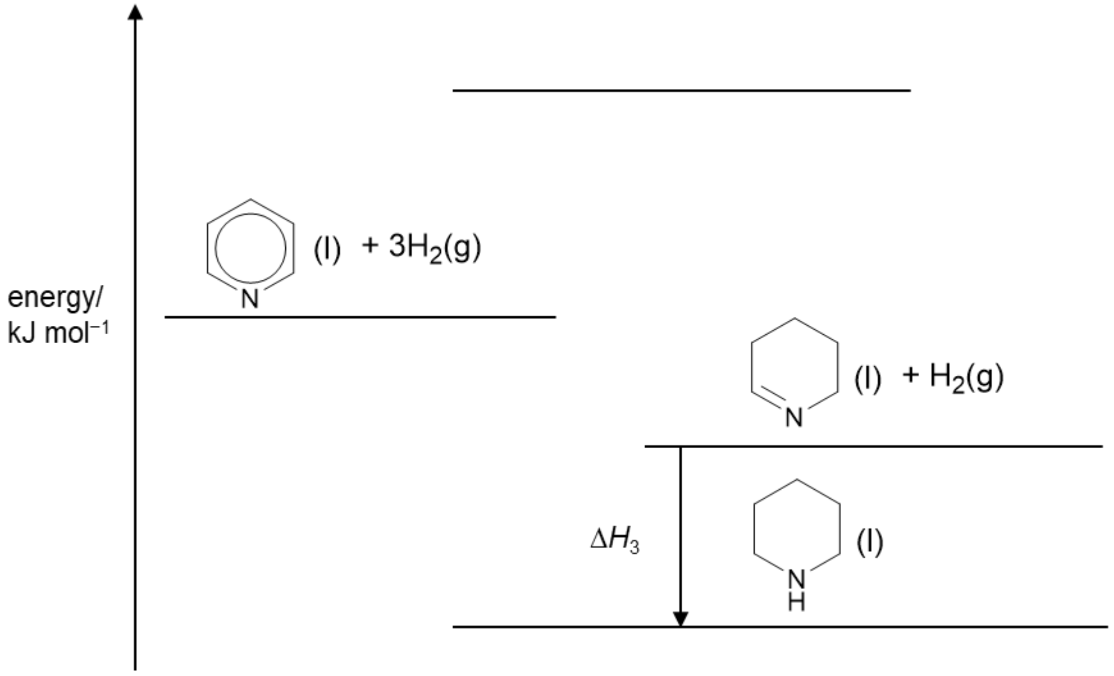
$\Delta H_1 = -194$ kJ mol^{-1}



E

$\Delta H_2 = -240$ kJ mol^{-1}

Using the information above and relevant data from Table 4.1, complete the energy diagram below and use it to calculate ΔH_3.



ΔH_3 = ………………………….. kJ mol^{-1}

[3]

[Total: 23]

END OF PAPER

HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**18S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

20 September 2019

2 hours

Candidates answer on separate answer booklet.

Additional Materials: 12-Page Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** 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.

Begin each question on a **<u>new</u> page of writing paper**.

A Data Booklet is provided.

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

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

At the end of the paper, submit only the 12-Page Answer Booklet and any additional booklets you have used.

This document consists of **11** printed pages.

Section A

Answer **all** the questions in this section.

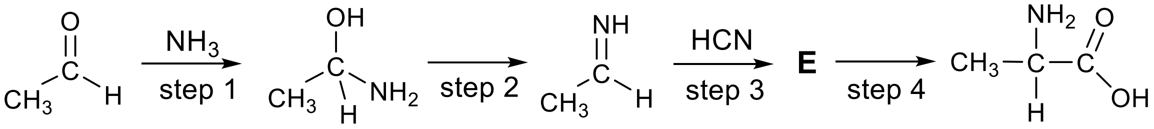
1 **(a)** **(i)** Write an equation for the thermal decomposition of $MgCO_3$. [1]

(ii) Explain how the magnitude of the lattice energy of $MgCO_3$ differs from that of the solid product formed in **(a)(i)**. [2]

(iii) The thermal decomposition of $MgCO_3$ is an endothermic process. Explain whether the decomposition of $MgCO_3$ is spontaneous at high or low temperature. [2]

(iv) State whether $MgCO_3$ or $BaCO_3$ has the lower decomposition temperature. Explain your answer. [3]

(b) The Strecker synthesis is a method used to prepare amino acids. Alanine, 2-aminopropanoic acid, can be prepared from ethanal via Strecker synthesis as shown below.

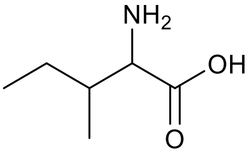


(i) Suggest the type of reaction occurring in steps 1 and 2. [2]

(ii) Draw the fully displayed structure of compound **E**. [1]

(iii) Suggest why step 3 produces an equimolar mixture of two stereoisomers. [2]

(iv) Another amino acid, isoleucine, can be prepared from aldehyde **F** via Strecker synthesis.



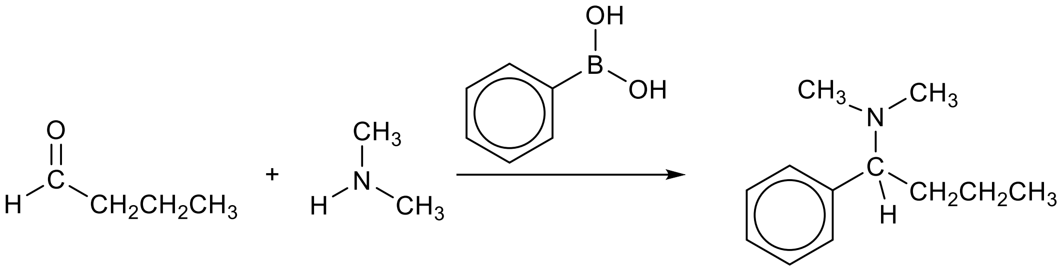
isoleucine

Draw the structure of aldehyde **F**. [1]

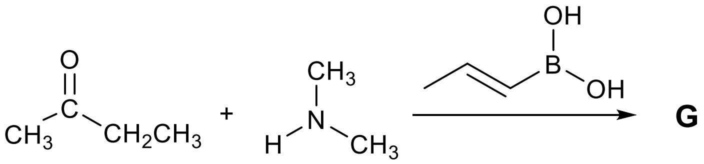
(c) In the Petasis reaction, carbonyl compounds, amines and suitable boronic acids can react to form substituted amines.

The general structure of a boronic acid is $B(OH)_2R$ where R is an alkyl or aryl group.

An example of the Petasis reaction is given below.

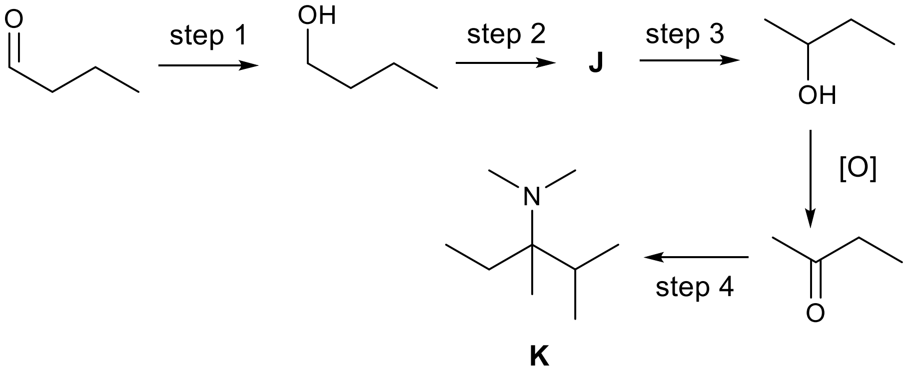


Consider the following Petasis reaction:



(i) Draw the structure of compound **G**. [1]

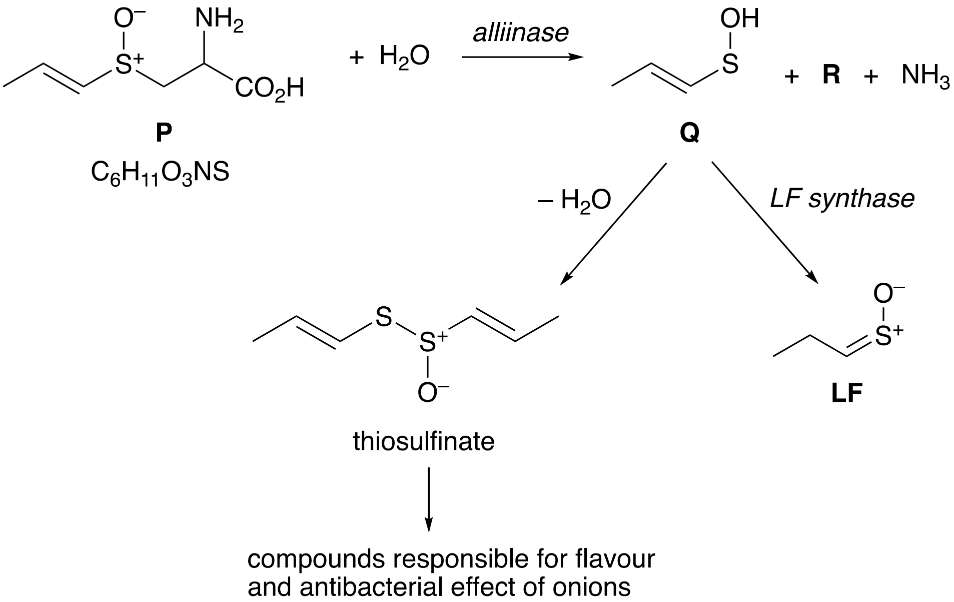
(ii) The Petasis reaction can be used in step 4 of the following synthesis of compound **K** from butanal.



Suggest reagents and conditions for steps 1 to 4, and the structure of compound **J**. [5]

[Total: 20]

2 When an onion is cut, the damaged tissues release the lachrymatory factor molecule, **LF**, that makes eyes water. The diagram below shows how **LF** is produced in the cut onion, starting from compound **P**.



(a) In the first step, **P** reacts with a water molecule, in the presence of the enzyme *alliinase*, to give **Q**, **R** and ammonia.

(i) Find the molecular formula of compound **R**. [1]

(ii) Compound **R** reacts in a 1:1 ratio with PCl_5 and gives a yellow precipitate with alkaline aqueous iodine. Draw the structure of compound **R**. [1]

(b) State the isomeric relationship between **Q** and **LF**. [1]

(c) **LF** is very soluble in water. Explain why **LF** dissolves well in water. [1]

(d) **LF** is also volatile. For years, the conversion of **Q** to **LF** was thought to be direct, but in 2002, scientists discovered the pathway requires an enzyme *LF synthase*.

Two methods, found on the internet, claim to prevent eyes from watering while cutting onions. Suggest how **each** of these methods could work, considering the volatility of **LF**, and the pathway that produces **LF**.

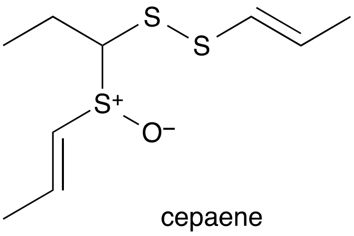
(i) "Cool the onion before cutting it." [1]

(ii) "Heat the onion before cutting it." [1]

(e) In 2016, scientists developed "tearless" onions by irradiating seeds with heavy-ion beams to reduce *LF synthase* levels. This mutation causes increased thiosulfinate production from **Q** via the alternate pathway above.

(i) In this alternate pathway, two molecules of **Q** react to form thiosulfinate, losing a water molecule. Name the type of reaction that occurs. [1]

Increased thiosulfinate means higher amounts of compounds which give onions flavor and antibacterial properties. One of these compounds is cepaene.



cepaene

The percentage of sulfur in an organic compound, such as cepaene, can be determined via the elemental analysis set-up in Fig. 2.1:

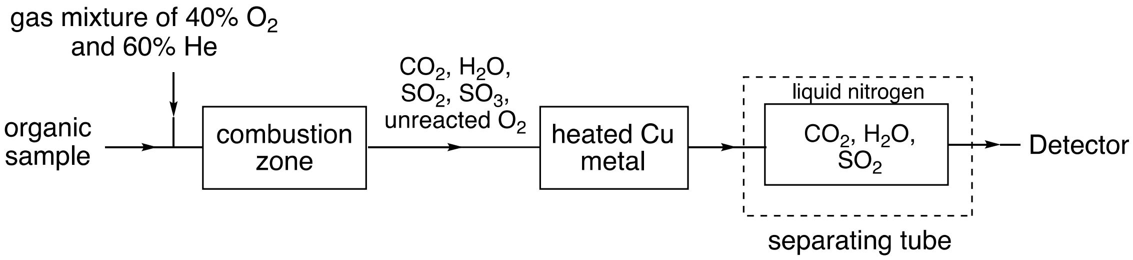


Fig. 2.1

The organic sample is first combusted in a gas mixture of 40% O_2 and 60% He, to form CO_2, H_2O and oxides of sulfur: SO_2 and SO_3.

The resultant gases then flow over a vessel containing heated copper metal to convert any SO_3 into SO_2. The heated copper also removes any unreacted O_2.

CO_2, H_2O and SO_2 gases are cooled in a separating tube immersed in liquid nitrogen at −196 °C, and then released one by one, by increasing the temperature, to the detector.

In one analysis, 5.0 mg of cepaene ($C_9H_{16}OS_3$, $M_r = 236.3$) is introduced into the combustion zone.

(ii) Write an equation for the combustion of cepaene in the combustion zone to form CO_2, H_2O and SO_3 only. [1]

(iii) Hence, calculate the minimum volume of the O_2/He gas mixture at r.t.p. (in cm^3) required for the combustion of 5.0 mg of cepaene. [2]

(iv) State the role of the heated copper metal, and hence write an equation to show how the unreacted O_2 is removed by the heated copper. [2]

(v) If the temperature of the heated copper metal is not high enough or insufficient copper is used, a sulfur-containing compound could be formed in the vessel as blue crystals. Identify the blue crystals and suggest how they may be formed. [1]

(vi) Predict the sequence in which the three compounds in the separating tube are released to the detector. Explain your answer fully. [3]

[Total: 16]

3 Cobalt is a *transition element* that can be found in the blue pigments used for jewellery and paints.

(a) Explain what is meant by the term *transition element*. [1]

(b) A cobalt-chrome alloy is a metal alloy of cobalt and chromium.

A sample of this alloy was dissolved in dilute HC*l* to form a solution containing 1.23×10^{-2} mol dm^{-3} of $Cr^{3+}(aq)$ and 5.77×10^{-3} mol dm^{-3} of $Co^{2+}(aq)$.

Aqueous NaOH was then added slowly to 1 cm^3 of the solution.

(i) Using the K_{sp} information below, show that the addition of NaOH will **not** allow for the separation of the Cr^{3+} and Co^{2+} metal cation ions in the above solution.

compound	K_{sp}
$Cr(OH)_3$	1.60×10^{-20}
$Co(OH)_2$	5.92×10^{-15}

[3]

(ii) A better way to separate the two aqueous ions is to add excess NaOH into the solution as $Cr(OH)_3$ dissolves.

With the aid of equations, explain why the precipitate of $Cr(OH)_3$ dissolves in excess NaOH using *Le Chatelier's Principle*. [3]

(c) When cobalt(II) chloride is dissolved in water, it forms a pink solution. Upon addition of excess aqueous potassium thiocyanate, KSCN, the solution turns blue.

(i) Draw a fully labelled diagram to account for the splitting of the degenerate d orbitals into two energy levels in an octahedral ligand field.

Explain how you arrived at your answer, taking into account the shape and the orientation of the d orbitals. [2]

(ii) Using your diagram in **(c)(i)**, account for the pink colour of the solution when cobalt(II) chloride is dissolved in water. [2]

(iii) Identify the type of reaction responsible for the colour change from pink to blue. [1]

(iv) Different proportions of 0.1 mol dm^{-3} $Co^{2+}(aq)$ and 0.2 mol dm^{-3} $SCN^-(aq)$ were mixed. The intensity of the blue colour of the resultant solution was measured using a colorimeter. The maximum colour intensity was observed when 2 cm^3 of $SCN^-(aq)$ was added to 1 cm^3 of $Co^{2+}(aq)$. Deduce the identity of the species responsible for the blue solution. [2]

(d) When cobalt(II) chloride is dissolved in aqueous ammonia, it forms $[Co(NH_3)_6]^{2+}$ which is oxidised by air to the +3 oxidation state.

(i) Explain why cobalt shows variable oxidation states as compared to a main group element like calcium. [2]

(ii) With the aid of the *Data Booklet* and the information below, calculate the $E^{\ominus}_{cell}$ for the oxidation of $[Co(NH_3)_6]^{2+}$ by atmospheric oxygen.

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E = +0.17\text{ V}$$

[1]

(e) **S** and **T** are ionic compounds which contain six-coordinate cobalt(III) complex ions, whose ligands are either NH_3 or Cl^-.

When excess aqueous $AgNO_3$ is added to 1 mole of **S** and 1 mole of **T** separately, 2 moles of a white precipitate is formed from **S** while 1 mole of the same white precipitate is formed from **T**.

(i) Identify the white precipitate and explain why different amounts of the white precipitate are formed from **S** and **T**. [2]

(ii) Draw the cobalt(III) complex ion in **S**, showing clearly how the ligands are bonded to the central metal ion. [1]

(iii) The cobalt(III) complex ion in **T** exhibits *cis-trans* isomerism. Suggest the structure of the *trans* isomer. [1]

(f) Cobalt is used as a heterogeneous catalyst in the synthesis of aldehydes from carbon monoxide and water.

Describe the mode of action of the cobalt catalyst in the reaction. [3]

[Total: 24]

Section B

Answer **one** question from this section.

4 (a) The world's first implantable cardiac pacemaker is powered by zinc and platinum electrodes which are placed directly within the body tissues.

These electrodes in the body fluid at a pH of 7.4 form a 'biogalvanic' cell in which zinc is oxidised to zinc hydroxide and oxygen is reduced.

(i) State the polarities of the zinc and platinum electrodes and write a half-equation for the reaction that occurs at **each** electrode. [3]

(ii) Given that the value of $\Delta G^\ominus$ at 298 K for the reaction in the biogalvanic cell is –637 kJ per mole of oxygen reduced, calculate a value for $E^\ominus_{cell}$.

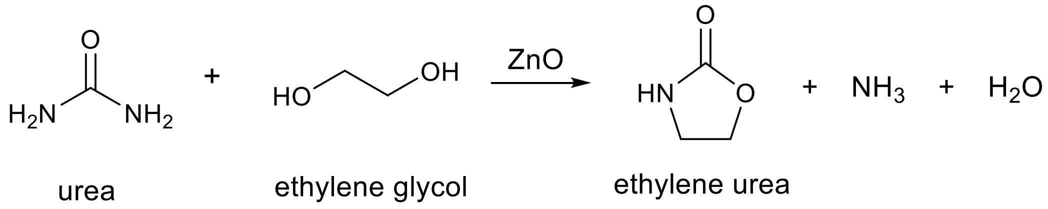
Hence, determine the value of the standard reduction potential of zinc hydroxide. [2]

(iii) A pacemaker operates at an average current of 8.0×10^{-4} A. Calculate how long the pacemaker will last when 5.0 g of zinc electrode is used before it needs to be replaced. Give your answer to the nearest day. [3]

(b) Zinc and silver are often present as impurities in crude copper obtained from minerals.

Explain, in terms of electrode reactions, how zinc and silver are removed in the industrial process of the purification of copper, using relevant data from the *Data Booklet*. Illustrate your answer with a labelled diagram. [4]

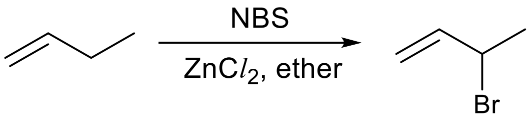
(c) Zinc oxide is used as a catalyst in the condensation of ethylene glycol and urea. One of the products formed is ethylene urea (M_r = 87.0),



(i) The reaction between ethylene glycol and urea also produces two other molecules, **X** (M_r = 86.0) and **Y** (M_r = 88.0). Suggest the structures of **X** and **Y**. [2]

(ii) Suggest the products formed when ethylene urea is heated with aqueous sodium hydroxide. [2]

(d) Zinc chloride may be used in the free radical substitution of but-1-ene as shown below. N-bromosuccinimide (NBS) is the source of molecular bromine, Br_2.



reaction 1

In the initiation step below, $ZnCl_2$ (initiator•) reacts with Br_2 to form Br• radicals:

initiator• + Br–Br → initiator–Br + Br•

(i) Draw curly arrows to show the movement of electrons in the initiation step shown above. [1]

(ii) Write equations for the propagation steps in the mechanism for reaction 1, starting from the Br• radical. The use of curly arrows is **not** required. [2]

(iii) NBS is a preferred source of Br_2 as it maintains a low concentration of Br_2 in this reaction. Suggest why liquid bromine is not directly added to but-1-ene instead. [1]

[Total: 20]

5 **(a)** Describe and explain the trend and variations in first ionisation energies of the Period 3 elements from sodium to chlorine. [3]

(b) The halogens can form many interhalogen compounds. Most interhalogen compounds contain two halogens and have the general formula XY_n where n = 1, 3, 5 or 7.

ClF_3 is an interhalogen compound which exists as a colourless gas.

(i) ClF_3 and Cl_2 react to form another interhalogen compound. No other product is formed in the reaction.

State the oxidation numbers of chlorine in ClF_3 and Cl_2 and write an equation for the reaction between ClF_3 and Cl_2. [2]

The standard enthalpy change of formation, $\Delta H^\ominus_f$, of $ClF_3(g)$ is –163 kJ mol^{-1}.

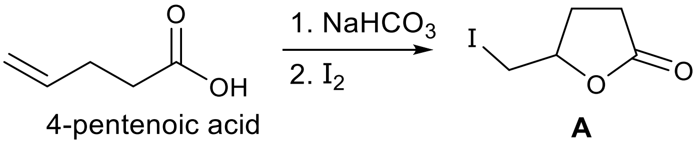
(ii) What can you infer about the stability of ClF_3 from its standard enthalpy change of formation? [1]

(iii) Use the standard enthalpy change of formation, $\Delta H^\ominus_f$, of $ClF_3(g)$ and data from the *Data Booklet* to determine a value for the bond energy of the Cl–F bond. [2]

Another interhalogen compound is ICl_3. In the solid state, ICl_3 exists as a dimer, I_2Cl_6, which consists of two bridging Cl atoms. The shape around each iodine atom is square planar.

(iv) Draw the structure of the I_2Cl_6 dimer including its co-ordinate (dative covalent) bonds. [2]

Cyclic esters are called lactones. One of the most effective ways to synthesise lactones is iodolactonisation, which involves the addition of an oxygen and iodine across a carbon-carbon double bond. An example using 4-pentenoic acid is shown below.



(c) **(i)** Draw the structure of the organic product formed when 4-pentenoic acid reacts with $NaHCO_3$. [1]

(ii) Hence, suggest a mechanism for the formation of compound **A** from your product in **(c)(i)**.

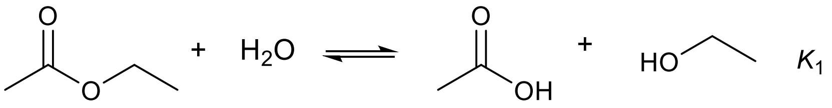
Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(d) Compound **B** contains only carbon, hydrogen and oxygen and exhibits stereoisomerism. 1 mole of **B** produces 4 moles of carbon dioxide gas when heated with acidified potassium manganate(VII). No other carbon-containing product is formed in the reaction with potassium manganate(VII).1 mole of **B** also reacts with 2 moles of aqueous NaOH.

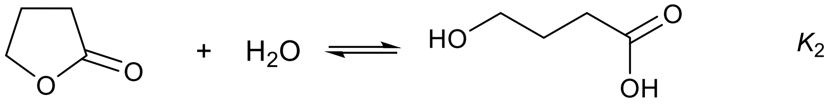
Deduce the structure of **B**, giving your reasoning. [3]

(e) Both non-cyclic esters and lactones undergo hydrolysis reactions.

reaction 1



reaction 2



(i) State the reagents and conditions needed to carry out the hydrolysis. [1]

(ii) State and explain whether the ΔH for the two reactions would be similar or different. [1]

(iii) The ΔS for reaction 1 is more positive than the ΔS for reaction 2. Use this information, and your answer to **(e)(ii)**, to compare the ΔG for both reactions and hence the magnitudes of the equilibrium constants, K_1 and K_2. [2]

[Total: 20]

END OF PAPER

HWA CHONG INSTITUTION
C2 Preliminary Examination
Higher 2

NAME		**CT GROUP**	**18S**

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2019

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	
Total	

This document consists of **18** printed pages.

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

1 Determination of the enthalpy change of neutralisation, ΔH_{neut}, of a strong acid by a strong base

The enthalpy change of neutralisation, ΔH_{neut}, is the enthalpy change when one mole of water is formed during a neutralisation reaction as shown in equation 1.

equation 1 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

FA 1 is a solution of sulfuric acid, H_2SO_4
FA 2 is 1.50 mol dm^{-3} sodium hydroxide, NaOH

You will perform a series of experiments using different volumes of **FA 1** and **FA 2** which together give a total volume of 50 cm^3. The change in temperature, ΔT, for each experiment will be determined and used to plot a graph of ΔT against volume of **FA 1** used.

You will then use data from the graph to determine the concentration of sulfuric acid in **FA 1**, and a value for the enthalpy change of neutralisation, ΔH_{neut}.

(a) (i) Determining the change in temperature for a series of reactions between FA 1 and FA 2

1. Place the Styrofoam cup in a 250 cm^3 beaker to prevent it from tipping over. Use a measuring cylinder to transfer 10.0 cm^3 of **FA 1** into the cup.

2 Use a measuring cylinder to measure 40.0 cm^3 of **FA 2.**

3. Measure the temperature of the **FA 1** solution using the thermometer. Record the initial temperature of **FA 1** as T_{FA1}.

4. Add **FA 2** to **FA 1** in the Styrofoam cup. Stir the mixture using the thermometer and record the maximum temperature, T_{max}, reached.

5. Wash and dry the Styrofoam cup.

6. Repeat steps 1 to 5 using 20.0 cm^3, 25.0 cm^3, 30.0 cm^3, 35.0 cm^3 and 40.0 cm^3 of **FA 1** and appropriate volumes of **FA 2** each time such that the total volume of the reacting mixture is 50.0 cm^3.

Keep the remaining FA 1 and FA 2 solutions for use in questions 2 and 4.

In an appropriate format in the space provided on **page 3**, record:

- all measurements of volumes used,
- all temperatures measured and the change in temperature, ΔT.

Results

[4]

(ii) On the grid provided, plot a graph of ΔT (y-axis) against volume of **FA 1** (x-axis) using the data you obtained in **1(a)(i)**.

Draw two lines of best fit.

- The first best-fit line should be drawn using the plotted points before the maximum change in temperature.
- The second best-fit line should be drawn using the plotted points after the maximum change in temperature.

Extrapolate these lines until they cross.

[3]

(iii) Determine from your graph, the maximum change in temperature, ΔT_{max}, and the volume, V_{max}, of **FA 1** required to obtain this value.

ΔT_{max} = ... V_{max} = ...

[1]

(b) Using your answers in **1(a)(iii),** calculate

(i) the concentration, in mol dm^{-3}, of H_2SO_4 in **FA 1**.

concentration of H_2SO_4 in **FA 1** = ...[1]

(ii) the heat change for the neutralisation reaction at ΔT_{max}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and the density of the final solution is 1.00 g cm^{-3}.

heat change = ...[1]

(c) Using your answers from **1(b)(i)** and **1(b)(ii),** calculate a value for the enthalpy change of neutralisation, ΔH_{neut}.

ΔH_{neut} =.. [1]

(d) Predict the effect on ΔH_{neut} if the experiment was repeated with malonic acid, $HO_2CCH_2CO_2H$, of the same concentration instead of sulfuric acid. Explain your answer.

……….

……….

……………………………………………………………………………………………………….[1]

(e) State one significant source of error in the experiment and suggest an improvement that can be made to reduce this error.

……….

……….

……………………………………………………………………………………………………….[1]

[Total: 13]

2 Determination of water of crystallisation in a hydrated iron(III) salt

FA 3 is hydrated iron(III) sulfate with formula $Fe_2(SO_4)_3.nH_2O$. The addition of excess zinc to a solution of **FA 3** reduces the Fe^{3+} ions to Fe^{2+} ions.

The amount of Fe^{2+} ions can be determined quantitatively by titration against a standard solution of potassium manganate(VII), $KMnO_4$. The reaction is shown in equation 2.

equation 2 $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

In this experiment, you will prepare a standard solution using **FA 3** and perform titrations to determine the value of *n*, the water of crystallisation in **FA 3**.

You are also provided with
FA 4, 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$,
zinc powder.

You will also need access to the **FA 1** solution you used earlier.

(a) Preparation of standard solution of hydrated iron(III) salt

1. Weigh accurately the sample of **FA 3** provided with the weighing bottle. Transfer all the solid into a 250 cm^3 beaker. Determine the mass of solid **FA 3** used and record all your weighings, to an appropriate level of precision, in the space below.

[1]

2. Use a measuring cylinder to add about 100 cm^3 of **FA 1** to the beaker. Stir the mixture with a glass rod for 3 minutes. Ignore any cloudiness that remains.

3. Transfer the solution into a 250 cm^3 volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.

4. Make up to the 250 cm^3 mark with deionised water, stopper and mix thoroughly by inverting the flask a number of times.

5. Label this solution **FA 5**.

(b) **Preparation of Fe^{2+} solution from FA 5**

6. Use a measuring cylinder to transfer 100 cm^3 of **FA 5** into a **dry** 250 cm^3 beaker.

7. Add all the zinc powder provided in the bottle into the beaker. Cover the beaker with a watch glass.

8. Allow the reaction to take place for about 5 minutes, stirring the reaction mixture from time to time. Record your observations in the space below.

Observations in step 8

[1]

9. Filter the mixture into the **dry** conical flask provided using **dry** filter paper and filter funnel. Ignore any reaction that may still be taking place.

10. Label the filtrate as **FA 6**. Proceed to **2(c)** once you have collected sufficient filtrate.

(c) **(i)** Titration of **FA 6** against **FA 4**

11. Fill a burette with **FA 4**.

12. Use a pipette to transfer 10.0 cm^3 of **FA 6** into a 250 cm^3 conical flask.

13. Use a measuring cylinder to add about 10 cm^3 of **FA 1** to this flask.

14. Run **FA 4** from the burette into this flask until the appearance of the first permanent pale-pink colour.

15. Record your titration results, to an appropriate level of precision, in the space below.

16. Repeat steps 12 to 15 until consistent results are obtained.

Keep the remaining FA 1 and FA 4 solutions for use in question 4.

Titration results

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{\text{FA 4}}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{\text{FA 4}}$ = ……………………………………………[3]

(d) **(i)** Calculate the amount of Fe^{2+} in 10.0 cm^3 of **FA 6**.

amount of Fe^{2+} in 10.0 cm^3 of **FA 6** = …………………………………………… [1]

(ii) In step 7, an excess of zinc was added to convert the Fe^{3+} to Fe^{2+}.

Calculate the amount of Fe^{3+} in 250 cm^3 of **FA 5**.

amount of Fe^{3+} in 250 cm^3 of **FA 5** = …………………………………………… [1]

(iii) Use your answer from **2(d)(ii)** to calculate the M_r of the hydrated iron(III) sulfate, $Fe_2(SO_4)_3.nH_2O$, in **FA 3**.

M_r of the hydrated iron(III) sulfate = …………………………………

Hence, deduce the value of n, the water of crystallisation in the hydrated iron(III) sulfate.

[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

n = ………………………………..

[5]

(e) Explain all the observations in step 8 in terms of the chemical processes involved.

………………………………………………………………………………………………...

………………………………………………………………………………………………...

…………………………………………………………………………………………….. [1]

(f) In step 9, excess zinc was filtered off before titration of **FA 6** against **FA 4** to avoid any possible reaction between zinc and **FA 4**.

Suggest another reason why it was necessary to filter off the excess zinc metal, and what effect failing to do it would have on the titre values.

………………………………………………………………………………………………...

………………………………………………………………………………………………...

…………………………………………………………………………………………….. [1]

[Total: 17]

3 Planning

Iron(III) ion, $Fe^{3+}(aq)$, and thiocyanate ion, $SCN^{-}(aq)$, react to give the thiocyanatoiron(III) complex ion, $FeSCN^{2+}(aq)$, as shown in equation 3.

equation 3 $Fe^{3+}(aq) + SCN^{-}(aq) \ll FeSCN^{2+}(aq)$

(a) Write an expression for the equilibrium constant, K_c, of the reaction between $Fe^{3+}(aq)$ and $SCN^{-}(aq)$.

[1]

The colour of $FeSCN^{2+}(aq)$ varies from deep red to orange depending on its concentration. It is possible to determine the concentration of a solution of $FeSCN^{2+}(aq)$ by placing 3 cm^3 of the solution inside a glass sample holder, known as a *cuvette*, into the spectrophotometer. The machine measures the amount of light absorbed when blue light is shone through the solution. The amount of light absorbed is expressed as an *absorbance value*. The more concentrated the solution, the higher the absorbance value.

(b) A plot of absorbance against concentration is known as a *calibration line*. Fig. 3.1 shows the calibration line obtained when the absorbance values of a series of standard solutions containing $FeSCN^{2+}(aq)$ were measured.

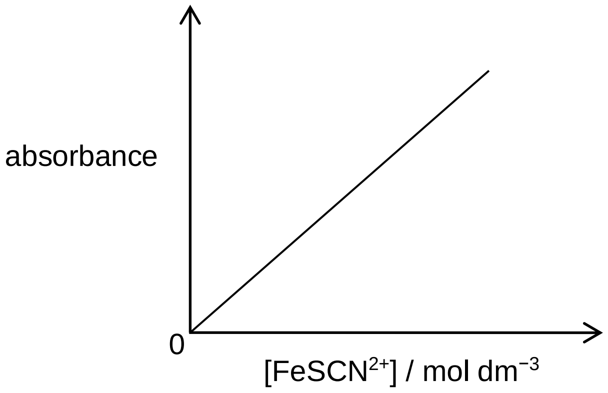


Fig. 3.1

One of the standard solutions was prepared by mixing 5.00 cm^3 of 0.200 mol dm^{-3} aqueous iron(III) nitrate, $Fe(NO_3)_3$, and 5.00 cm^3 of 2.00×10^{-3} mol dm^{-3} potassium thiocyanate, KSCN.

Show that the concentration of $FeSCN^{2+}(aq)$ is 1.00×10^{-3} mol dm^{-3} in this standard solution, and explain why the amount of aqueous iron(III) nitrate used must be in large excess in the standard solutions used to obtain the calibration line.

………..................

…… [2]

To determine a value for K_c, known amounts of $Fe^{3+}(aq)$ and $SCN^-(aq)$ are mixed to produce a solution of $FeSCN^{2+}(aq)$. The absorbance of this solution is then measured. Using the calibration line in Fig 3.1, the concentration of $FeSCN^{2+}(aq)$ can be determined. This can be used to calculate the concentrations of $Fe^{3+}(aq)$ and $SCN^-(aq)$ in the equilibrium mixture and hence K_c.

The following equation represents the relationship between K_c and temperature in kelvin, T:

$$\ln K_c = -\frac{\Delta H^\ominus}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\ominus}{R}$$

R is the molar gas constant with a value of 8.31 J K^{-1} mol^{-1}.
$\Delta H^\ominus$ is the standard enthalpy change of reaction.
$\Delta S^\ominus$ is the standard entropy change of reaction.

A plot of $\ln K_c$ against 1/T can then be used to graphically determine $\Delta H^\ominus$ and $\Delta S^\ominus$.

(c) Plan an investigation to determine the effect of temperature, T, on the equilibrium constant, K_c of the reaction between $Fe^{3+}(aq)$ and $SCN^-(aq)$.

You may assume that you are provided with:
- 2.00×10^{-3} mol dm^{-3} iron(III) nitrate,
- 2.00×10^{-3} mol dm^{-3} potassium thiocyanate,
- a cuvette,
- access to a spectrophotometer and instructions for its use,
- the equipment normally found in a school or college laboratory.

In your plan you should include:
- an outline of how you would prepare a solution of $FeSCN^{2+}(aq)$,
- an outline of how you would determine the concentration of $FeSCN^{2+}(aq)$ in the solution at different temperatures,
- brief, but specific, details of how the concentrations, in mol dm^{-3}, of $Fe^{3+}(aq)$ and $SCN^-(aq)$ in the equilibrium mixture can be determined, and how you would use these concentrations to determine K_c for one of your chosen temperatures.

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………[6]

(d) **(i)** Given that the reaction between Fe^{3+}(aq) and SCN^{-}(aq) is exothermic, sketch a graph you would expect to obtain using data obtained from **3(c)** on the axes in Fig 3.2.

Explain your answer.

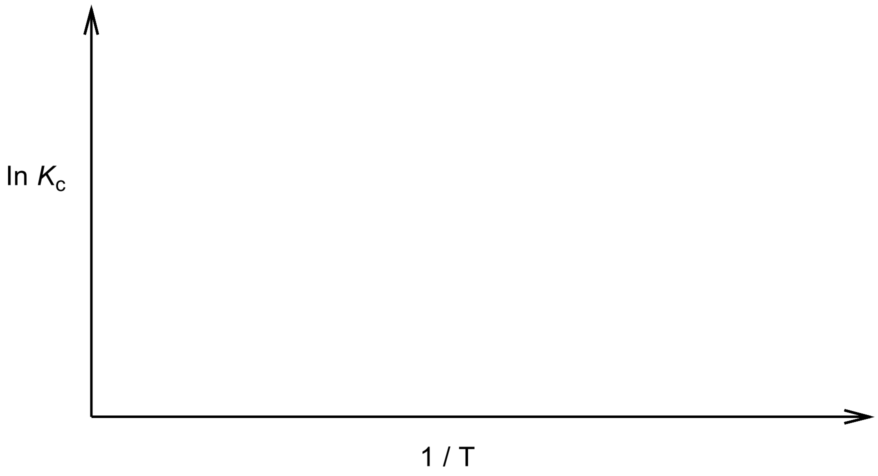


Fig. 3.2

Explanation ……………………………………………………………………………………………

………………………………………………………………………………………………………

[2]

(ii) Describe how would you use your graph in **3(d)(i)** to determine values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$.

………………………………………………………………………………………………………

………………………………………………………………………………………………………

………………………………………………………………………………………………………

………………………………………………………………………………………………………

[2]

[Total: 13]

4 Investigation of some reactions involving manganese compounds

FA 7 is solid manganese dioxide, MnO_2.
FA 8 is an aqueous solution of hydrogen peroxide, H_2O_2.

In addition to access to the usual bench reagents, you are also provided with the following.

- aqueous sodium thiosulfate, $Na_2S_2O_3$(aq)

You will also need access to the **FA 1**, **FA 2** and **FA 4** solutions you used earlier.

Perform the tests described in Tables 4.1, 4.2 and 4.3 and record your observations. Test any gases produced.

Table 4.1

	test	observations
(a)	Place 1 cm depth of **FA 1** in a test-tube. Add a spatula of **FA 7** to this test-tube, followed by another 2 cm depth of aqueous potassium iodide. Filter the mixture into a clean test-tube and collect the filtrate. To the filtrate, add aqueous sodium thiosulfate dropwise, with shaking, until the solution first becomes colourless. Divide the filtrate into two portions.	
	To the first portion, add **FA 2** slowly until no further change is seen.	
	To the second portion, add aqueous ammonia slowly until no further change is seen.	[3]

(b) Suggest the role of **FA 7** in the reaction occurring in **4(a)**. Explain your answer with **two** observations from your experiment.

Role of **FA 7** ……………………………………………………………

Explanation

……………………………………………………………………………………………………

……………………………………………………………………………………………………

…………………………………………………………………………………………………… [2]

Table 4.2

	test	observations
(c)	Place 3 cm depth of **FA 8** into a test-tube. Add a spatula of **FA 7** to this test-tube.	[1]

(d) The mixture in **4(c)** was filtered and the filtrate divided into two portions. When **FA 2** and $NH_3(aq)$ were added to the two portions respectively, no precipitate was formed.

Explain why this observation shows that **FA 7** plays a different role in the reaction taking place in **4(c)** as compared to **4(a)**.

………

………[1]

(e) Hence, suggest the role of **FA 7** in the reaction in **4(c)** and justify your answer with an observation from your experiment.

Role of **FA 7**…………………………………………………………

Explanation

………

………[1]

Question 4 continues on the next page.

Table 4.3

	test	observations
(f)	Place 1 cm depth of **FA 2** into a test-tube. Add 5 drops of aqueous potassium iodide and shake. Add **FA 4** to the mixture dropwise, with shaking, until 10 drops have been added. Then add 1 cm depth of aqueous barium nitrate slowly, with shaking, into the same test-tube. Filter the mixture into a boiling tube. Wash the residue thoroughly with deionised water. Discard the washings. Retain the residue for use in **4(g)**.	
(g)	Place the filter funnel with the residue from **4(f)** over a clean test-tube. Carefully add **FA 1** slowly until it covers the residue. Observe until no further changes are seen.	[2]

(h) When aqueous barium nitrate was added to the mixture in **4(f)**, a Mn-containing species was precipitated and collected as residue on filtration. When **FA 1** was then added to this residue in **4(g)**, two Mn-containing species, **X** and **Y**, were produced which could be found in the final residue and filtrate respectively.

Suggest the identities of **X** and **Y**.

Identity of **X** in the residue ……………………

Identity of **Y** in the filtrate …………………….. [1]

(i) A white precipitate is also formed after adding **FA 1** in **4(g)** but it is unlikely that you will have noticed it. Suggest the identity of this white precipitate.

………………………………………………………………………………………….. [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 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 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

HWA CHONG INSTITUTION
2019 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 1

ANSWERS:

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

Comments

1 D

The definition for atomic mass is the ratio of the average mass of one atom of an element to one-twelfth the mass of one atom of ^{12}C. In option **D**, the mass of one mole of atoms of an element has already taken into account all the isotopes and their relative abundances.

2 A

The electronegativity increases across Period 3 as the effective nuclear charge increases.

The electrical conductivity of the metals Na to A*l* increases while Si is a semiconductor and the non-metals P, S and C*l* are non-conductors.

The atomic radii across Period 3 shows a generally decreasing trend due to the increase in effective nuclear charge across the period.

The melting point increases from Na to A*l* on account of the increasing metallic bonding strength; the trend peaks at Si which has a giant covalent structure with extensive strong covalent bonding, before showing a decreasing trend for the simple covalent compounds which only have weak dispersion forces between molecules.

3 D

Ice has a simple covalent structure. There is hydrogen bonding between water molecules, and covalent bonding between atoms of H and O in each molecule of water.

Iodine has a simple covalent structure. There are dispersion forces between iodine molecules, and covalent bonding between atoms of iodine in each molecule of iodine.

Aluminium chloride has an ionic lattice structure with a large amount of covalency in the solid state at room temperature. Its structure becomes simple covalent just below its melting point resulting in dispersion forces between Al_2Cl_6 molecules. Hence permanent dipole interactions are not found in the solid state.

Graphite has a giant covalent structure with dispersion forces holding the sheets of carbon atoms together.

4 **B**

Species	**NH_4^+**	**XeF_4**
Shape	Tetrahedral	Square planar
Bond Angle	109.5^{o}	90^{o}
Species	**NF_3**	**NH_3**
Shape	Trigonal pyramidal	Trigonal pyramidal
Bond Angle	102^{o}	107^{o}
	F is more electronegative than N and so the electron cloud of the N–F bond is distorted towards F. This causes the electron density about N to decrease. Thus, bond pair-bond pair repulsion is weaker around the central N atom in NF_3 than in NH_3. Hence, bond angle in NF_3 is smaller.	
Species	**NO_2^+**	**SO_2**
Shape	Linear	Bent
Bond Angle	180^{o}	$<120^{o}$
Species	**BCl_3**	**PCl_3**
Shape	Trigonal planar	Trigonal pyramidal
Bond Angle	120^{o}	107^{o}

5 **C**

Since the number of moles of gas in the three containers did not change before and after the taps are opened, the number of moles of gas found in the individual containers before and after the taps are opened should be the same.

$$\eta_{\text{gas in first container}} + \eta_{\text{gas in second container}} + \eta_{\text{gas in third container}} = \eta_{\text{gas in overall container}}$$

Note that there is no gas in the second container since it contains a vacuum. Thus it is not included in the calculation of the total number of moles of gas.

$$\frac{P_1V_1}{T_1} + \frac{P_2V_2}{T_2} = \frac{P_{final} \times V_{final}}{T_{final}}$$

$$\frac{1 \times 420}{293} + \frac{2 \times 75.5}{273} = \frac{P_{final} \times (420 + 75.5 + 13)}{298}$$

P_{final} = 1.16 bar

6 C

No. of moles of sodium percarbonate = 10.0 x 10^{-3} x 0.100 = 0.00100

1 mole of sodium percarbonate produces x moles of CO_2.
No. of moles of carbon dioxide = 48 ÷ 24000 = 0.00200

$$x = \frac{0.00200}{0.00100} = 2$$

No. of moles of $KMnO_4$ = 0.0500 x 24.0 x 10–3 = 0.00120
No. of moles of H_2O_2 = 0.00120 x 5 ÷ 2 = 0.00300

1 mole of sodium percarbonate produces y moles of H_2O_2.

$$y = \frac{0.00300}{0.00100} = 3$$

Ratio of $y : x = 3 : 2$

7 A

$\Delta G = \Delta H - T\Delta S$

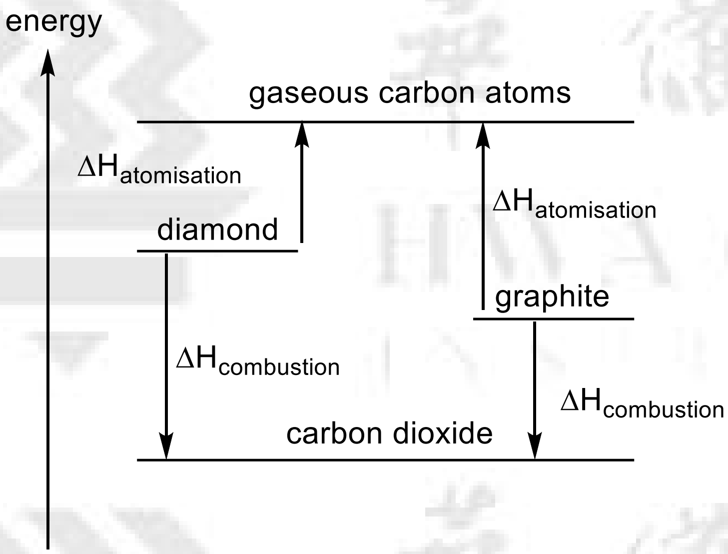
In general, ΔH & ΔS hardly changes with temperature unless there is a change in the physical state of the reactants or products. Normally, ΔG is dependent on the temperature as seen from the equation above.

For this particular reaction, ΔS is almost 0 regardless of the temperature since there are equal number of moles of gas on both sides of the arrow. Since $\Delta S \approx 0$, therefore $T\Delta S \approx 0$ and so $\Delta G \approx \Delta H$. Thus the ΔG of the reaction becomes relatively independent of temperature.

Note also that the equilibrium constant, K, is always affected by temperature unless $\Delta H = 0$.

8 B

The diagram below shows that the magnitude of the ΔH_{atom} for graphite is larger than that for diamond but the magnitude of ΔH_c for graphite is smaller than that for diamond.



In graphite, each C atom has a 2p orbital containing one electron that is not used in the formation of C–C bonds. The 2p orbitals can overlap with each other to form a two-dimensional delocalised π bonding system spreading throughout the whole sheet of atoms. Thus, the C–C bonds in graphite have partial double bond character. Thus the C–C bonds in graphite are stronger than those in diamond. This is also evident from the larger magnitude of ΔH_{atom} of graphite.

The rearrangement of atoms in a tetrahedral structure of carbon atoms in diamond to the trigonal planar structure of carbon atoms in graphite requires a lot of energy as many strong covalent bonds are broken. This constitutes a very high activation energy such that conversion of diamond to graphite is kinetically unfavorable despite the process having a negative ΔG.

9 C

The number of half-lives that it takes rock sample to decay to a ratio of 2:3 for thorium-234 to protactinium-234 is calculated as follows. Hence fraction of thorium-234 in the rock sample = $\frac{2}{2+3} = \frac{2}{5}$

$$1 \times \left(\frac{1}{2}\right)^n = \frac{2}{5}$$

n = 1.32 half-lives

where 1 = amount of thorium-234 at the start, and $\frac{2}{5}$ is the amount of thorium at the end of the time period of radioactive decay.

Time taken = 1.322 x 24.1 = 31.9 hr

In this question, the strategy is to recognize that more than one half-life, but less than two half-lives, have passed. So the logical answer would lie between 24.1 h and 48.2 h.

10 B

In order to find the correct rate equation based on the suggested reaction mechanisms, the following steps must be taken.

The species found in the rate equation should only include the reactants and not any of the intermediates formed in the mechanism. It is helpful to write down the overall chemical equation so that the reactants are not confused with any of the intermediates.

The stoichiometry of each reactant in the slow step of a mechanism is reflected as the order of reaction of that reactant in the overall rate equation.

1. Overall equation: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
The reactants in the slow step consist of those found in the overall equation. This means that two NO molecules and one H_2 molecule are involved in the rate determining step. The rate equation should reflect this. Hence the rate equation should be rate = $k[NO]^2[H_2]$.

2. Overall equation: $2NO + O_2 \rightarrow 2NO_2$
The reactants in the slow step contain the intermediate N_2O_2 and reactant O_2. Hence the rate law based on the slow step would look like this.

rate = $k[N_2O_2][O_2]$ --- equation 1

However, N_2O_2 should not appear in the rate equation. We need to substitute $[N_2O_2]$ with the concentration of reactants that produced this intermediate into equation 1, giving rate = $k[NO_2]^2[O_2]$. Although the rate equation seems to indicate a termolecular reaction mechanism, the suggested mechanism shows otherwise.

3. Overall equation $2O_3 \rightarrow 3O_2$
In the slow step, one molecule of O_3 reacts with one atom of C*l*. Hence the overall rate equation should be rate = $k[O_3][Cl]$. The species C*l* is a homogenous catalyst since it is used up in step one and regenerated in step 2. It should appear in the rate equation as it affects the rate of reaction even if it does not appear in the overall equation.

11 **B**

	$2SO_3$ (g)	+	O_2 (g)	⇌	$2SO_3$ (g)
I / mol	0.50		1.00		–
C / mol	– 0.30		– 0.15		+ 0.30
E / mol	0.20		0.85		0.30

The equilibrium constant expression for the formation of SO_3 is written as follows:

$$K=\frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$$

$$K=\frac{\left(\frac{0.30}{0.5}\right)^2}{\left(\frac{0.20}{0.5}\right)^2\left(\frac{0.85}{0.5}\right)}=\frac{45}{34}$$

The equilibrium constant expression for the equation $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is written as follows:

$$K_c = \frac{P_{SO_3}}{P_{SO_2}\left(P_{O_2}\right)^{1/2}}$$

$$K_c = \sqrt{K} = 1.15$$

12 B

Adding a catalyst to a reversible reaction increases the rate of the forward and backward reactions equally. The equilibrium position is not affected, so the yield of the reaction is not affected by the catalysis. The catalyst merely causes equilibrium to be reached at a faster rate. The catalyst does **not** lower the activation energy of the <u>original</u> reaction pathway, but provides an <u>alternative reaction pathway with a lower activation energy for both the forward and backward reactions</u>.

13 B

See Topic 15, page 14. The graph for α vs V should be similar to that for pH vs V. As the volume of acid increases due to adding more water to dilute the acid, the pH will keep increasing while the extent of dissociation increases to almost 1 (i.e. almost complete dissociation). The pH should not exceed 7, which is the pH of water. K_a only changes with temperature.

14 A

The chemical equation for the oxidation process at the anode is given as follows:

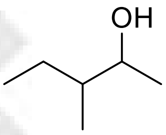
$$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3\,(s) + 6H^+(aq) + 6e^-$$

$Q = I \times t = n_e \times F$
$n_e = It/F$ ------ (1)
$n_e : n_{Al_2O_3} = 6 : 1$ from the equation. Hence, $n_e = 6 \times n_{Al_2O_3}$ ------ (2)
Therefore, substituting (2) into (1): $n_{Al_2O_3} = It/(6F)$
mass of $Al_2O_3 = It/(6F) \times M_r(Al_2O_3)$

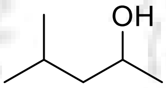
As can be seen, the mass of Al_2O_3 produced is <u>only</u> dependent on the current that passes through the circuit, and the time in which the current has passed through.

15 C

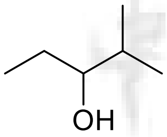
For the molecular formula $C_6H_{14}O$ to be a secondary alcohol with a branched chain, we should start with a five-carbon backbone and the –OH group in the 2nd position first, then in the 3rd position. Then explore a four-carbon backbone and place the –OH group in the 2nd position. Hence, there are a total of 4 constitutional isomers.



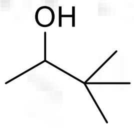
3-methylpentan-2-ol



4-methylpentan-2-ol



2-methylpentan-3-ol

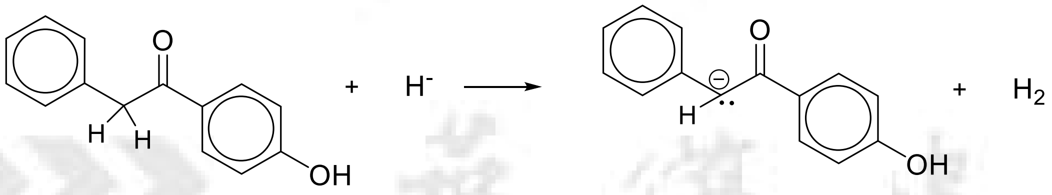


3,3-dimethylbutan-2-ol

16 D

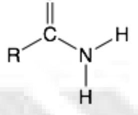
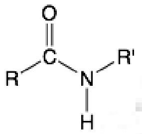
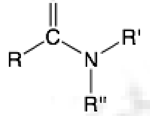
Step 1 involves the attack of the electron-deficient C atom on the C=O group of the phenylethanoic acid (the electrophile) on the benzene ring of phenol. The electrophile substitutes the H atom on the benzene ring of phenol. Hence reaction 1 is an electrophilic substitution.

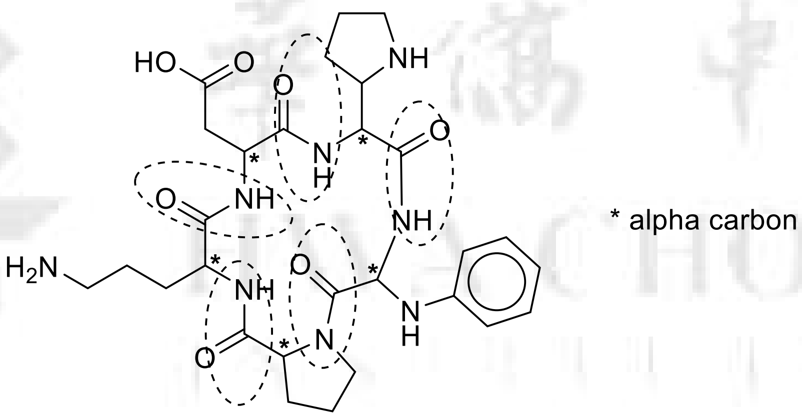
In **Step 2**, NaH provides the H^- anion, which abstracts a H^+ from the carbon next to the C=O group. This is an acid-base reaction with the ketone acting as the acid since it donates a H^+ ion, while the H^- acts as the base in receiving the H^+.



17 A

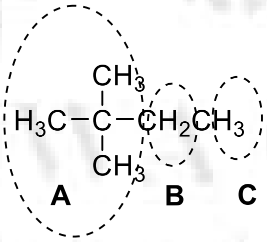
Identify the alpha-carbons in the backbone of the oligopeptide (in *). You can then easily identify the amide linkages in compound W (circled below). If you are confused as to what is an amide, refer to the table below.

Primary amides	**Substituted amides**	
		

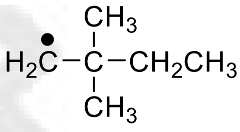


18 B

There are three different types of environments in which the hydrogens in 2,2-dimethylbutane are in, which are circled below.

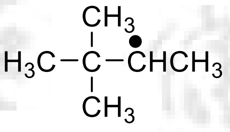


Hence, the 3 different radicals you can obtain from abstracting each type of hydrogen respectively are:



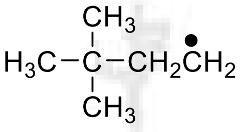
$\overset{\bullet}{H_2C}-C(CH_3)_2-CH_2CH_3$

A



$H_3C-C(CH_3)_2-\overset{\bullet}{C}HCH_3$

B

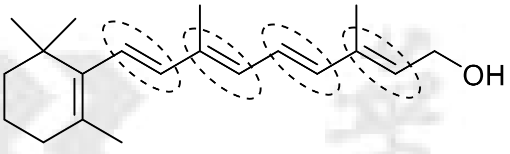


$H_3C-C(CH_3)_2-CH_2\overset{\bullet}{C}H_2$

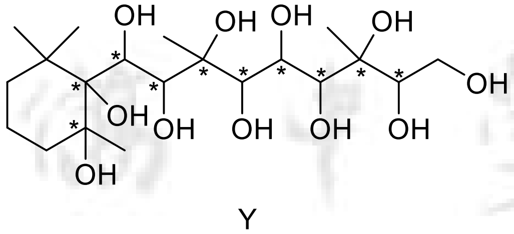
C

19 C

The C=C in retinol (except that in the cyclic ring) will exhibit cis-trans isomerism, hence 2^4. After mild oxidation to form the diol, all 5 C=C will undergo addition and give 10 chiral carbons, hence 2^{10}.



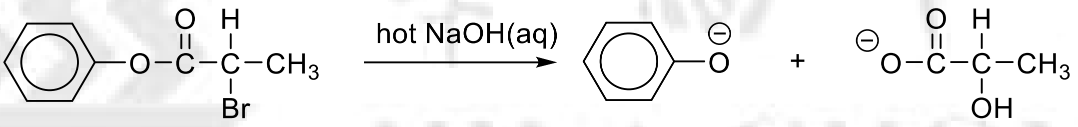
retinol



Y

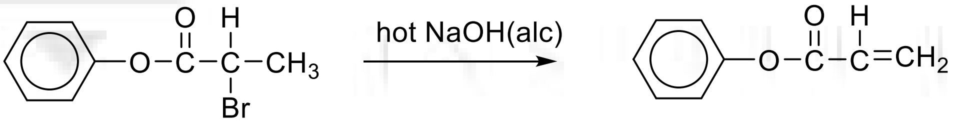
20 C

The bromoalkane undergoes nucleophilic substitution and the ester group undergoes alkaline hydrolysis with hot NaOH(aq).



(option 2)

Bromoalkane can undergo elimination with hot ethanolic NaOH.

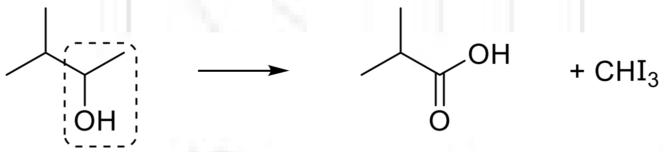


(option 3)

There are other possible products that can form from the reaction above, but they are not in the options provided. Option 1 will not be formed no matter what as no reaction would yield a benzoate ion as a possible product.

21 D

Identify the presence of $CH_3CH(OH)-$ group in the alcohol. The products formed after acidification are the carboxylic acid below and iodine.



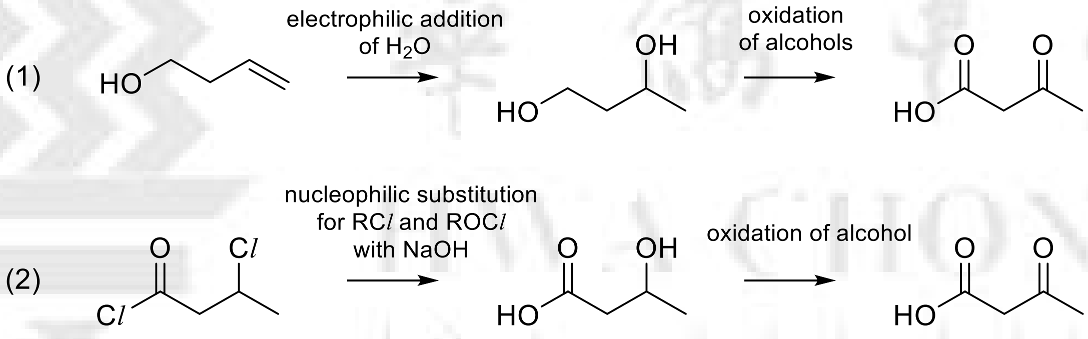
2-methylpropanoic acid

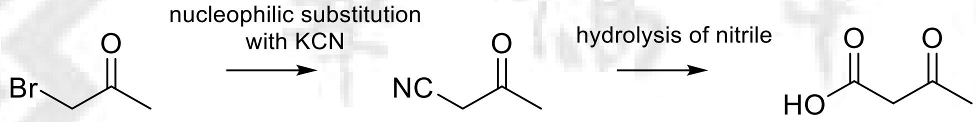
22 D

There must be 2 acidic groups in compound X which undergo acid-base reaction with NaOH(aq) since 2 mol of water is formed. Only phenols and carboxylic acids are strong enough acids to react with NaOH, but alcohols are too weak to donate a proton to NaOH.

23 D

Think of the possible transformations to form a ketone and carboxylic acid.



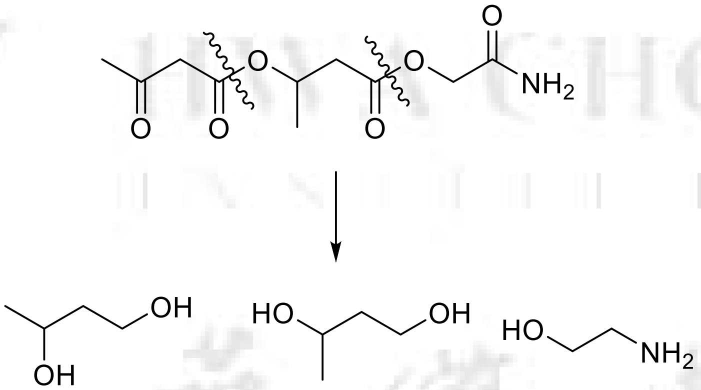
(3) 

24 A

Ketones and nitriles can be reduced by H_2/Ni but <u>not</u> carboxylic acids. Refer to summary of oxidising and reducing agents on pg 105 of Organic Chemistry (II) lecture notes.

25 C

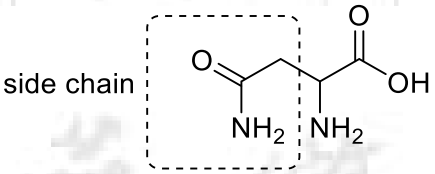
Apply the same pattern of reduction across the ester bonds to alcohols, bearing in mind that ketones are also reduced to secondary alcohols and amides are reduced to amines. Hence a total of three fragments are produced after the reaction.



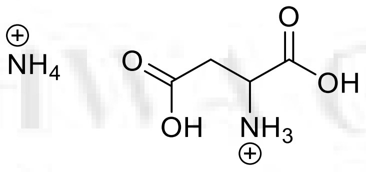
26 B

(1) Asparagine exists in solution as a zwitterion as it undergoes an intramolecular acid-base reaction.

(2) α-amino acids have the amino and carboxyl groups bonded directly to the same α-carbon, differing only in the side chain bonded directly to the α-carbon. The amide functional group in the side chain is neutral.



(3) The side chain of asparagine will undergo acidic hydrolysis to give the two products below. No ammonia gas is evolved.



27 A

Ionic oxides tend to be basic in nature, hence higher pH. Covalent oxides tend to be acidic oxides, hence lower pH. SiO_2 is insoluble in water, hence neutral pH. Refer to summary of properties of oxides on pg 15 of Inorganic Chemistry lecture notes.

28 C

Al_2O_3 is an inorganic ionic compound, but is insoluble in water, hence it shouldn't conduct electricity when dissolved in water. When molten, however, its ions are mobile and it will be able to conduct electricity.

$SiCl_4$ exists as simple discrete covalent molecules and cannot conduct electricity. However, it undergoes complete hydrolysis in water to give HCl(aq), which dissociates to give H^+ and Cl^- ions which are mobile charge carriers.

NaF is an inorganic ionic compound, dissolving in water to give Na^+ and F^- ions, which are mobile charge carriers.

29 D

$E^\ominus([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}) = +0.36V$
To oxidise $[Fe(CN)_6]^{4-}$, we need to find an oxidising reagent (which can be reduced) and whose $E^\ominus$ is more positive than +0.36V.

In your data booklet, SO_2 and NO_2 are both reducing agents as they can only be oxidized (found on right hand side of half-equations), hence both cannot be used. Cu^{2+} and I_2 are both oxidising agents, and their $E^\ominus$ values are +0.34V and +0.54V respectively, hence I_2 is the only one which can be used.

30 C

A homogeneous catalyst operates in the same phase as the reactants. Iron exhibits variable oxidation states which allows it to perform its role.

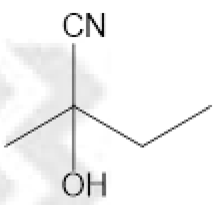
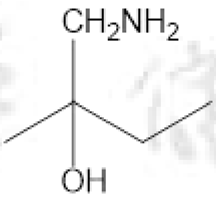
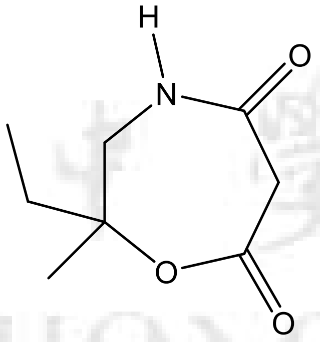
$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$ $E^\ominus_{cell} = 2.01 - 0.77 = +1.24\ V$
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ $E^\ominus_{cell} = 0.77 - 0.54 = +0.23\ V$

HWA CHONG INSTITUTION
2019 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 2

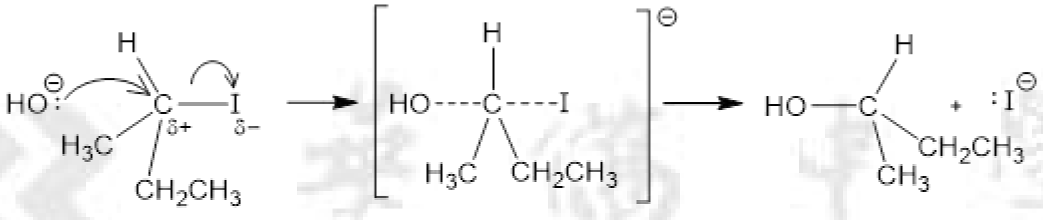
1 (a) (i) HCN with trace amount of KCN (or NaOH(aq)), cold **[1]**

(ii)

 **A**	 **B**	 **C**

[1] for each correct structure

(b) (i) Mechanism: **Bimolecular** Nucleophilic Substitution (**S$_N$2**) **[1]**

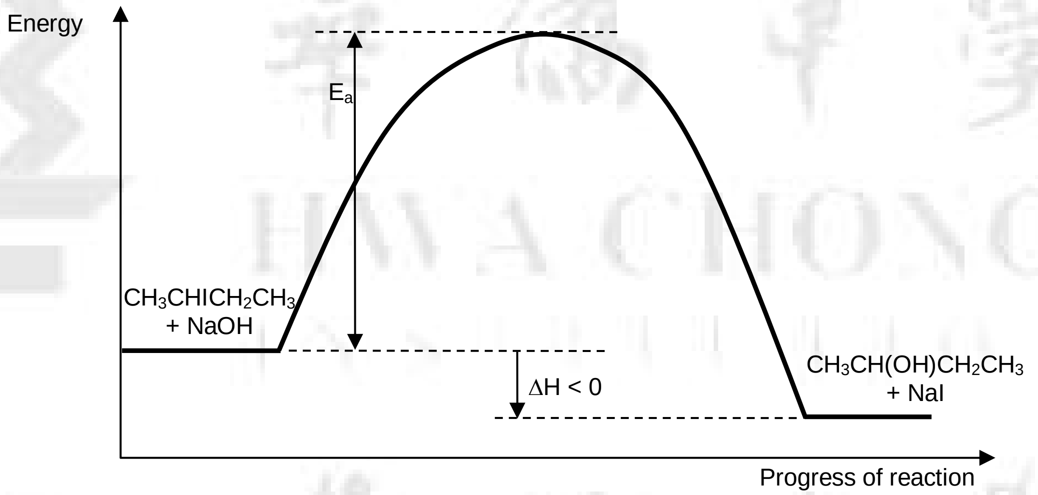


[1] for:
- ✓ OH^- is the nucleophile that attacks $C^{\delta+}$ of C–I (attack from the side that's opposite to the I)
- ✓ partial charges: $C^{\delta+}$–$C/^{\delta-}$
- ✓ curly arrow going from <u>lone pair</u> of OH^- to $C^{\delta+}$ of C–I
- ✓ curly arrow going from C–I bond, to I

[1] for:
- ✓ transition state negatively charged (need not label "transition state")
- ✓ I^- is produced at the end of the reaction
- ✓ no slow or fast step

−½m for every mistake

(ii)



[1] shape of graph
[1] labelling graph
✓ label E_a
✓ label ΔH
✓ label "reactants" and "products"
✓ label axes
−½m for every mistake

(c) The halogens Cl_2, Br_2 and I_2 exist as simple non-polar covalent molecules. From Cl_2 to Br_2 to I_2, the size of the electron cloud and hence, the polarisability of the halogen molecule increases [1]. More energy is needed to overcome the stronger dispersion forces between the molecules. Hence, the volatility of the halogens decreases [1] from chlorine to iodine.

(d) **(i)** $2HX \rightarrow H_2 + X_2$ **[1]**

(ii) Down the group, as atomic radius increases from C*l* to I, the bond length of the H–X bond increases / bond strength decreases **[1].**
Hence, less energy is needed to break the H–X bond. Thus, the thermal stability of the hydrogen halides decreases down the group **[1].**

Remarks: can also justify by quoting the bond energy data, H–Cl = +431, H–Br = +366, H–I = +299 kJ mol^{-1}*. Weaker H–X bond needs less energy to break during thermal decomposition*

(e) From *Data Booklet*,

	$E^{\ominus}$/V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Bromine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$, which will be further oxidised to SO_2 and subsequently SO_4^{2-}.
$E^{\ominus}_{cell}$ = +1.07 − (+0.09) = +0.98 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +1.07 − (+0.51) = +0.56 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +1.07 − (+0.17) = +0.90 V > 0 (spontaneous)

Iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ but there is no further oxidation of $S_4O_6^{2-}$ to SO_2.
$E^{\ominus}_{cell}$ = +0.54 − (+0.09) = +0.45 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +0.54 − (+0.51) = +0.03 V > 0 (spontaneous but extent of reaction is too small)

[1] $E^\ominus_{cell}$ for reaction with bromine or showing that the $E^\ominus_{(Br2/Br-)}$ > all the 3 $E^\ominus$
[1] $E^\ominus_{cell}$ for reaction with iodine or showing that $E^\ominus_{(I2/I-)}$ > +0.09 V but only slightly larger than +0.51 V
[½] spontaneous since $E^\ominus_{cell} > 0$
[½] spontaneous but extent of reaction too small

2 (a) (i) $K_a = [H^+][A^-] / [HA]$
$K_a = (10^{-5.5})(1) / 4$
$K_a = 7.91 \times 10^{-7}$ mol dm^{-3}
$pK_a = -\lg(7.91 \times 10^{-7}) = 6.10$ **[1]**

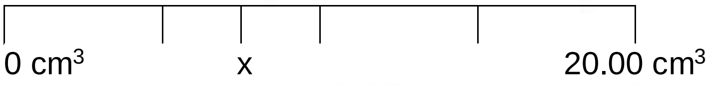
OR

pH = pKa + lg[A$^-$]/[HA]
5.5 = pKa + lg(1/4)
$pK_a = 6.10$ **[1]**

(ii) 1:1 **[1]**

(iii) Let x be the volume of NaOH required to achieve maximum buffer capacity

For visualization:



Since the ratio of the [A$^-$]:[HA] in the buffer is 1:4, a titre value of 20.00 cm^3 must correspond to 4 units. Hence, maximum buffer capacity must occur when there are 2.5 units of [A$^-$] and 2.5 units of [HA]. **[1]**

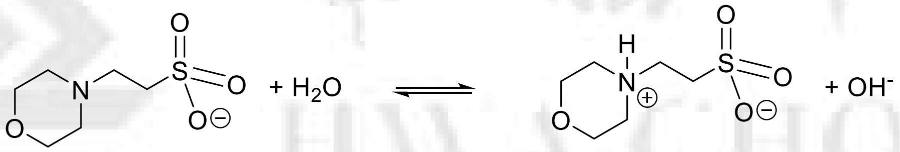
Therefore, the volume of NaOH required, x, corresponds to 1.5 units.

Volume of NaOH required = 20.00/4 × 1.5 = 7.5 cm^3 **[1]**

OR

Let x be the volume of NaOH required to achieve maximum buffer capacity
Since the ratio of the [A$^-$]/[HA] in the buffer is 1:4,
(20 – 2x) / (20) = 1/4 **[1]**
2(10 – x) = 20/4
x = 7.5 cm^3 **[1]**

(iv)



[1]

(v) Given that the **region of rapid pH change will be at about pH 9.4,** I would use an indicator with a **working range that coincides with that pH range [1]**, which would be **cresolphthalein**. **[1]**

(b) (i) Initially, the graph is a straight line/increases steadily. This is because the reaction is **first order wrt to [sugar]/ rate is directly proportional to [sugar]/ more enzyme-substrate complex can be formed by increasing [sugar]. [1]** Thus, the rate of reaction increase.

The graph plateaus/becomes horizontal/becomes zero order wrt [sugar] **because the enzyme is now saturated/all active sites are occupied [1],** thus, the rate of reaction cannot be increased by increasing [sugar].

(ii)

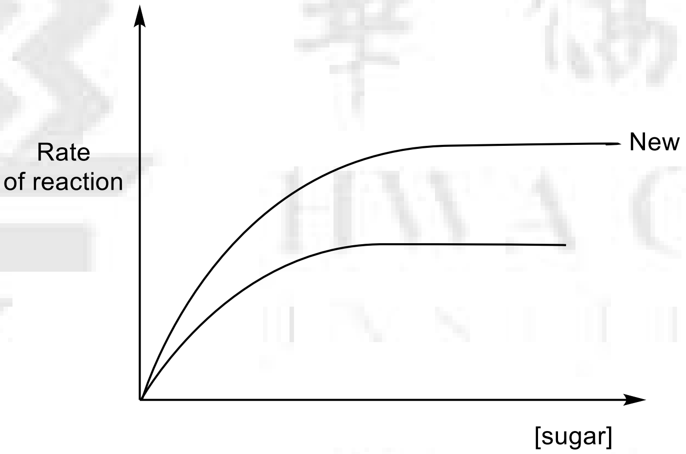


Fig. 2.1

[1]

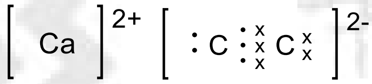
Key points

- Initial rate increases more quickly
- Plateau occurs at a higher concentration of sugar
- Plateau occurs at a higher rate

(iii) Order wrt to [sugar]:
Comparing experiment 1 and 2,
When [sugar] is doubled from 0.20 mol dm^{-3} to 0.40 mol dm^{-3}, the relative rate of reaction doubled.
Thus, [sugar] is directly proportional to the rate of reaction, and is first order.
[1] for explanation

Order wrt to [zymase]:
Comparing experiment 1 and 3,
When [sugar] is halved from 0.20 mol dm^{-3} to 0.10 mol dm^{-3}, the relative rate of reaction is expected to halve.
When [zymase] is doubled from 0.010 mol dm^{-3} to 0.020 mol dm^{-3}, the relative rate is doubled from ½ to 1
Thus, [zymase] is directly proportional to the rate of reaction, and is first order.
[1] for explanation
[½] x 2 for each correctly identified order

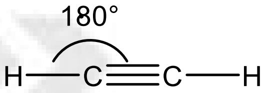
3 (a) (i)



Anion:
additional electrons of opposite symbol were accepted
additional electrons of third symbol were accepted
dative bonds were rejected
[½] for each ion

(ii) $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$ [1]
[1] balanced equation with correct state symbols

(b) (i)



[1] for correct bond angle (only one needs to be labelled on the diagram itself), and correct Lewis structure which must show linear shape.

Type of hybridisation: sp **[1]**

(ii) Two characteristics of ethyne, and explanation:

1. Ethyne has a small molecular size, which means the volume of the particles of ethyne is small compared to the volume of the container, and so can be considered negligible just as for ideal gases; and
2. Ethyne is a non-polar molecule, so it has relatively weak intermolecular dispersion forces, which could therefore be considered negligible, just as for ideal gases.

[1] x 2 for each characteristic

(c) (i) Total initial pressure = $x + y$
= 760 mm Hg **[1]**

(ii) Since p mm Hg is the change in partial pressure of ethyne during the combustion:

	$C_2H_2(g)$	+	$5/2\ O_2(g)$	→	$2CO_2(g)$	+	$H_2O(l)$
Initial partial pressure / mm Hg	x		y		0		-
Change / mm Hg	$-p$		$-5/2p$		$+2p$		-
Final partial pressure / mm Hg	$x - p$		$y - 5/2p$		$2p$		-

Total pressure after combustion $= (x - p) + (y - \frac{5}{2}p) + 2p$
$= [(x + y) - \frac{3}{2}p]$ mm Hg

[1] Correct expression of total pressure after combustion in terms of x, y and p

(iii) Total initial pressure = $(x + y)$ mm Hg
Total pressure after combustion = $(x + y) - \frac{3}{2}p$ mm Hg

Since a reaction occurs, p must be > 0
so $(x + y) - \frac{3}{2}p < (x + y)$,
i.e. (final pressure) < (initial pressure)
and ∴ the term "$-\frac{3}{2}p$" represents a fall in pressure from the original $(x + y)$ mm Hg (shown)

[1] Convincing argument in which there is a comparison of initial and final pressures in terms of x, y and p.

(iv) From **(ii)** and **(iii)**, we know that the fall in pressure inside the flask corresponds to difference in height (atmospheric pressure remains unchanged):

$\frac{3}{2}p = 65$
$p = 65 \div (3/2)$
$= \underline{\underline{43.3}}$ (to 1 d.p.) (in mm Hg)

[1] Answer must be to 1 d.p. to get the full credit.

(v) **(I)** Since final partial pressure of CO_2 is $2p$
∴ $P_{CO2} = 2p = \underline{86.7 \text{ mm Hg}}$ **[1]** (to 3 s.f.)

(II) If all oxygen was used up, then $y - 5/2p = 0$
∴ $y = 5/2p$
$y = 5/2\ (65 \div 3/2) = 108.3$ mm Hg (1 d.p.)
$= \underline{\underline{108}}$ mm Hg (3 s.f.) **[½]**

And $x = 760 - 108.3 = 651.7$ mm Hg (1 d.p.)
$= \underline{\underline{652}}$ mm Hg (3 s.f.) **[½]**

(d) (i) pV = nRT
From graph, $\eta_{H2} = \underline{1.06}$ mol (accepted 1.04 – 1.06)
[1] for correct reading of no. of moles of H_2 from graph

$P_{H2} = nRT/V = (1.06)(8.31)(1250 + 273) / (0.100)$
$= 134,155$ Pa
$= \underline{1.34 \times 10^5 \text{ Pa}}$
$= \underline{134 \text{ kPa}}$ (to 3 s.f.)
[1] for correct use of ideal gas equation, and answer

ALTERNATIVE:
From graph, $\eta_{(total)} = (1.06 + 0.30 + 0.26)$
$= 1.62$ mol

$P_{(total)} = n_{(total)}RT/V = (1.62)(8.31)(1250 + 273) / (0.100)$
$= 205{,}029$ Pa

P_{H2} = (mole fraction of H_2) x $P_{(total)}$
= (1.06/1.62) x 205,029
= 134,155 Pa = $\underline{1.34 \times 10^5 \text{ Pa}}$ = $\underline{134 \text{ kPa}}$ (to 3 s.f.)

(ii)

$$\left.\begin{aligned} K_p &= \frac{(P_{H2})^3(P_{C2H2})}{(P_{CH4})^2} \\ &= \frac{(\frac{n_{H2}RT}{V})^3(\frac{n_{C2H2}RT}{V})}{(\frac{n_{CH4}RT}{V})^2} \\ &= \frac{(n_{H2})^3(n_{C2H2})}{(n_{CH4})^2} \times \left(\frac{RT}{V}\right)^{4-2} \\ &= \frac{(n_{H2})^3(n_{C2H2})}{(n_{CH4})^2} \times \left(\frac{RT}{V}\right)^{2} \end{aligned}\right\}$$

[1] for convincing proof and use of pV = nRT

$$= \frac{1.06^3 \times 0.30}{0.26^2} \times \left(\frac{8.31 \times 1523}{0.100}\right)^2$$

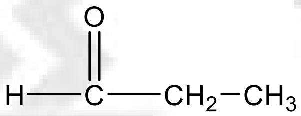
[1] for substitution of correct terms from graph

$= \underline{8.47 \times 10^{10} \text{ Pa}^2}$ (3 s.f.) **[1]** for correct answer and units

Other accepted units of K_p: (J^2 m^{-6})
≡ Pa^2

(iii) When the temperature is changed from 1250 °C to 1000 °C, the value of K_p would decrease / be smaller **[1]**.

(e) (i)



$H-C(=O)-CH_2-CH_3$ **[1]**

Propanal **[1]** (must be spelt clearly and correctly, no benefit of doubt)

(ii) To each separate samples of propyne and propanal, (any of the following):

	Chemical test	**Observations**	
		propyne	**propanal**
1	Add 2,4-DNPH	No orange ppt	Orange ppt formed
2	warm with Tollen's reagent	No silver mirror	Silver mirror produced
3	warm with Fehling's solution	No brick-red ppt	Brick-red ppt formed
4	add aqueous bromine	Yellow-orange aqueous bromine decolourised	Yellow-orange colour remains
5	Add $Br_2(l)$ (at r.t., no UV) or Br_2 in CCl_4 (at r.t., no UV)	Reddish-brown liquid bromine decolourised Orange-red Br_2 in CCl_4 decolourised	Reddish-brown colour remains Orange-red colour remains

6	Heat with acidified potassium dichromate	Orange colour remains	Orange solution turns green

Careful! hot acidified or alkaline $KMnO_4$ is not ideal here as both propyne and propanal can undergo oxidation (propyne undergoes oxidative cleavage, while propanal will be oxidsed to propanoic acid). However, students who added hot *acidifed* $KMnO_4$ to both compounds and used the effervescence of CO_2 to identify propyne (effervescence not seen for propanal) were awarded the mark.

Careful! Cold $KMnO_4$ to form the diol for propyne is a dubious choice, as propanal may still get oxidized in cold conditions, so decolourisation might happen for both compounds.

[1] correct choice of test
[1] correct distinguishing observation (incorrect colours of ppts or solutions were penalized)

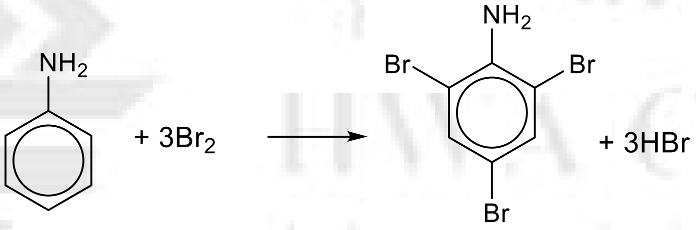
Ecf was only awarded if product drawn in (e)(i) was an aldehyde or ketone

4 **(a)** The π cloud has high electron density/ is electron-rich that will attract electron-deficient electrophiles but will repel electron-rich nucleophiles. **[1]**

(b) Electrophilic addition destroys the delocalisation in the π electron cloud/disrupts aromaticity which requires a significant amount of energy, whereas electrophilic substitution retains aromaticity. **[1]**

(c) **(i)** Step 1: Conc. HNO_3, conc. H_2SO_4, maintained at 55 °C **[1]**
Step 2: 1. Sn, (excess) conc. HC*l*, heat 2. NaOH(aq) **[1]**

(ii)

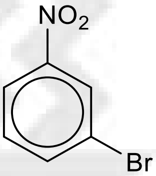


X

[1] for X
[1] for equation (ecf for equation if X is monosubstituted)

(iii) Nitrobenzene < benzene < phenylamine.**[½]**

The nitro group is electron withdrawing and withdraws electron density from the π electron cloud on the benzene ring **[½]**, reducing the susceptibility of the benzene ring towards electrophiles/deactivating the ring towards electrophiles **[½]**. The NH_2 group on phenylamine is electron-donating as it can donate its lone pair of electrons to the ring and increases electron density of the π electron cloud in the benzene ring. **[½]**
(only need to mention susceptibility towards electrophiles/activating or deactivating towards electrophiles once)

(iv) 

[1]

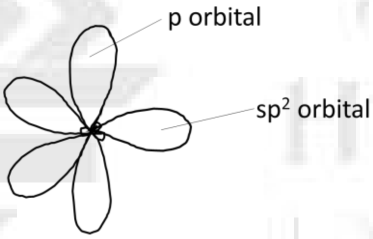
(d) **D** has only 4 π electrons in the ring, so it doesn't satisfy criteria 4. **[1]**

F has two carbon atoms in the ring that are sp^3 hybridised, so those carbons do not have available p orbitals, so it doesn't satisfy criteria 2

OR

F does not satisfy criteria 3, since the p orbitals are not overlapped in a continuous fashion/ since the structure is not planar at the carbons that are sp^3. **[1]**

(e) **(i)**



[1] for correct shape, arrangement and label for p orbital
[1] for correct shapes, arrangement and label for sp^2 orbitals

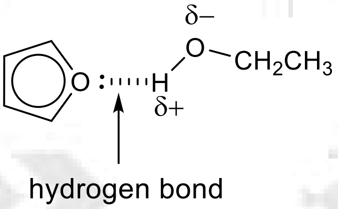
(ii) <u>2</u> **[1]**

(iii) p orbital. **[1]**

(iv) The <u>lone pair</u> on N of pyrrole is <u>delocalised</u> into the π cloud and is <u>less/not available</u> for donation to a H$^+$. **[1]**

(f) **(i)** Furan has very low resonance energy of <u>80 kJ mol^{-1}</u> **[1]**, so disrupting its aromaticity requires very little energy OR formation of strong σ bonds in an addition can compensate for the loss in its small resonance energy **[1]**.

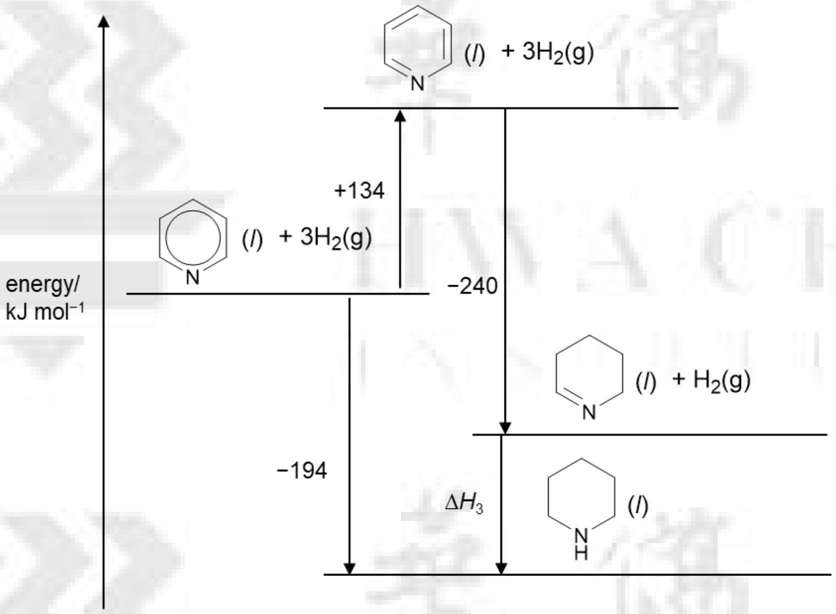
(ii)



[1] (correct bond, lone pair, partial charges and label) (-1/2 per mistake)

The <u>hydrogen</u> atom <u>bonded to the</u> highly <u>electronegative O</u> on ethanol has a very significant <u>δ+ charge</u> and the electron density in the covalent bond is highly polarised towards the oxygen atom. As a result, the H can form a very strong <u>attraction to the lone pair of electrons</u> on the highly electronegative <u>oxygen atom on furan</u>. This is a hydrogen bond. **[1]**

(g)



Cycle: **[2]**

–[½]m per mistake (max ½ m for cycle if students put the diene on the highest energy level, the ½ m can only be awarded if they put in -194 at the correct position)

By Hess' Law,

$\Delta H_3 = -(-120 - 120) - 134 + (-194) = -88$ kJ mol^{-1} **[1] ecf for correct use of Hess' Law.**

HWA CHONG INSTITUTION
2019 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 3

1 **(a)** **(i)** $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ **[1]**

(ii) $\text{L.E}\ \alpha\ \frac{q_+q_-}{r_+ + r_-}$ **[1]**

Both $MgCO_3$ and MgO have the <u>same charges and cationic radius</u> **<u>[0.5]</u>**
<u>Anionic radius for CO_3^{2-} is bigger than O^{2-}</u> [**0.5**]
Magnitude of L.E. of $MgCO_3$ is smaller than that of MgO.

(iii) **Δ*S* is positive** as **gaseous CO_2 is evolved [1]**. Hence, –TΔ*S* term is negative.
$\Delta G = \Delta H - T\Delta S$
Since the decomposition of $MgCO_3$ is endothermic, Δ*H* is positive.
So for the decomposition to be spontaneous, **for Δ*G* to be negative**, the decomposition should take place at **high temperature [1]**.

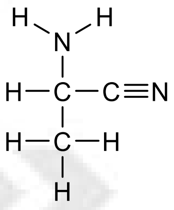
(iv) **$MgCO_3$** has the lower decomposition temperature. **[0.5]**

Both Mg^{2+} and Ba^{2+} have the same charge. The **ionic radius of Mg^{2+} is smaller than Ba^{2+} (0.5)**. So Mg^{2+} has a **higher charge density (0.5)** and a **greater polarizing power** and it can **distort the electron cloud of the CO_3^{2-} to a greater extent (0.5 for either point)**, **weakening** the C−O **covalent bonds** in CO_3^{2-} to a **greater extent (0.5)**, hence **less energy is needed for decomposition (0.5).**

(b) **(i)** Type of reaction (reaction 1): Nucleophilic Addition **[1]**

Type of reaction (reaction 2): Elimination/Dehydration **[1]**

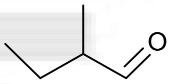
(ii)



[1]

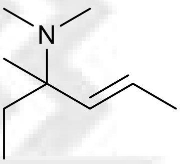
(iii) The geometry about the center C is **trigonal planar [1]**. Hence, there is **equal probability for the CN^- ion to attack from either side of the plane [1]**, giving rise to an equimolar mixture of two stereoisomers.

(iv)



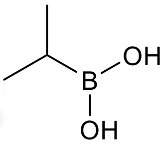
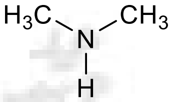
[1]

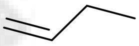
(c) **(i)**



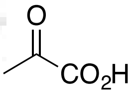
G **[1]**

(ii) Reagents and Conditions:
Step 1: $LiAlH_4$ in dry ether **[1]**
Step 2: excess concentrated H_2SO_4, heat **[1]**
Step 3: steam, concentrated H_3PO_4, high T high P **[1]**

Step 4:  ,  **[1]**

J:  **[1]**

2 **(a)** **(i)** $C_3H_4O_3$ **[1]**

(ii)  **[1]**

(b) constitutional/structural/functional group isomerism **[1]**

(c) The **LF** molecule is polar and can form strong/favourable permanent-dipole permanent-dipole interactions/hydrogen bonding/ion-dipole interactions with water molecules. **[1]**

(d) **(i)** When the onion is cooled, less **LF** will vaporise and come into contact with the eyes. **[1]**

(ii) Heating the onion can denature the enzyme *LF synthase* so that **LF** will not be formed. **[1]**

(e) **(i)** condensation **[1]**

(ii) $C_9H_{16}OS_3 + 17O_2 \rightarrow 9CO_2 + 8H_2O + 3SO_3$ **[1]**

(iii) n(cepaene) = $5 \times 10^{-3} / 236.3 = 2.116 \times 10^{-5}$ mol **[½]**
$n(O_2) = 2.116 \times 10^{-5} \times 17 = 3.597 \times 10^{-4} = 3.60 \times 10^{-4}$ mol **[½] ecf from ii**
volume of O_2 mixture at r.t.p. = $3.597 \times 10^{-4} \times 24000 = 8.63$ cm^3 **[½]**
volume of mixture = $8.63 \times 100/40 = 21.6$ cm^3 **[1]**

(iv) Role of copper: reducing agent **[1]**
$Cu + ½O_2 \rightarrow CuO$ **[1]**

(v) The blue crystals are $CuSO_4$ **[1]**, which can be formed from the reaction of CuO with SO_3. **[1]**

$CuO + SO_3 \rightarrow CuSO_4$

(vi) Order of gases released: CO_2, then SO_2, then water. **[1]**

CO_2 is a non-polar molecule, hence intermolecular forces are the weakest – only dispersion forces, so it is released first at a lower temperature. followed by SO_2.

SO_2 is a polar molecule with *both* intermolecular permanent-dipole permanent-dipole interactions, which are stronger than dispersion forces, *and* dispersion forces, which are also stronger than those of CO_2 due to SO_2 having more electrons and the larger electron cloud size than CO_2.

Water has intermolecular hydrogen bonding, which are the strongest intermolecular forces, and most energy required to vapourise it, and hence it is released last.

[1] correct types of intermolecular forces for all 3 molecules
[1] correct comparison of the strength of the 3 different intermolecular forces and relate to energy required to overcome the intermolecular forces for the gas to escape to the detector.

3 (a) Transition elements are **d-block elements** that **form one or more stable ions** with **partially filled d-subshell**. **[1]**

(b) (i) Precipitation occurs when I.P. = Ksp

For Cr^{3+}:
$Ksp = [Cr^{3+}][OH^-]^3$

$1.6 \times 10^{-20} = 1.23\times10^{-2}[OH^-]^3$
$[OH^-] = 1.09\times10^{-6}$ mol dm^{-3} **[1]**

For Co^{2+}:
$Ksp = [Co^{2+}][OH^-]^2$

$5.92 \times 10^{-15} = 5.77\times10^{-3}[OH^-]^2$
$[OH^-] = 1.01\times10^{-6}$ mol dm^{-3} **[1]**

Since the $[OH^-]$ required for IP = Ksp is similar for both precipitates to form, it does not allow for the separation of the two metal ions. **[1]**

(ii) **either**

$Cr(OH)_3$ is sparingly soluble and dissolves to give small concentrations of Cr^{3+} and OH^-.

$Cr(OH)_3 \ll Cr^{3+}(aq) + 3OH^-(aq)$ (1) **[1]**

When excess OH^- is added, complex formation takes place.
$Cr^{3+}(aq) + 6OH^-(aq) \ll [Cr(OH)_6]^{3-}$ **[1] (accept if $[Cr(OH)_4^-]$)**

The $[Cr^{3+}]$ falls shifting the position of equilibrium of (1) to the right, causing the precipitate to dissolve. **[1]**

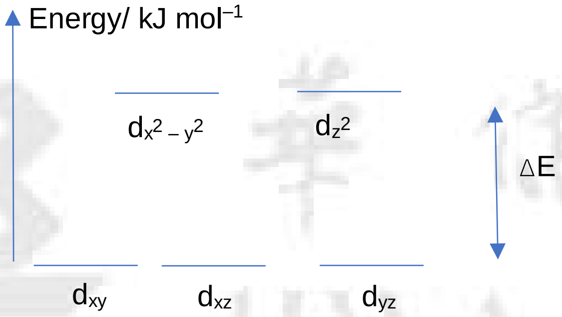
or

$[Cr(H_2O)_3(OH)_3]$ (s) + $3OH^-$ (aq) $\ll$ $[Cr(OH)_6]^{3-}$ +$3H_2O$ (*l*) **[2]**

([1] for $[Cr(H_2O)_3(OH)_3]$ and $[Cr(OH)_6]^{3-}$, [1] for balancing equation)

When the $[OH^-]$ increases, position of equilibrium shifts forward to offset the increase in the $[OH^-]$ concentration. This causes the solid to dissolve. **[1]**

(c) (i)



[1] (no need to show axes and ΔE)

The 5 *d* orbitals can be classified into two groups. The $d_{x^2-y^2}$ and d_{z^2} have their lobes along the axis, while the d_{xz}, d_{xy} and d_{yz} have lobes in between the axis. Since the ligands approach the central metal ion along the axis, **the repulsion felt by the d_{xz}, d_{xy} and d_{yz} orbitals is less than for the $d_{x^2-y^2}$ and d_{z^2} orbitals**. **[1]** As such the d_{xz}, d_{xy} and d_{yz} orbitals are at the lower energy.

(ii) When an electron is promoted from the lower energy d-orbitals, **energy is absorbed corresponding to a wavelength in the visible spectrum**. **[1]**

The colour observed is the **complement** of the colours absorbed. **[1]**

(iii) **Ligand exchange** reaction. **[1]**

(iv) Identify the 1:4 ratio for Co^{2+}: SCN^- **[1]**

$[Co(SCN)_4]^{2-}$ **[1]**

(d) (i) The **energy levels of 3d and 4s electrons in cobalt are similar**, hence once the 4s electrons are removed, some or all of the 3d electrons may also be removed without requiring much more energy. **[1]**

However in calcium, once the 4s electrons are removed, the subsequent removal of electrons must come **from an inner quantum shell which requires too much energy**. **[1]**

(ii) $[Co(NH_3)_6]^{3+} + e \ll [Co(NH_3)_6]^{2+}$ E = +0.17 V

$O_2 + 2H_2O + 4e \ll 4OH^-$ E = +0.40 V

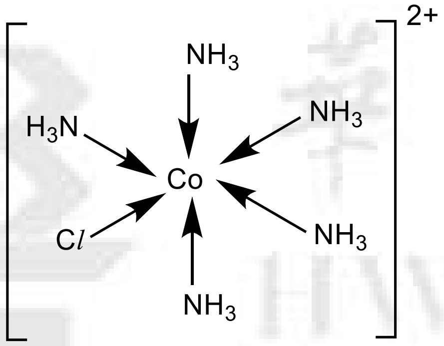
E_{cell} = +0.40 – (+0.17) = +0.23V **[1]**

(e) **(i)** AgC*l* **[1]**

The number of moles of **free** C*l*⁻ ions/ C*l*⁻ **counter ions** are different in both the complexes. **[1]**

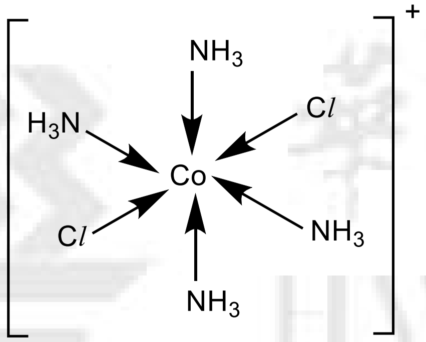
S has one C*l*⁻ ion datively bonded to the Co^{3+} while **T** has two C*l*⁻ ion datively bonded to the Co^{3+} central metal ion.

(ii) **complex from S**



[1] (mark for dative bonds and positive charge)

(iii) **complex from T**



[1] (as long as *trans* structure is shown, ignore dative bonds/charges etc.)

(f) Reactant molecules, CO and H_2O are **adsorbed onto the active sites** of the catalyst surface by formation of weak attractive forces.

This brings the **molecules closer together, weakens the C˜O and O–H bond**, **orientating them in the right position for reaction**, hence lowering the activation energy. (**[2]** for all 3 points, **[1]** for any 2 points)

Once the reaction has taken place, the aldehyde formed **desorbs and diffuses away** from the catalyst surface so that the **active sites are exposed** for further reaction.

[1] adsorb and desorb + active sites

4 **(a)** **(i)** Zn(−): $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$ **[1]**
Pt(+): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **[1]**
[1] on polarity

(ii) $\Delta G = -nFE^\ominus_{cell}$

$-637 \times 1000 = -(4)(96500)E_{cell}$

$E^\ominus_{cell} = 1.65$ V **[1]**

$E_{cell} = E_{O2/OH^-} - E_{Zn(OH)2/Zn}$

$+1.65 = 0.40 - E_{Zn(OH)2/Zn}$

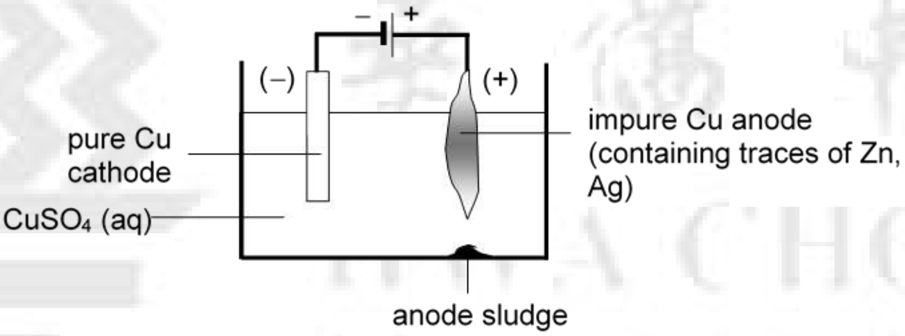
$E_{Zn(OH)2/Zn} = -1.25$ V **[1] ecf**

(iii) Amount of Zn = $\frac{5}{65.4}$ = 0.0765 mol **[0.5]**
Amount of electrons = 2 × 0.0765 = 0.153 mol **[0.5]**
Since charge on 1 mol of electron = 96500 C
∴ charge = 0.153 × 96500 = 14755 C

$t = \frac{Q}{I} = \frac{14755}{0.8\times10^{-3}}$ **[1] substitution, ecf**

$= 1.84 \times 10^7$ s
= 213 days **[1] ecf; conversion to exact days**

(b)



[1] deduct 0.5 for every mistake

$E^\ominus_{Zn2+/Zn} = -0.76$ V
$E^\ominus_{Cu2+/Cu} = +0.34$ V
$E^\ominus_{Ag+/Ag} = +0.80$ V **(0.5 for these 3 values correctly quoted)**

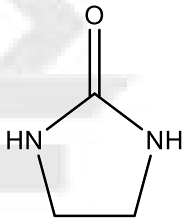
At the anode, Zn is oxidised to Zn^{2+} (can be described in equation form) as $E^\ominus_{Zn2+/Zn}$ is more negative than $E^\ominus_{Cu2+/Cu}$ and dissolves into the electrolyte. **[0.5]**

Ag will not be oxidised as $E^\ominus_{Ag+/Ag}$ is more positive than $E^\ominus_{Cu2+/Cu}$, **[0.5]** hence Ag drops off as anode sludge. **[0.5] can be drawn in diagram**

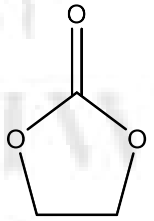
At the cathode, only Cu^{2+} is reduced as $E^\ominus_{Cu2+/Cu}$ is more positive than $E^\ominus_{Zn2+/Zn}$. **[0.5]** Hence Cu is collected, whereas Zn^{2+} is not reduced/remains in solution. **[0.5]**

(c) **(i)**

X:



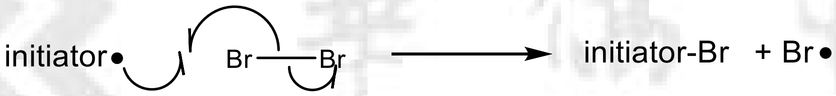
Y:



[1] each; deduct 1m if X and Y are swapped

(ii) CO_3^{2-} or HCO_3^- **[1]**
$HOCH_2CH_2NH_2$ **[1]**

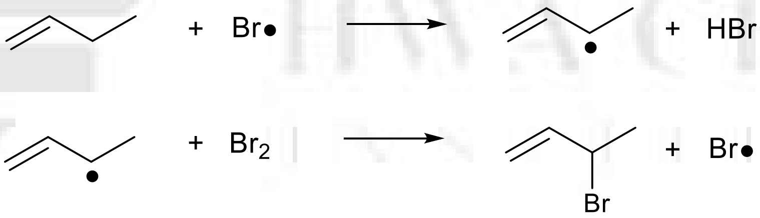
(d) **(i)**



[1]

[1/2] if only the arrows of the homolytic fission is shown

(ii)



[1] per step

(iii) If liquid bromine were added, the high concentration of Br_2 will result in electrophilic addition across the C=C bond. **[1]**

5 **(a)** First ionisation energy (I.E.) generally increase across Period 3. **[½]**
Across the period, nuclear charge (or number of protons) increases but shielding effect remains relatively constant so effective nuclear charge increase and the outermost electrons are more strongly attracted to the nucleus. **[½]**

The 1st I.E. of Al, $[Ne]3s^2 3p^1$, is lower than that of Mg, $[Ne]3s^2$. **[½]**
The electron is removed from the 3p subshell in Al, which is further away from the nucleus compared to the 3s subshell in Mg. **[½]**

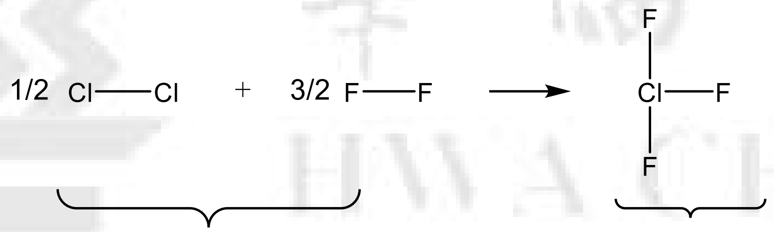
The 1st I.E. of S, $[Ne]3s^2 3p^4$, is lower than that of P, $[Ne]3s^2 3p^3$. **[½]**
The inter-electronic repulsion between the paired 3p electrons in S is absent in P as the 3p electrons are unpaired. **[½]**

(b) **(i)** Oxidation number of chlorine in ClF_3 is +3; in Cl_2 is 0 **[½, ½]**
$ClF_3 + Cl_2 \rightarrow 3ClF$ **[1]** no ecf

(ii) ClF_3 is (energetically) more stable than its constituent elements (Cl_2 and F_2).**[1]**

Accept:
The decomposition of ClF_3 into its elements is not feasible.
The formation of ClF_3 from its elements is feasible.

(iii)



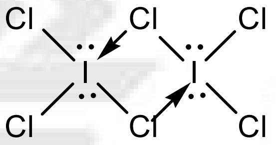
bonds broken = 1/2 × 244 + 3/2 × 158   bonds formed = 3 × BE(C*l*–F)

–163 = 1/2 × 244 + 3/2 × 158 – **3** × BE(C*l*–F)

BE(C*l*–F) = 522 ÷ 3 = **174 kJ mol⁻¹**

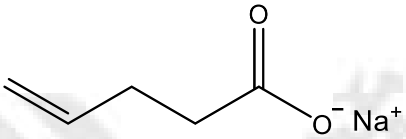
Correct BE(C*l*–C*l*), BE(F–F) and three C*l*–F bonds in one C*l*F_3 molecule **[1]**
Correct BE(C*l*–F) with units (no negative sign) **[1]**

(iv)



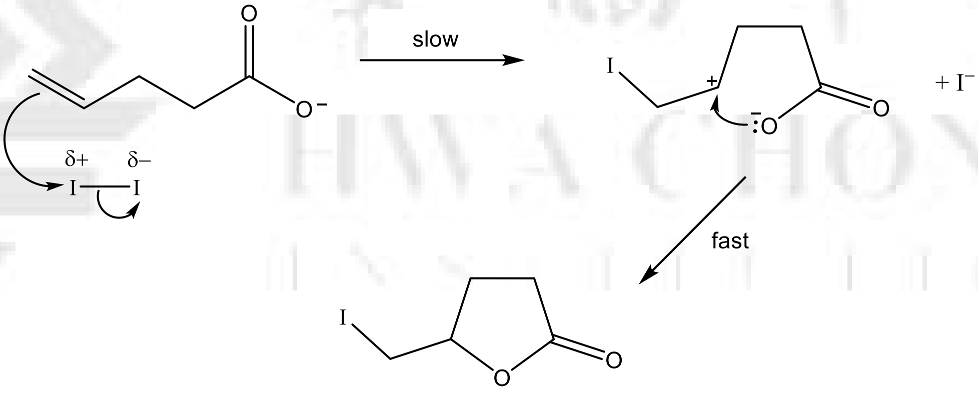
correct shape and lone pairs **[1]**
correct dative bonds (from C*l* to I) **[1]**

(c) **(i)**



[1]

(ii)



Partial charges on I–I, positive charge on carbocation, lone pair on O atom, 3 curly arrows, first step is slow step **[2]**

–½ mark for each mistake

(d)

1 mol **B** undergoes <u>oxidative cleavage</u> to give only 4 mol CO_2 ⇒ **B** contains <u>4 C atoms</u> and one <u>C=C bond</u>
1 mol **B** undergoes <u>neutralisation</u> with 2 mol NaOH ⇒ **B** contains <u>two $–CO_2H$</u>
B exhibits stereoisomerism ⇒ **B** exhibits <u>cis-trans isomerism</u>

5-6 correct **[2]**
any 4 **[1.5]**

any 3 **[1]**
any 2 **[½]**

B is  (not required to show cis or trans arrangement) **[1]**

(e) **(i)** dilute HC*l*, heat
(accept NaOH(aq), heat followed by dilute aqueous acid e.g. HC*l*) **[1]**

(ii) ΔH would be <u>similar</u> (or the same) as the <u>same bonds are broken and formed</u>. **[1]**

(iii) Reaction 1 has a <u>more negative / less positive ΔG</u> (from $\Delta G = \Delta H - T\Delta S$). **[1]**
ecf from **(e)(ii)**

Hence, <u>K_1 is larger</u> than K_2 (from $\Delta G = -RT\ln K$). **[1]**
ecf from ΔG

HWA CHONG INSTITUTION
2019 C2 H2 CHEMISTRY PRELIMINARY EXAM
SUGGESTED SOLUTIONS

Paper 4

1 (a) (i)

- Tabulates volumes and temperature data in **(a)(i)**
  Table should contain correct headers and units. Data headers to include volume of **FA 1,** volume of **FA 2**, T_{FA1}, T_{max} and ΔT. **[1]**

Volume of **FA 1** / cm^3	Volume of **FA 2** / cm^3	$T_{FA\,1}$ / °C	T_{max} / °C	ΔT / °C
10.0	40.0	32.0	36.0	4.0
20.0	30.0	32.0	39.5	7.5
25.0	25.0	32.0	41.5	9.5
30.0	20.0	32.0	41.0	9.0
35.0	15.0	32.0	38.5	6.5
40.0	10.0	32.0	36.0	4.0

- Complete 6 sets of volume/temperature readings in **(a)(i)**
  Required volumes: Volume of **FA 1** = 10.0 cm^3, 20.0 cm^3, 25.0 cm^3, 30.0 cm^3, 35.0 cm^3 and 40.0 cm^3
  and
  use appropriate volume of **FA 2** such that the total volume of reacting mixture in each set of data is 50 cm^3 **[1]**

- Records all temperature data in **(a)(i)** to 0.5°C,
  all volumes for **FA 1** and **FA 2** in **(a)(i)** to 1 d.p. **[1]**

- Correctly calculates all ΔT values to 1 d.p. in **(a)(i)** **[1]**

(a) (ii)

- Axes correct way round **and** correct labels **and** units **and** scale **[1]**
  Note: Scale chosen must allow for the lines to be extrapolated to cross each other. The plotted points should occupy at least half the grid in both directions.

- All points are correctly plotted to within ± ½ small square. **[1]**
- All drawn graph lines are <u>straight</u> best-fit lines and are extrapolated to cross each other.
  and
  there are at least three points on each side of the graphically determined ΔT_{max}
  [1]

(a) **(iii)** $\Delta T_{\max}$ and $V_{\max}$ are read correctly to ± ½ small square from graph

From the sample graph, $\Delta T_{\max} = 10.4\ °C$ $V_{\max} = V(H_2SO_4) = 27.25\ cm^3$

[1]

(b) **(i)** $H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$

$V(NaOH) = 50.0 - 27.25 = 22.75\ cm^3$
$n(NaOH) = 1.50 \times (22.75/1000) = 0.03413\ mol$

$n(H_2SO_4) = 0.03413 / 2 = 0.01706\ mol$
$[H_2SO_4] = 0.01706 / (27.25/1000) = 0.626\ mol\ dm^{-3}$ **[1]**

(ii) Heat change = $m_{solution}c\Delta T_{\max} = 50.0 \times 4.18 \times 10.4 = 2174\ J$ **[1]**

(c) $n(H_2O) = n(NaOH) = 0.03413\ mol$
$\Delta H_{neut} = -2174 / 0.03413 = -6.37 \times 10^4\ J\ mol^{-1} = -63.7\ kJ\ mol^{-1}$ (Sign must be negative) **[1]**

(d) ΔH_{neut} would be less exothermic as malonic acid is a weak acid. Energy is absorbed to ionise the un-ionised weak acid. **[1]**

(e) Suggested sources of errors **and** its appropriate improvements: **[1]**

heat loss to the surrounding **and** use a cup lid to minimise heat exchange with the surrounding air

$V_{FA\,1}$ and $V_{FA\,2}$ is to 1 d.p. as measured using less precise measuring cylinders **and** can be measured using more precise burettes to give 2 d.p.

initial temperature of **FA 2** was not accounted for **and** weighted initial temperature should be calculated where

$$T_{\text{weighted initial}} = \frac{(\text{Volume of FA 1} \times T_{FA1}) + (\text{Volume of FA 2} \times T_{FA2})}{\text{Volume of FA 1} + \text{Volume of FA 2}}$$

heat capacity of the calorimeter (Styrofoam cup) was not accounted for **and** heat absorbed by the styrofoam cup can be included in the calculation of heat change

2 **(a)**

Mass of weighing bottle and **FA 3** / g	
Mass of weighing bottle and residual **FA 3** / g	
Mass of **FA 3** used / g	

Tables have correct **headers and units** (*included in the header or with each entry in the table*) **[1]**

(b) Effervescence observed. **[0.5]**
and
Yellow / greenish yellow / yellow green solution turned colourless / very pale green. **[0.5]**

(c) (i)

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 4** used / cm^3	

- Tables have correct headers and units (included in the header or with each entry in the table) **[1]**
  Note: Mark is lost if any final and initial burette readings are inverted or 50 is used as the initial burette reading.

- All mass reading in **(a)** are recorded to the nearest **0.01 g** and burette readings & volume used for all accurate titres in the titration table are recorded to the nearest **0.05 cm^3**. **[1]**

- At least two uncorrected titres for end-point within ±0.10 cm^3. **[1]**

(c) (ii)

- Student obtains average titre, to **2 d.p.**, from any experiments with end-point titre values within 0.10 cm^3 **[1]**

Mark is lost if there are arithmetic errors in the table.
Mark is lost if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.

- Accuracy

  Supervisor's $V_{FA\ 4} / m_{FA\ 3} = 1.530$
  Difference between student's and supervisor's $V_{FA\ 4} / m_{FA\ 3}$
  If difference is $\leq$ **0.045 $cm^3\ g^{-1}$** **[2]**
  If difference is **> 0.045** but $\leq$ **0.075 $cm^3\ g^{-1}$** **[1]**
  For a difference **> 0.075** **[0]**

(d) (i) If $V_{FA\ 4} = 10.10\ cm^3$

$\eta(Fe^{2+}) = 10.10 \times 10^{-3} \times 0.020 \times 5 = 1.01 \times 10^{-3}$ mol (3 s.f) **[1]**

(d) (ii) $\eta(Fe^{3+}) = 1.01 \times 10^{-3} \times 250 / 10.0 = 0.0253$ mol (3 s.f) **[1]**

(d) (iii) $m_{\mathbf{FA\ 3}} = 6.60$ g

Mole ratio of $Fe_2(SO_4)_3.nH_2O : Fe^{3+} = 1 : 2$

Number of moles of $Fe_2(SO_4)_3.nH_2O = 0.0253 \div 2 = 0.01265$ mol

M_r of $Fe_2(SO_4)_3.nH_2O = 6.60 / 0.01265 = 521.7$ **[1]**

$n = \{521.7 - [2(55.8) + 3(32.1) + 12(16.0)]\} \div 18.0$
$= 7$ (nearest whole number) **[1]**

- Shows working in **1(b)(i)**, **1(b)(ii)**, **1(c)**, **2(d)(i)**, **2(d)(ii)** and **2(d)(iii)**. All calculations must be relevant although they may not be complete or correct. ***Any calculation not attempted loses this mark.*** **[1]**

- Shows appropriate significant figures (3 or 4 sf) in all final answers (in the blank) in **1(b)(i)**, **1(b)(ii)**, **1(c)**, **2(d)(i)** and **2(d)(ii)**. For **2(d)(iii)**, M_r can be given to 1 d.p. or 3 s.f. but *n* should be given as a whole number. ***Any calculation not attempted loses this mark.*** **[1]**

- Shows appropriate units in all final answers (in the blank) in **1(a)(iii)** (°C, cm^3), **1(b)(i)** (mol dm^{-3}), **1(b)(ii)** (J or kJ), **1(c)** (J mol^{-1} or kJ mol^{-1}), **2(c)(ii)** (cm^3), **2(d)(i)** (mol), **2(d)(ii)** (mol). Units should not be given for M_r or *n* in **2(d)(iii)**. ***Any calculation not attempted loses this mark.*** **[1]**

(e) Effervescence was observed as zinc reacted with acid to form H_2 gas. **[0.5]**

Yellow solution turned colourless / very pale green as Fe^{3+} was reduced to Fe^{2+}. **[0.5]**

(f) Zinc metal that is not removed will continue to reduce Fe^{3+} formed during the titration to Fe^{2+}, resulting in a higher than expected titre. **[1]**

3 (a) $K_c = \dfrac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$ **[1]**

(b) no. of moles of $FeSCN^{2+}$ formed $\approx$ no. of moles of SCN^- added

$= 2.00 \times 10^{-3} \times (5/1000) = 1.00 \times 10^{-5}$ mol

$[FeSCN^{2+}] = (1.00 \times 10^{-5})/(10/1000) = 1.00 \times 10^{-3}$ mol dm^{-3} **[1]**

Large excess of Fe^{3+} is used to drive the equilibrium **almost completely** to the right. **[1]**
Hence, the amount of $FeSCN^{2+}$ produced will be essentially equal to the amount of SCN^- added.

(c) **Procedure** (sample answer)

1. Using separate burettes, transfer 5.00 cm^3 of $Fe(NO_3)_3$ and 5.00 cm^3 of KSCN into a boiling tube. Stopper and shake to ensure a homogeneous solution.
2. Rinse and fill a cuvette with 3 cm^3 of the mixture.
3. Place the cuvette in a thermostatically controlled water bath maintained at 50 °C for about 5 min.
4. Measure and record the temperature of the solution using a thermometer.

5. Remove the cuvette from the water bath, and immediately measure and record the absorbance (at wavelength of blue light 447 nm) using a spectrophotometer.
6. Repeat steps 3 – 5 at 40 °C, 30 °C, 20 °C and 10 °C.
   or
   Repeat steps 2 – 5 (total volume must then be at least 5×3=15 cm^3) at 40 °C, 30 °C, 20 °C and 10 °C.

M1 – Logical sequence [1] (minus ½ mark for each missing point)

- Mixing known volumes of $Fe(NO_3)_3$ and KSCN, amount of Fe^{3+} not more than 10 times of $SCN^–$, total volume > 3 cm^3
- Measure (and record) the temperature of the mixture
- Measure (and record) the absorbance of the mixture

M2 – Apparatus [1] (½ mark for each point)

- separate burettes for $Fe(NO_3)_3$ and KSCN (or other precise apparatus e.g. micropipette or pipette)
- thermostatically controlled water bath

M3 – Essential details [1] (½ mark for each point)

- Shake boiling tube / test-tube/ swirl conical flask (with stopper) or stir beaker (with glass rod)
- Allow time for the mixture to equilibrate in the water bath (e.g. 5 - 10 min) **and** measure absorbance immediately

M4 – Choice of temperatures [1] (½ mark for each point)

- at least 5 different temperatures
- with at least 5 °C difference, 0 ºC < T < 100 ºC

M5 and M6 – Treatment of results [2] (½ mark for each point)

- use calibration line to determine $[FeSCN^{2+}]$ (accept if show how on calibration line)
- correct $[Fe^{3+}]_{initial}$ and $[SCN^–]_{initial}$
- correct $[Fe^{3+}]_{eqm}$ and $[SCN^–]_{eqm}$; ecf from initial conc
- correct expression for K_c in terms of $[FeSCN^{2+}]_{eqm}$; ecf from eqm conc

Sample answer:

For each absorbance obtained, read off the calibration line to determine the corresponding $[FeSCN^{2+}]$ at each temperature.

	Fe^{3+}	+	$SCN^–$	⇌	$FeSCN^{2+}$
initial / mol $dm^{–3}$	$\frac{2\times10^{-3}\times5}{10}$ $= 1.00 \times 10^{–3}$		$\frac{2\times10^{-3}\times5}{10}$ $= 1.00 \times 10^{–3}$		0
change / mol $dm^{–3}$	– x		– x		+ x
eqm / mol $dm^{–3}$	0.001 – x		0.001 – x		$[FeSCN^{2+}]$ = x

$K_c = \frac{x}{(0.001-x)^2}$

(d) (i)

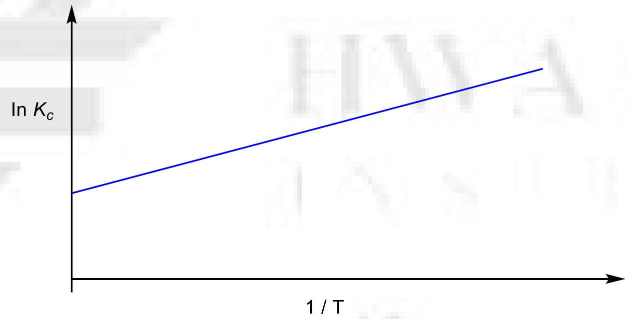


Fig. 3.1 **[1]**

Compare the equation given to y = mx + c, gradient = −Δ*H* / *R*.
As Δ*H* < 0 and *R* > 0, gradient is positive **[1]**

Accept correct explanation using LCP.
Mark for explanation may be lost if graph is incorrect.

(d) (ii) gradient = Δy / Δx = −Δ*H* / *R*
Hence, Δ*H* = − gradient × *R* = − gradient × 8.31 **[1]**

y-intercept = Δ*S* / *R*
Hence, Δ*S* = y-intercept × *R* = y-intercept × 8.31 **[1]**

Correct expressions for Δ*H* and Δ*S* (i.e. both must be the subject). Accept correct descriptions instead of expressions.

4 (a)

1. Black/dark brown/grey residue obtained.
2. Brown/orange/yellow filtrate obtained.
3. Off-white/light brown/yellow/orange ppt formed insoluble in excess NaOH(aq). (REJECT: brown ppt).
4. Off-white ppt which turned brown/darkened on standing (must appear at least once either with NaOH(aq) or NH_3(aq)).
5. Off-white/light brown/yellow/orange ppt formed insoluble in excess NH_3(aq) (insoluble must appear at least once in point 3 or 5).

(c)

6. Effervescence observed (REJECT: gas evolved).
7. Gas relit glowing splint.

(f)

8. Solution turned green
9. Then darker green.
10. Dark blue/dark green/blue-green residue obtained.
11. Colourless filtrate.

(g)

12. Purple/Pink filtrate obtained.
13. Residue turned brown/black/grey (must show a change in colour from point 10)

Observation points
11 – 13 = 6 marks
9 – 10 = 5 marks
7 – 8 = 4 marks
5 – 6 = 3 marks
3 – 4 = 2 marks
1 – 2 = 1 mark
0 = 0 mark **[6]**

(b) Oxidising agent **[1]**
Evidence 1: Since a brown/orange/yellow solution is formed that decolourises with $S_2O_3^{2-}$, I^- was oxidised to I_2. **[½]**
Evidence 2: MnO_2 was reduced to Mn^{2+}, as seen by the off-white/light brown ppt formed with NaOH(aq) that darkened on standing. **[½]**

(d) Since there was no ppt with NaOH(aq), MnO_2 was not reduced to Mn^{2+} or an off-white ppt will be formed, hence it is not acting as an oxidising agent. **[1]**

(e) Heterogeneous catalyst **[½]**
Since there was brisk effervescence, it indicates that rate of decomposition of H_2O_2 is faster. **[½]**

(h) **X**: MnO_2 **[½]**
Y: MnO_4^- **[½]** (no credit if colour of filtrate is not correct)

(i) $BaSO_4$. **[1]**

NAME ______________________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY
9729/01

Higher 2
26 September 2019

Paper 1 Multiple Choice
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 **12** printed pages.

1 In which of the following pairs do the molecules have similar shapes?

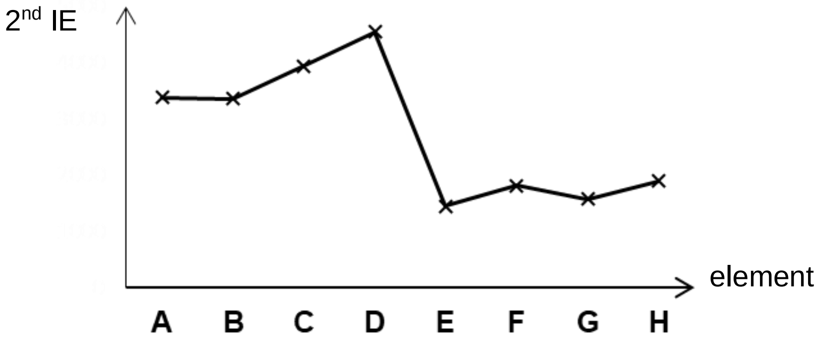
A CO_2 and SO_2

B BF_3 and NH_3

C H_2O and ClO_2^-

D NO_2^+ and ClO_2

2 **A** to **H** are consecutive elements with atomic numbers less than 20. The graph below shows their second ionisation energies (2nd IE).



Which of the following statements is **incorrect**?

A Element **E** is from Group 2.

B **H** exists as tetratomic molecules.

C The compound formed between **A** and **G** is a gas at room temperature.

D The 2nd IE of **B** is lower than that of **A** due to inter–electronic repulsion between its paired p electrons.

3 After an oil spillage at sea, a liquid hydrocarbon layer floats on the surface of the water.

Which statements help to explain this observation?

1 Hydrocarbon molecules are not solvated by water.

2 There are only instantaneous dipole–induced dipole interactions between hydrocarbon molecules.

3 Hydrogen bonding between water molecules causes water molecules to be packed closely together.

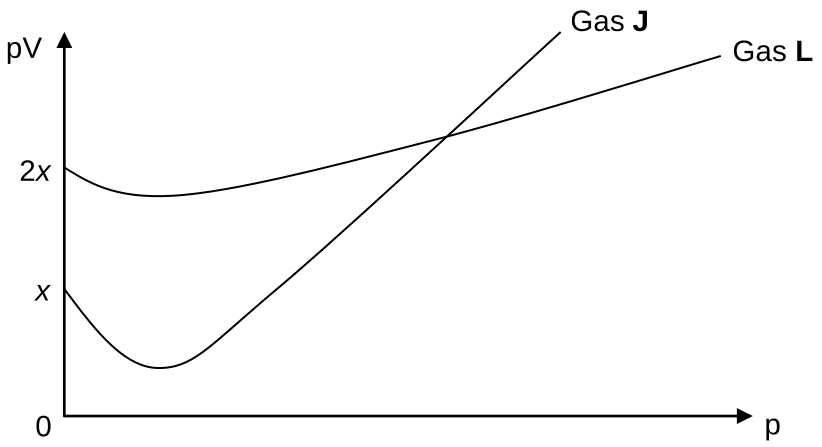
A 2 only

B 1 and 2 only

C 2 and 3 only

D 1, 2 and 3

4 The value of pV is plotted against p for two gases, **J** and **L**, where p is the pressure and V is the volume of the gas.



Which of the following could be the identities of the gases?

	Gas **J**	Gas **L**
1	0.5 mol of H_2O at 25 °C	0.5 mol of H_2 at 50 °C
2	0.5 mol of NH_3 at 25 °C	1 mol of CH_4 at 25 °C
3	0.25 mol of SO_2 at 25 °C	0.5 mol of H_2 at 25 °C

A 2 only

B 3 only

C 2 and 3 only

D 1, 2 and 3

5 *Use of the Data Booklet is relevant to this question.*

Which statement about 28.0 g of nitrogen gas is correct?

A It contains the same number of atoms as one mole of neon gas.

B It contains the same number of molecules as 71.0 g of chlorine gas.

C It has the same mass as one mole of carbon dioxide gas.

D The gas occupies a volume of 24 dm^3 at standard temperature and pressure.

6 *Use of the Data Booklet is relevant to this question.*

An element **M** can exist in a few oxidation states.

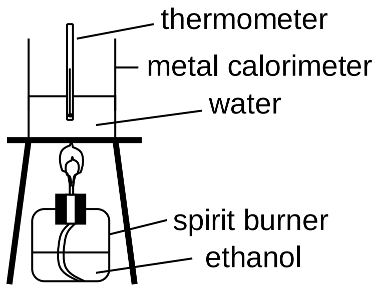
15.00 cm^3 of an aqueous solution of 0.100 mol dm^{-3} of M^{n+} required 20.00 cm^3 of 0.0250 mol dm^{-3} of acidifed $K_2Cr_2O_7$ solution for a complete reaction.

What is the change in oxidation state of **M**?

A 2 **B** 3 **C** 4 **D** 5

7 *Use of the Data Booklet is relevant to this question.*

A student carried out an experiment under laboratory conditions and the following results were obtained.



initial temperature of the water	28.0 °C
final temperature of the water	50.4 °C
mass of ethanol burner before burning	259.400 g
mass of ethanol burner after burning	259.286 g
mass of water used	30.000 g

Given that the enthalpy change of combustion of ethanol is –1367 kJ mol^{-1}, what is the efficiency of heat transfer in the above experiment?

A 60.7% **B** 81.1% **C** 82.9% **D** 83.2%

8 Hydrogen can be made from steam as shown.

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

The Gibbs free energy change of the reaction is +78 kJ mol^{-1} at 378K.

Which statement about the reaction is not correct?

A The entropy change is positive.

B The products are energetically less stable than the reactants

C The E_{cell} value of the reaction is positive.

D The reverse reaction is spontaneous.

9 The table below gives data for the reaction between **N** and **Q** at constant temperature.

Experiment	[**N**] / mol dm^{-3}	[**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.003	0.2	4.0×10^{-4}
2	0.006	0.4	1.6×10^{-3}
3	0.006	0.8	6.4×10^{-3}

Which statement about the reaction is not correct?

A The reaction is elementary.

B The rate constant k has the units of mol^{-1} dm^{3} min^{-1}.

C The half–life of **N** is not constant.

D The order of reaction with respect to [**Q**] is 2.

10 Poly(tetrafluoroethene) is a polymer used as a coating in non–stick kitchen utensils and for replacement of bone joints. One of the stages in the manufacture of the polymer is

$$2CHClF_2(g) \rightleftharpoons C_2F_4(g) + 2HCl(g) \qquad \Delta H_c = +128 \text{ kJ mol}^{-1}$$

Which statement correctly describes the effect of the change applied?

A The equilibrium position will shift to the left when the reaction vessel is expanded.

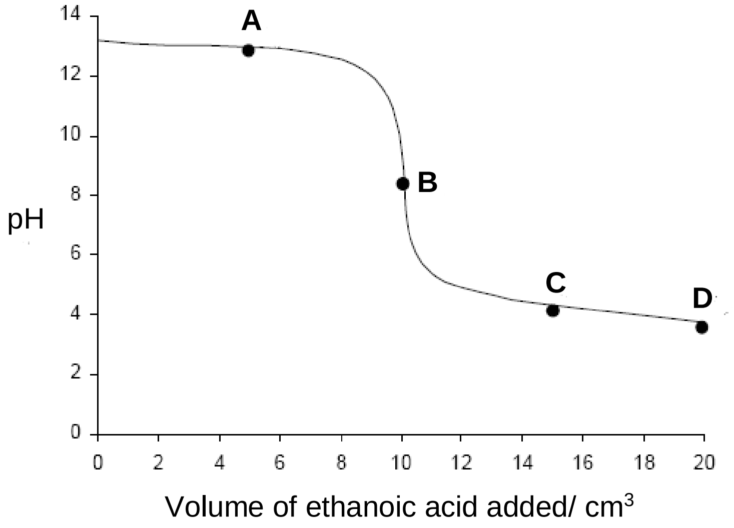
B The equilibrium concentration of $CHClF_2$ decreases when the reaction vessel is cooled.

C The addition of a catalyst will increase the equilibrium concentration of C_2F_4.

D The equilibrium constant, K_c, increases when the reaction vessel is heated.

11 The diagram below shows the change of pH produced by gradually adding 0.100 mol dm^{-3} aqueous ethanoic acid to 10.0 cm^3 of 0.100 mol dm^{-3} aqueous sodium hydroxide.

At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of ethanoic acid?



12 The following tests were performed on an aqueous solution to identify the unknown ions it contains.

Step	Test	Observations
1	Add $AgNO_3$(aq) followed by excess dilute NH_3(aq). Swirl and filter the mixture.	Yellow residue and colourless filtrate obtained.
2	Add Cl_2(aq) to filtrate.	Orange solution formed.

Which statements are correct?

1 I^- ion is present in the mixture as the yellow AgI residue was obtained due to the low K_{sp} of AgI.

2 Br^- ion is present in the mixture as it undergoes disproportionation reaction with Cl_2(aq).

3 Br^- ion and $[Ag(NH_3)_2]^+$ ion are present in the filtrate.

A 1, 2 and 3

B 1 and 3 only

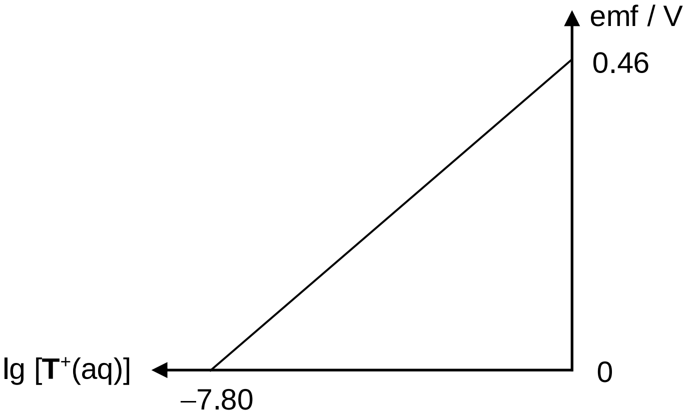
C 2 and 3 only

D 1 only

13 *Use of the Data Booklet is relevant to this question.*

The graph below shows the variation in electromotive force (emf) of the following electrochemical cell with lg [**T**$^+$(aq)] at 298 K.

Cu(s) | Cu^{2+}(aq, 1 mol dm^{-3}) || **T**$^+$(aq) | **T**(s)



Which statement is not correct?

A **T**(s) is the positive electrode.

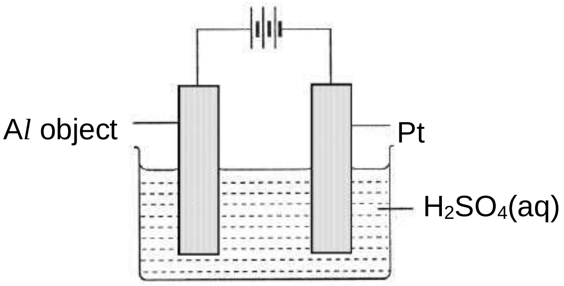
B The direction of electron flow in the external circuit will be reversed when the concentration of **T**$^+$(aq) is 1.00×10^{-5} mol dm^{-3}.

C The emf of the given cell under standard conditions will be +0.46 V.

D The standard electrode potential of the **T**$^+$(aq) | **T**(s) half–cell is +0.80 V.

14 *Use of the Data Booklet is relevant to this question.*

A piece of aluminium object was placed in dilute sulfuric acid and anodised with a direct current of 1.5 A. After *t* minutes, the mass of the oxide layer formed is 3.7 g.



What is the time taken, *t*, for this anodisation process?

A 38.9 **B** 58.3 **C** 117 **D** 233

15 Consider the following sequence of compounds:

NaF MgO A*l*N SiC

What conclusions can be drawn about this sequence of compounds from left to right?

1 The electronegativity difference between the elements in each compound increases.
2 These compounds are isoelectronic.
3 The bonding becomes increasingly covalent.

A 1 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

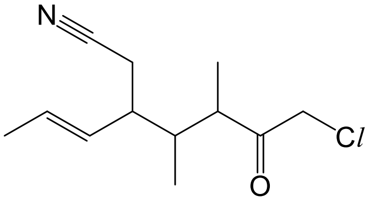
16 A student carried out two experiments involving copper(II) sulfate.

Experiment 1: Addition of aqueous ammonia causes a pale blue precipitate to form which dissolves in excess ammonia to give a deep-blue solution.
Experiment 2: Addition of aqueous potassium iodide produces a white precipitate and a brown solution.

What can be deduced from the experiments?

A The pale blue precipitate dissolves in excess ammonia due to the formation of a complex ion in experiment 1.
B There is a redox reaction occurring in experiment 1.
C The white precipitate formed in experiment 2 is CuI_2.
D The brown solution in experiment 2 decolourises upon addition of sodium thiosulfate due to a ligand exchange reaction.

17 Which of the following options about the structure below is correct?



	Number of *sp* hybridised C	Number of sp^2 hybridised C	Number of sp^3 hybridised C
A	1	3	8
B	1	3	6
C	0	4	8
D	0	4	6

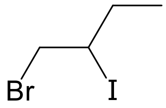
18 3–methylpentane can undergo reaction with chlorine to form monosubstituted compounds that are optically active.

How many possible stereoisomers can be formed in the reaction?

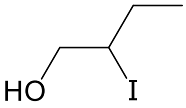
A 4 **B** 5 **C** 6 **D** 8

19 Which of the following is not the product formed when but–1–ene reacts with IBr(aq)?

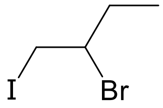
A



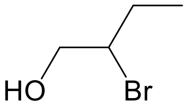
B



C



D



20 Fly paper is used as a non–toxic method of trapping houseflies. To increase its effectiveness and attractiveness, Muscalure, which is a fly sex pheromone, is added to the paper during its manufacture. Mascalure has the following structure:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3$$

Which of the following statements about Muscalure is not correct?

A In the presence of excess bromine and UV light, it undergoes free radical substitution.

B It exists as a pair of cis–trans isomers.

C It gives a diol with cold dilute acidified potassium dichromate(VI).

D It can be extracted from the fly paper by soaking the paper in benzene.

21 In which of the following reactions do benzene and methylbenzene behave differently?

1 Reacting with hot aqueous alkaline potassium manganate(VII)
2 Reacting with bromine in the presence of an iron catalyst
3 Reacting with bromine in the presence of light

A 1 only
B 1 and 2 only
C 1 and 3 only
D 2 and 3 only

22 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 of the following compounds will result in precipitate formation only after 8 minutes?

A iodoethane
B ethanoyl bromide
C bromobenzene
D chloroethane

23 *Use of the Data Booklet is relevant to this question.*

Which of the following statements are likely to be true for the reaction:

$$(CH_3)_3SiCl + C_2H_5O^- \rightarrow (CH_3)_3SiOC_2H_5 + Cl^-$$

1 It is likely to undergo a S_N1 mechanism.
2 $C_2H_5O^-$ plays the role of the nucleophile.
3 Reaction proceeds faster if $(CH_3)_3CCl$ is used instead.

A 1, 2 and 3
B 1 and 3 only
C 2 and 3 only
D 1 only

24 Geraniol is found in rose oil and is used for the preparation of artificial scents.

Upon controlled oxidation, geraniol yields CH_3COCH_3, $CH_3COCH_2CH_2COOH$ and $(CO_2H)_2$.

A possible structure of geraniol is:

A $CH_3CH{=}C(CH_3)CH_2CH_2C(CH_3){=}CHCH_2OH$

B $(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OH$

C $(CH_3)_2C{=}C(CH_3)CH_2C(CH_3){=}CHCH_2OH$

D $(CH_3)_2C{=}CHCH_2CH_2C(CH_2OH){=}CHCH_3$

25 The table below shows the relative rates of reaction for the addition of hydrogen cyanide to ketones under different conditions.

condition	*relative rate*
In water	slow
With small amount of acid	virtually zero
With small amount of base	very rapid

Which of the following statement can explain the above observations?

A H_2O is involved in the rate–determining step.

B The small amount of base added acts as a catalyst.

C Reaction in water is slow due to the low concentration of CN^-.

D H^+ is not a nucleophile.

26 Which of the following compounds react with both $NaBH_4$ and Tollens' reagent?

A Both aldehydes and ketones

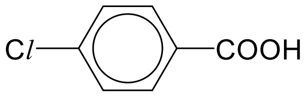
B Aldehydes only

C Ketones only

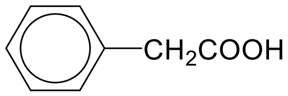
D Neither aldehydes nor ketones

27 Which of the following compounds has the lowest pK_a value?

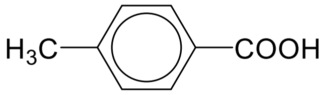
A



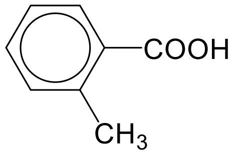
B



C



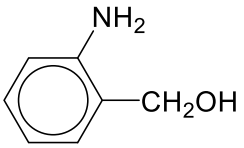
D



28 A compound **U** releases carbon dioxide from aqueous sodium hydrogencarbonate, and it readily decolourises aqueous bromine.

Which of the following could be **U**?

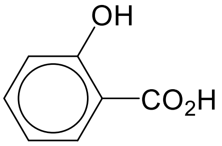
A



B $HOCH_2CO_2H$

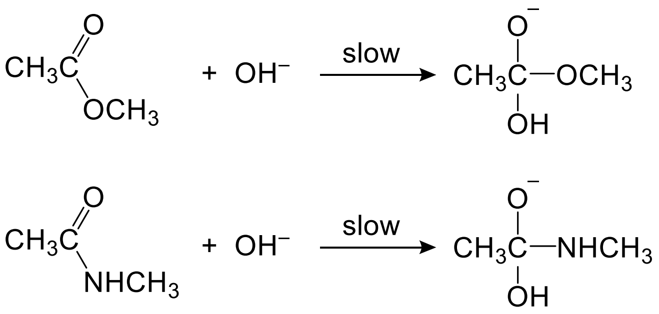
C $CH_2{=}CHCH_2CO_2Na$

D



29 1 mol of an ester ($CH_3CO_2CH_3$) and an amide ($CH_3CONHCH_3$) underwent base hydrolysis separately and the initial rate of reaction was measured. It was found that the ester undergoes hydrolysis approximately three times faster than the amide.

The slow step of the base hydrolysis of the ester and amide is the same and shown below.



Which statements help to explain the faster rate of base hydrolysis of the ester?

1 Oxygen is more electronegative then nitrogen.

2 The lone pair of electrons on the nitrogen atom in the amide interacts more with the carbonyl group.

3 There are two lone pairs of electrons on the oxygen atom in the ester and only one lone pair of electron on the nitrogen atom in the amide.

A 1, 2 and 3

B 1 and 2 only

C 1 and 3 only

D 2 and 3 only

30 **X** is synthetic nonapeptide that is resynthesised from the amino acids found in honey bee venom. To investigate the sequence of amino acids in **X**, the nonapeptide was first hydrolysed by two enzymes. The protein fragments were then separated and their sequence determined.

The following protein fragments were obtained from the first enzyme which hydrolysed the peptide chain at the carboxylic end of the amino acid isoleucine, Ile.

Arg–Ile
Ser–Lys–Trp–Ile
Lys–Leu–Arg

The second enzyme, which hydrolysed the peptide chain at the carboxylic end of the amino acid lysine, Lys, yielded the following fragments

Arg–Ile–Ser–Lys
Trp–Ile–Lys
Leu–Arg

Which of the following is the correct primary structure of the nonapeptide **X**?

A Lys–Leu–Arg–Ile–Ser–Lys–Trp–Ile–Lys

B Trp–Ile–Lys–Leu–Arg–Ile–Ser–Lys–Trp

C Arg–Ile–Ser–Lys–Trp–Ile–Lys–Leu–Arg

D Arg–Ile–Ser–Lys–Leu–Arg–Trp–Ile–Lys

NAME ____________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY **9729/02**

Higher 2

Paper 2 Structured Questions

17 September 2019
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	**17**
2	**17**
3	**19**
4	**22**
Penalty (delete accordingly)	
Bond linkages	**–1 / NA**
Total	**75**

This document consists of **18** printed pages.

Answer **all** the questions.

1 Copper, a transition element, and iodine, a Group 17 halogen, are both shiny crystalline solids. The crystal structures of copper and iodine are both face−centred cubic. **Figure 1.1** shows the arrangement of the particles in this type of crystal lattice.

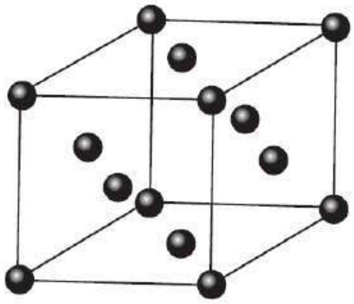


Figure 1.1

In **Figure 1.1**, the particles present are represented by ●.

(a) **(i)** What type of particles is present in the copper crystal? State the interactions within the crystal.

Particles : ....

Interactions : .... [1]

(ii) What type of particles is present in the iodine crystal? State the interactions within the crystal.

Particles : ....

Interactions : .... [1]

(b) Explain why copper is malleable and ductile.

....

....

.... [1]

(c) Give an example of another physical property that is present in one of the above solids but absent in the other. Explain.

....

....

....

.... [2]

(d) A sample of copper contains the two isotopes ^{63}Cu and ^{65}Cu only. An experiment is conducted to find the relative atomic mass of this sample and is found to be 63.9.

(i) Explain why the value found is not a whole number.

.... [1]

(ii) Suggest why the relative atomic mass stated above differs from the value obtained from the Periodic Table.

....

.... [1]

(e) When separate beams of $^{63}Cu^{2+}$ and $^{127}I^{-}$ are passed through an electric field in **Figure 1.2**, they behave differently.

On **Figure 1.2**, sketch the paths taken by beams of $^{63}Cu^{2+}$ and $^{127}\ I^{-}$ in the presence of electric field, given that the angle of deflection of the Cu^{2+} beam is 7.0 °.

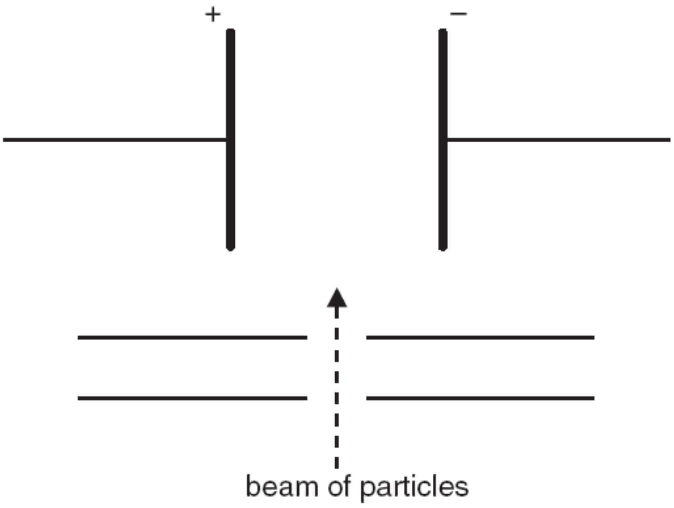


Figure 1.2

[2]

(f) Group 17 halogens Cl_2, Br_2 and I_2 are often used as oxidising agents in chemical reactions.

Describe, using relevant *E* values from the *Data Booklet*, the trend in the reactivity of the halogens, Cl_2, Br_2 and I_2 as oxidising agents.

....

....

....

....

.... [2]

(g) In acidic solutions, H_2O_2 is one of the most powerful oxidising agents known and is stronger than the halogens. H_2O_2 reacts with aqueous iodine as shown in equation **1**.

equation **1** $I_2(aq) + 5H_2O_2(aq) \rightarrow 2IO_3^-(aq) + 2H^+(aq) + 4H_2O(l)$

$E_{cell} = +0.57\ V$

(i) Write the half–equations for the above reaction between H_2O_2 and I_2. Hence, use relevant data from the *Data Booklet to* calculate *E* (IO_3^-/I_2).

[2]

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(ii) Draw a fully labelled diagram of the electrochemical cell you would set up in order to measure the cell potential of reaction **1** under standard conditions.

In your answer, you should include the following:

- describe the measurement you would make determine the cell potential,
- polarity of electrodes and,
- direction of electron flow.

[4]

[Total: 17]

2 **Table 2.1** lists the solubility of the Group 2 carbonates at 25 °C.

Table 2.1

Group 2 element, **M**	Solubility of **M**CO_3 / mol dm^{-3}
Mg	1.87×10^{-4}
Ca	6.16×10^{-5}
Sr	1.05×10^{-5}

(a) By considering the relationship between ΔH_{soln}, lattice energy and ΔH_{hyd}, explain why the solubility of Group 2 carbonates, decreases down the group.

....

....

....

....

....

.... [2]

(b) Selective precipitation is a technique of separating two or more ions from a solution by adding a suitable reagent that selectively precipitates one ion over the other ions.

A student carried out a selective precipitation experiment by slowly adding, dropwise, volumes of aqueous $Sr(NO_3)_2$ solution to 1.0 dm^3 solution containing 0.020 mol of CO_3^{2-}(aq) and 0.10 mol of F^-(aq) at 25 °C.

You may assume that the volume of aqueous $Sr(NO_3)_2$ added is negligible to the total volume of the solution in the experiment.

(i) Calculate the value of K_{sp} for strontium carbonate, $SrCO_3$.

[1]

(ii) Given that at 25 °C, the numerical value of the solubility product, K_{sp}, for strontium fluoride, SrF_2, is 2.5×10^{-9} and using your answer in **(b)(i)**, deduce which salt will precipitate first in the selective precipitation experiment.

Show your working clearly.

[3]

(c) A teacher asked the students in her class to explain which compound, calcium carbonate or strontium carbonate, has a higher decomposition temperature.

The following response was given by one of her students:

> *'Calcium carbonate has a higher decomposition temperature than strontium carbonate. The Ca^{2+} ion is a smaller ion than Sr^{2+}, hence the lattice energy of calcium carbonate is more exothermic than that of strontium carbonate.'*

Comment on the student's response.

....

....

....

....

....

.... [3]

(d) A current is passed through three cells connected in series, as shown in **Figure 2.2**.

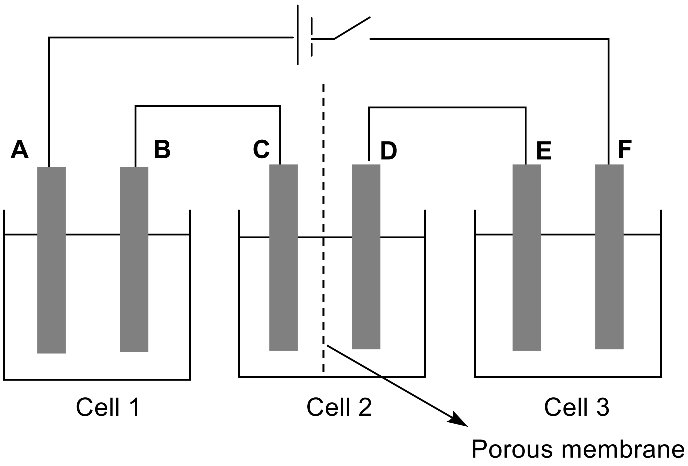


Figure 2.2

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

Cell 2 contains platinum electrodes, **C** and **D**, and electrolyte $Mg(OH)_2$(*l*).

Cell 3 contains platinum electrodes, **E** and **F**, and electrolyte containing X^{n+}(aq).

(i) Give the ion–electron equations for the reactions that occur at each of the electrodes, **A** to **C**, when the switch is closed.

Electrode **A**: ....

Electrode **B**: ....

Electrode **C**: .... [3]

(ii) It was found that 3240 coulombs of electricity cause the deposition of 1 g of **X** (A_r = 119) at electrode **F** in Cell 3.

Find the value of n in $\mathbf{X}^{n+}$ (aq).

[2]

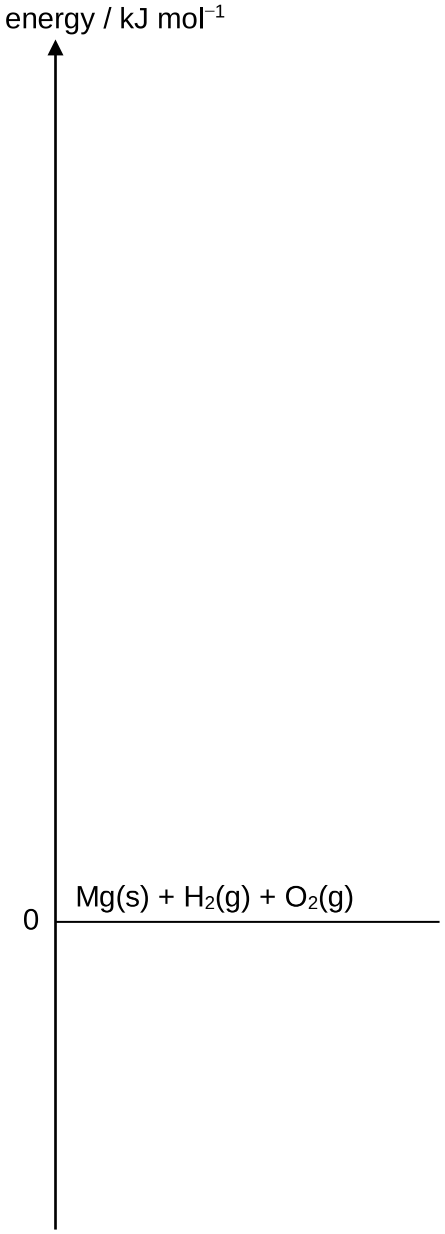
(e) The equation for the formation of the gaseous hydroxide ion is shown below.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) + e^- \rightarrow OH^-(g) \qquad \Delta H^\ominus_f(OH^-(g))$$

Using the data in **Table 2.3** and relevant data from the *Data Booklet*, complete the energy level diagram to calculate $\Delta H^\ominus_f(OH^-(g))$.

Table 2.3

Enthalpy change of atomisation of Mg(s)	+148 kJ mol^{-1}
Enthalpy change of formation of $Mg(OH)_2(s)$	–925 kJ mol^{-1}
Lattice energy of $Mg(OH)_2(s)$	–2993 kJ mol^{-1}



[3]

[Total: 17]

3 **(a)** Amines are found commonly in polymers used in plastics or textiles.

Compound **D** is an amino–containing monomer, which is used in polymerisation to form plastic materials. **Figure 3.1** outlines the formation of compound **D** from **A**.

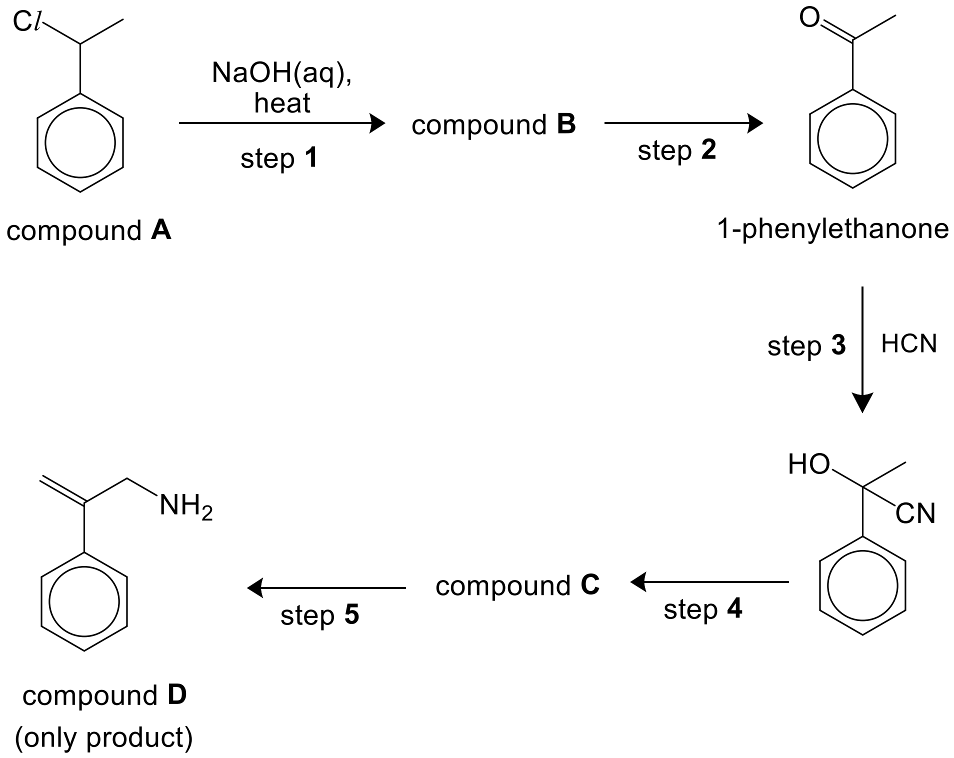


Figure 3.1

(i) Draw the structures of the compounds **B** and **C** in the boxes provided below.

Compound **B**	Compound **C**

[2]

(ii) Give the reagents and conditions for steps **2**, **4** and **5**.

step **2** : ....

step **4** : ....

step **5** : .... [3]

(iii) Name and describe the mechanism of the reaction that occurs in step **3**.

Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

Type of mechanism: ....

[4]

Question 3 continues on the next page.

(b) Compound **A**, $C_6H_5CH(CH_3)Cl$**,** undergoes hydrolysis reaction according to the following equation.

$$C_6H_5CH(CH_3)Cl + CH_3O^- \rightarrow C_6H_5CH(CH_3)OCH_3 + Cl^-$$

The graphs in **Figure 3.2** were obtained from two hydrolysis experiments. In each experiment, the overall $[CH_3O^-]$ remained virtually constant.

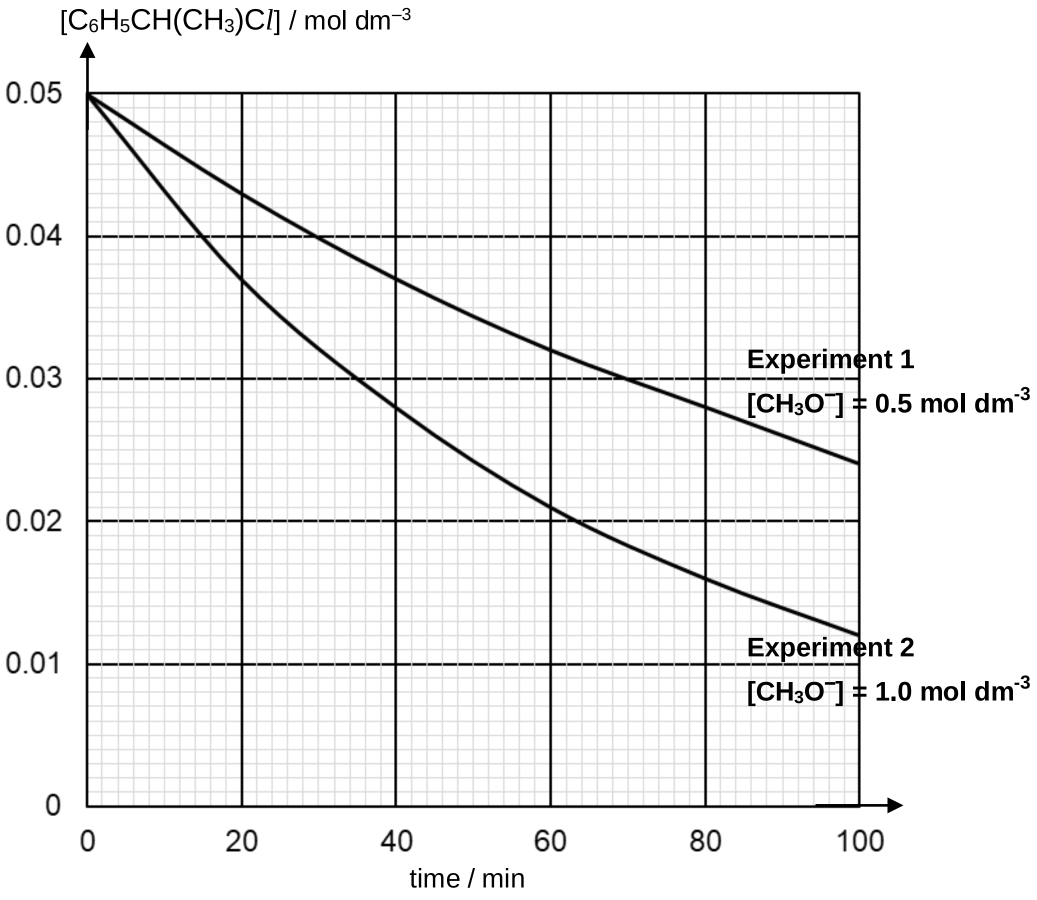


Figure 3.2

(i) Deduce the order of reaction with respect to $[C_6H_5CH(CH_3)Cl]$.

....

.... [2]

(ii) Deduce the order of reaction with respect to $[CH_3O^-]$.

[2]

(iii) Hence, construct a rate equation for the reaction, stating clearly the units for the rate constant.

....

.... [1]

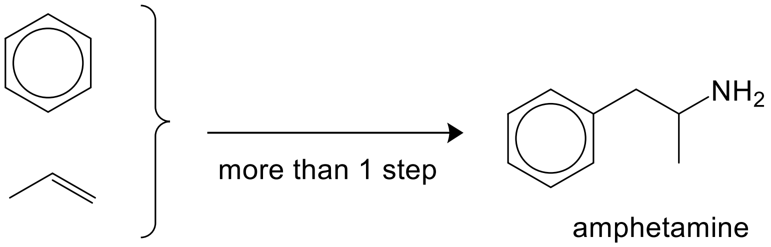
(iv) Determine the half–life of the reaction if Experiment 3 is repeated with both the concentrations of $CH_3O^-(aq)$ and $C_6H_5CH(CH_3)Cl$ doubled that in Experiment 2.

.... [1]

(c) Amphetamine, $C_6H_5CH_2CH(CH_3)NH_2$, is a central nervous system stimulant that is used to improve brain development and nerve growth, and the treatment of obesity.

Suggest a synthesis of amphetamine starting from benzene and propene.

Include reagents and conditions for all reactions and the structures of all other intermediate compounds, in your answer.



[4]

[Total: 19]

4 **(a)** Methanoic acid, HCO_2H, was formerly known as formic acid because it is present in the sting of ants and the Latin name for ant is *formica*. It was first isolated in 1671 by John Ray who collected a large number of dead ants and extracted the acid from them by distillation.

When stung by one typical ant, about 80 % of its methanoic acid is injected into the skin. This volume of methanoic acid injected is equivalent to 7.5×10^{-3} cm^3 of a laboratory–prepared solution **A** which contains 50 % by volume of pure methanoic acid.

The sting of bees also contain high amounts of methanoic acid. In a typical bee sting, the mass of methanoic acid injected into skin is 5.4×10^{-3} g.

The lethal dose of formic acid on mouse is 1.8 g per kg of mouse.

One simple treatment for ant or bee stings is to use washing soda, which contain sodium carbonate.

(i) Use the given information, calculate how many ants would have to be distilled to produce at least 1 cm^3 of pure methanoic acid.

[2]

(ii) Determine the number of ants required to inject a lethal dose on a 0.2 kg mouse.

The density of pure methanoic acid is 1.2 g cm^{-3}.

[2]

(iii) Write a balanced chemical equation for the reaction between methanoic acid and sodium carbonate.

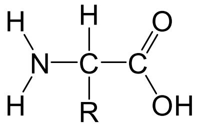
.... [1]

(iv) Calculate the mass of sodium carbonate required to neutralise one bee sting.

[2]

(b) Many ants forage at extrafloral nectar on plants and provide the plant with some measure of protection from herbivory. These nectars contain sugars, amino acids and, often, other compounds.

Amino acids are the building blocks of protein. The general structure of amino acid is as shown below



where R represents the side–chain on the α–carbon of amino acid.

Information on three amino acids is given in **Table 4.1**.

Table 4.1

Amino Acid	Formula of side–chain (R in $NH_2CHRCOOH$)	pK_a		
		α–COOH	α–NH_2	R group
aspartic acid (asp)	$-CH_2COOH$	1.88	9.60	3.65
glutamic acid (glu)	$-CH_2CH_2COOH$	2.19	9.67	4.25
lysine (lys)	$-(CH_2)_4NH_2$	2.18	8.95	10.53

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.

An electrophoresis experiment is run on a solution containing aspartic acid, lysine, and glutamic acid in **Table 4.1** at pH 5.60. The relative positions of the three amino acids obtained after electrophoresis is as shown **Figure 4.2**.

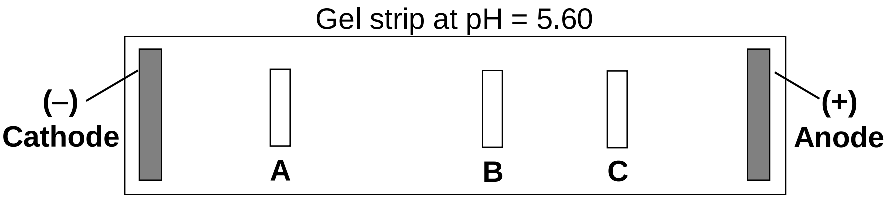


Figure 4.2

Draw the structural formulae of the species found at positions **A**, **B** and **C** at the end of the experiment.

A	B	C

[3]

(c) Compound **J**, which contains only carbon, hydrogen and oxygen atoms, is a non–narcotic analgesic commonly sold in pharmacy.

The chemical composition of liquid **J** can be analysed by combustion:

- 0.1 cm^3 of liquid **J** was burnt with 150 cm^3 of oxygen gas.
- Before cooling to room temperature, the gaseous mixture was passed through a tube containing anhydrous calcium chloride. The mass of the tube increased by 0.038 g.
- The resulting gas mixture was then cooled to room temperature and the volume of the gaseous mixture is 140 cm^3.
- The gaseous mixture further contracted by 90 cm^3 when it is passed through aqueous sodium hydroxide.
- All volumes are measured at room temperature and pressure.

(i) Using the combustion data of compound **J**, show that the molecular formula of compound **J** is $C_9H_{10}O_3$.

[3]

In another experiment, compound **J** is hydrolysed with hot NaOH(aq) and the resulting mixture acidified with a mineral acid such as sulfuric acid. Two products **K** and **M** are formed. Methanoic acid, HCO_2H, is **not** among the products.

Table 4.3 shows the results of the analysis of compounds **K** and **M** with the following reagents.

Table 4.3

Reaction	Reagent and condition	Result
1	excess Br_2(aq)	Only **K** forms a white solid, **L** (M_r = 295.8) but not **M**.
2	Na_2CO_3(aq)	Effervescence observed for **K** but not **M**.
3	Na(s)	Effervescence observed for both **K** and **M**.
4	NaOH(aq), I_2(aq), heat	Pale yellow precipitate observed for **M** but not **K**.

(ii) Name the functional group that reactions **1** and **2** show to be present in compound **K**.

reaction **1** ....

reaction **2** .... [2]

(iii) Give the molecular formula of compound **K**.

.... [1]

(iv) State the structural feature present in compound **M**.

.... [1]

(v) Use the deduction made in **(c)(i)** to **(c)(iv)**, suggest a possible structural formulae for the compound **J,** $C_9H_{10}O_3$.

[1]

Question 4 continues on the next page.

Values of the acid dissociation constants, K_a, for some organic acids are given in **Table 4.4** below.

Table 4.4

acid	**Formula**	**K_a / mol dm^{-3}**
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}
phenol	C_6H_5OH	1.3×10^{-10}
ethanoic acid	CH_3CO_2H	1.8×10^{-5}
trifluoroethanoic acid	CF_3CO_2H	5.0×10^{-3}

(vi) After compound **J** is hydrolysed with hot NaOH(aq), the resulting mixture acidified with a mineral acid such as sulfuric acid to give compound **K**.

Suggest, whether ethanoic acid or trifluoroethanoic acid, can be used as a replacement for sulfuric acid. Explain your answer.

....

....

....

....

.... [2]

(vii) With reference to **Table 4.4**, account for the difference in K_a values of:

- K_a of ethanoic acid is higher than that of phenol,

....

....

....

....

- K_a of trifluoroethanoic acid is higher than that of ethanoic acid.

....

....

....

.... [2]

[Total: 22]

NAME ______________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY

9729/03

Higher 2

23 September 2019

Paper 3 Free Response

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page for Answer
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 **14** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** When a red–hot wire is plunged into separate samples of the gaseous HCl and HI, a colour change was observed in one of the samples.

Suggest which sample gave the colour change. Use data from the *Data Booklet* to explain your answer. [2]

(b) Chlorine gas can be prepared by reacting concentrated hydrochloric acid with manganese(IV) oxide. Manganese(II) chloride and water are also formed. Chlorine gas evolved is passed through a drying agent.

(i) Write an ion–electron equation for the reduction of manganese(IV) oxide, MnO_2. [1]

(ii) The standard reduction potential, E , of the half–reaction in **(b)(i)** is +1.23 V.

Calculate ΔG , in kJ mol^{-1}, for the overall reaction and use it to explain why the reaction is unlikely to occur. [3]

(iii) Give **two** possible reasons why the reaction does occur. Explain your answer. [2]

(c) Alkenes or alcohols can react with gaseous HCl to form alkyl chlorides. However, carboxylic acids do not react with gaseous HCl.

(i) Describe the mechanism for the reaction of propene with HCl. [2]

(ii) With reference to your mechanism in **(c)(i)**, suggest how propene can act as a Bronsted–Lowry base. [1]

(iii) State the *type* of reaction that occurs between ethanol and gaseous HCl. [1]

(iv) Explain why ethanoic acid does not react with gaseous HCl. [1]

(d) HCl can be used to prepare perchloric acid, $HClO_4$.

In the presence of $HClO_4$, alcohols reacts with nitriles to form *N*–alkylamides. This is known as the *Ritter reaction*, as shown in **Fig. 1.1**.

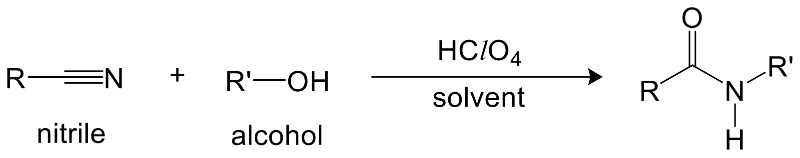


Fig. 1.1

Consider the following reaction which employs the *Ritter reaction* in the last step.

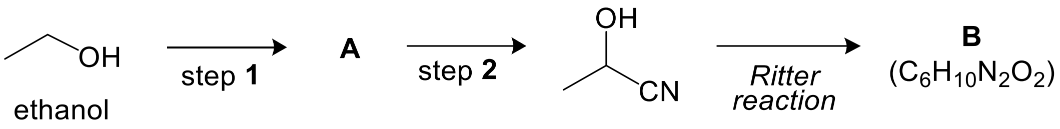


Fig. 1.2

Suggest appropriate reagents and conditions necessary for steps **1** and **2**, and draw the structures of the compounds **A** and **B**. [4]

(e) *Lingzhi* (*Ganoderma lucidum)* is a mushroom that has been used in Chinese medicines for more than 2000 years due to its numerous health benefits.

When *Lingzhi* is ingested, gastric juice in the stomach which comprises mainly hydrochloric acid, activates digestive enzymes to breakdown proteins into smaller peptides and amino acids.

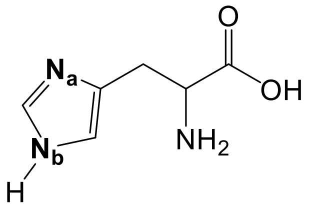
(i) A peptide, isolated from *Lingzhi*, consists of 10 amino acid residues. It is partially hydrolysed into the following tripeptides:

ala–val–ser, leu–gly–val, ser–gly–arg,

val–ala–val, arg–asn–leu, gly–arg–asn

Suggest the primary structure of this peptide. [1]

(ii) Histidine is an amino acid also found in *Lingzhi*.



histidine (his)

Both N_a and N_b are sp^2 hybridised.

By considering the hybridisation state and the orientation of the p orbitals of the two nitrogen atoms, explain why N_a is a stronger base than N_b. [1]

Histamine, which causes allergic reaction such as runny noses and itchy eyes, is synthesised in the body by decarboxylation of histidine with the aid of an appropriate enzyme catalyst.

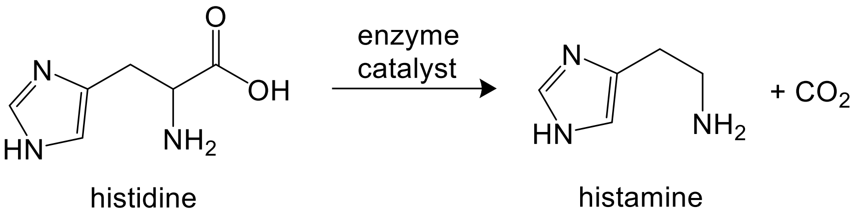


Fig. 1.3

(iii) With the aid of a Boltzmann distribution curve, explain how enzymes speed up the decarboxylation reaction. [3]

(iv) The reaction in **Fig 1.3** has a first–order kinetics.

Sketch a graph to illustrate the relationship between the rate of reaction and [histidine] in the presence of a very small amount of enzyme catalyst. [1]

[Total: 23]

2 **(a)** The kinetic theory of gases makes assumptions about the behaviour of an ideal gas. State **two** assumptions of the kinetic theory of gases. [2]

(b) Ozone, O_3, is produced naturally in the stratosphere when highly energetic solar radiation strikes molecules of oxygen, O_2.

$$3O_2(g) \ll 2O_3(g) \qquad \text{value of } K_p = 6.1 \times 10^{-62} \text{ at } 25\ °C$$

(i) Write K_p expression for this reaction. [1]

(ii) Assuming gaseous oxygen and ozone obey the ideal gas equation, use your answer in **(b)(i)** to express K_c in terms of K_p and hence, show that the value of K_c is 1.5×10^{-55}. [2]

(iii) Based on the numerical value of K_c given in **(b)(ii)**, how does the amount of product compare to the amount of reactant in this reaction at equilibrium? [1]

(iv) If a 4 dm^3 flask is initially filled with 10.0 moles of O_2, calculate the equilibrium concentration of ozone.

You may use your conclusion in **(b)(iii)** to make suitable approximation in your calculations. [2]

(c) Ozone reacts with water and sulfur dioxide, SO_2 to form sulfuric acid, H_2SO_4, as the only product.

(i) Construct a balanced equation for this reaction. [1]

H_2SO_4, a dibasic acid, dissociates in two stages.

$$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$$

$$HSO_4^- + H_2O \ll SO_4^{2-} + H_3O^+ \qquad K_a = 0.012 \text{ mol dm}^{-3}$$

(ii) Suggest a reason for the difference in the extent of dissociation of H_2SO_4 and HSO_4^-. [1]

(iii) Calculate the pH of the buffer solution formed when 5 cm^3 of 0.100 mol dm^{-3} HC*l* solution was added to 10 cm^3 of 0.200 mol dm^{-3} Na_2SO_4 solution. [2]

(d) Concentrated sulfuric acid can be used to form ester by reacting alcohol with ethanoic acid. However, under the same condition, phenol cannot react with ethanoic acid to form ester **E**.

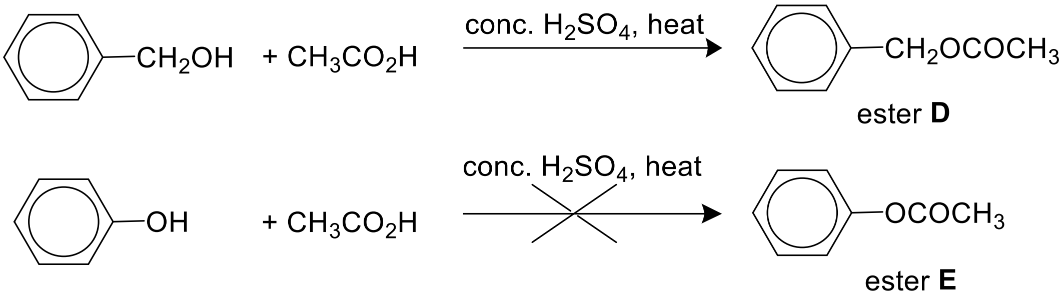


Fig. 2.1

Explain why ester **E** cannot be formed from phenol and ethanoic acid.

Suggest suitable reagent and conditions for the formation of ester **E** from phenol. [2]

(e) **Fig. 2.2** shows the reaction scheme for the conversion of a diester into salbutamol, a drug used to treat asthma.

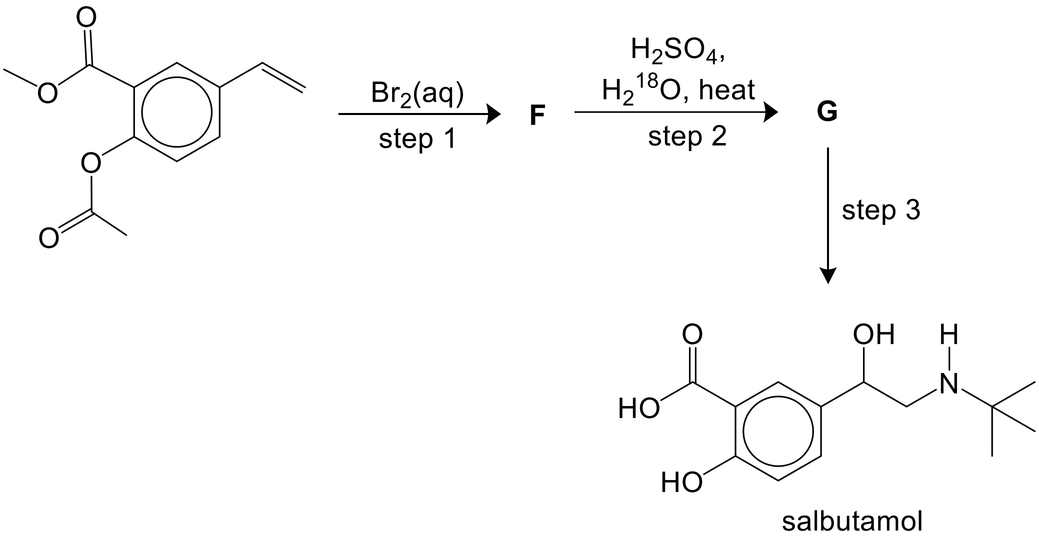


Fig. 2.2

(i) Draw the structure of **F**. [1]

(ii) Isotopic labelling experiment is often used to elucidate the mechanism of organic reaction. In step 2 of **Fig 2.2**, the water used in the hydrolysis of **F** was labelled using the oxygen isotope ^{18}O.

Draw the structure of **G**, stating clearly the ^{18}O isotope if present. [2]

(iii) Suggest the reagent and conditions necessary for step 3. [1]

(iv) Suggest why step 2 cannot be carried out before step 1. [1]

(v) Explain why the reaction in step 3 is likely to give a low yield of salbutamol. [1]

[Total: 20]

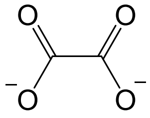
3 **(a)** **(i)** Write the full electronic configurations for a Cr atom. [1]

(ii) Transition elements exhibit a range of different oxidation states.

Describe and explain the pattern of **maximum** oxidation states for the elements from Sc to Zn. [2]

(iii) Explain why iron(III) salts are usually coloured while scandium(III) salts are white or colourless. [3]

(iv) When a solution of cobalt(II) sulfate is warmed with potassium ethanedioate, $K_2C_2O_4$, sulfuric acid and hydrogen peroxide, a complex with the formula $K_3[Co(C_2O_4)_3]$ is formed. The structure of ethanedioate ion is given below.



ethanedioate ion

Draw the three–dimensional diagram to show the shape of the cobalt–containing anion. [1]

(b) Copper in oxidation state of +1 is unstable in aqueous solution but can be stabilised as insoluble salts and in some complexes.

Step 1: On boiling with copper metal, 1 mole of blue aqueous $CuCl_2$ reacts with 2 moles of dilute HC*l* to give a colourless solution **P**, which contains complex ion of copper and chlorine.

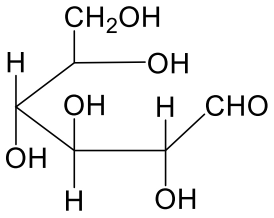
Step 2: After filtering off the excess copper metal and diluting the solution with water, a white solid **Q**, containing copper and chlorine only, is formed. The oxidation number of copper in **P** and **Q** are the same.

(i) Explain the observations in step 1.

Your answer should include the type of reactions that have occurred and give the formula of any insoluble salt and complex formed. Write an equation for the reaction that occurred. [2]

(ii) Identify the white solid **Q** formed in step 2. [1]

(c) Fehling's solution can be used to screen for glucose in urine, thus detecting diabetes. It gives a positive test due to the presence of an aliphatic aldehyde functional group in the open structure of glucose.

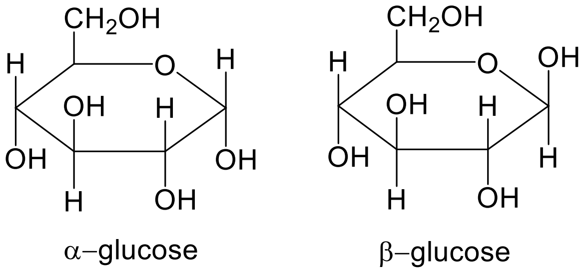


open structure of glucose

Fehling's solution is prepared by mixing $CuSO_4$(aq) and an alkaline solution of Roselle salt. The resulting solution contains a deep blue copper–containing complex ion, $[CuL_2]^{2-}$.

(i) State what would you observe when Fehling's solution is added to glucose. Draw the structure of the organic product formed. [2]

However, the open structure made up a very small amount of the glucose molecules in aqueous solution. The glucose molecules are present predominantly in cyclic ring structures, namely α–glucose and β–glucose, as shown in **Fig. 3.1**.



α–glucose β–glucose

Figure 3.1

(ii) This cyclic form of glucose exhibits both enantiomerism and cis–trans isomerism. One way of labelling the stereochemical configuration of α–glucose is (trans, cis) while that of β–glucose is (trans, trans).

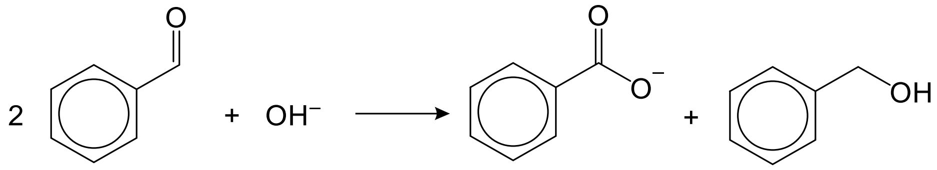
Explain why glucose can exhibit both enantiomerism and cis–trans isomerism. [2]

(iii) A 1.0 mol dm^{-3} α–glucose solution has an optical rotation angle of +113.4 ° while a 1.0 mol dm^{-3} β–glucose solution has an optical rotation angle of +19.0 ° at 298 K.

An equilibrium mixture containing both α–glucose and β–glucose has an optical rotation angle of +52.2 °.

Determine the percentage of α–glucose in the mixture. [2]

(iv) On the other hand, the complex ion in Fehling's solution has no reaction with benzaldehyde, which is an aromatic aldehyde. This is because under the influence of the alkaline medium, benzaldehyde reacts according to the below equation.



Suggest the type of reaction that has occurred. [1]

[Total: 17]

Section B

Answer **one** question from this section.

4 **(a)** There is said to be a 'diagonal relationship' between elements of the second and third periods of the Periodic Table, exemplified by lithium and magnesium, and by beryllium and aluminium. This relationship leads to diagonal pairs of elements having similar properties.

(i) By considering the trends in electronegativity across the period and down the group, suggest why beryllium and aluminium have similar properties. [1]

(ii) In terms of structure and bonding, explain why the boiling point of beryllium chloride is much lower than that of beryllium oxide. [2]

(iii) Beryllium chloride dissolves in water to give $[Be(H_2O)_4]^{2+}$.

Predict and explain the effect of adding beryllium chloride to a beaker of litmus solution. [2]

(b) Beryllium oxide was heated with a mixture of potassium fluoride and hydrogen fluoride. An ionic compound was formed, which dissolved in water. When the resultant solution was added to aqueous lead(II) nitrate, a white precipitate, **A**, containing only beryllium, fluorine and lead was obtained. The white precipitate contained 3.08 % by mass of beryllium.

(i) Given that the relative formula mass of **A** is approximately 290 and the empirical formula of **A** is $PbBe_xF_y$, determine the values of x and y.

Shows all working clearly. [2]

(ii) The anion in compound **A** is also formed when 1 mole of beryllium difluoride reacts with 2 moles of potassium fluoride.

Draw a 'dot–and–cross' diagram of this anion, showing the outer shell electrons only. In your diagram, use the symbols '•' and '×' to distinguish electrons from different atoms, and the symbol '☐' for any additional electrons responsible for the overall negative charge. [1]

Aryl esters can be converted to aryl ketones by a reaction known as the Fries rearrangement.

In the presence of $AlCl_3$, the acetyl group, $-COCH_3$, is transferred to the 2–position to form 2–hydroxyacetophenone, depending on the reaction conditions used. A proposed mechanism for the Fries rearrangement of phenyl ethanoate is shown **Fig. 4.1.**

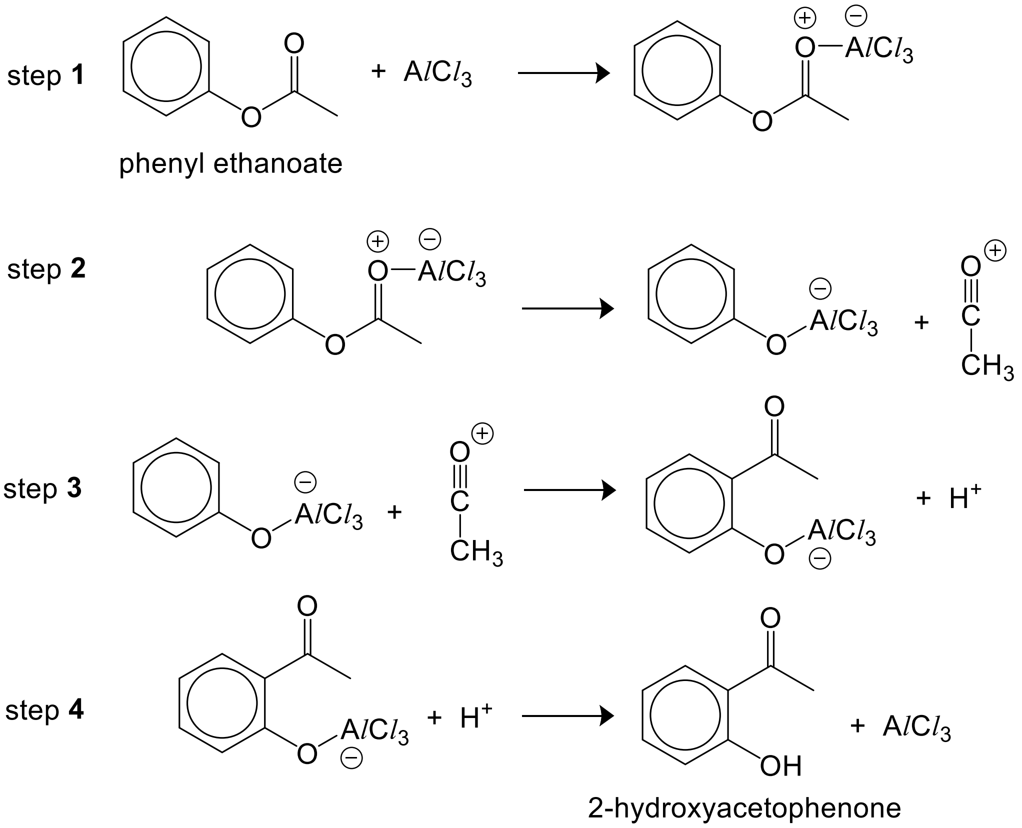


Fig. 4.1

(c) **(i)** Write an overall equation for the Fries rearrangement of phenyl ethanoate. [1]

(ii) Considering the mechanism in **Fig. 4.1** and your overall equation in **(c)(i)**, state and explain the roles of $AlCl_3$ in Fries rearrangement. [2]

(iii) Step **3** of the mechanism in **Fig. 4.1** occurs in two stages.

- In stage 1, benzene attacks the electron–deficient carbon atom of CH_3CO^+ to form an intermediate with delocalised positive charge.
- In stage 2, the loss of a proton restores the aromaticity of the compound.

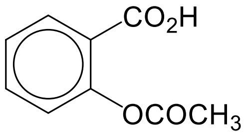
Using curly arrows to show the movement of electron pairs, complete the mechanism. Show all charges and relevant lone pairs. [3]

(iv) Describe a simple chemical test to confirm that 2–hydroxyacetophenone is formed during the reaction. State what you would observe. [2]

(v) 4–hydroxyacetophenone was also formed during the Fries rearrangement of phenyl ethanoate. However, 2–hydroxyacetophenone is likely to be formed in larger proportion than 4–hydroxyacetophenone due to the formation of favourable interactions between the ketone and alcohol functional groups.

Draw an appropriate diagram to illustrate the type of interactions formed, stating the interactions clearly. [2]

(d) Aryl ester **B** is an analog of phenyl ethanoate.



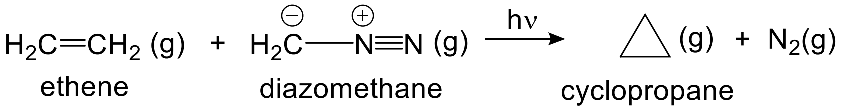
aryl ester **B**

Considering the mechanism in **(c)(iii)**, explain how the rate of Fries rearrangement might compare with phenyl ethanoate if aryl ester **B** was used instead. [2]

[Total: 20]

5 **(a)** **(i)** Explain what is meant by the term *bond energy*. [1]

(ii) In the presence of light, diazomethane gas reacts with ethene to give cyclopropane.



Use relevant bond energies data from the *Data Booklet* to calculate the standard enthalpy change of the reaction between diazomethane gas and ethene. [2]

(iii) Other than average bond energies in the *Data Booklet*, suggest why the theoretical value calculated in **(a)(ii)** is likely to be *significantly* less exothermic than the actual value. [1]

(b) Alkenes can be formed from alkyl halide, via elimination process, in the presence of a suitable base such as potassium hydroxide. Like nucleophilic substitution of alkyl halides, there are two possible mechanisms for the elimination reaction, namely E1 and E2.

E1 reaction is an unimolecular reaction which occurs via a two-step mechanism.

- In the first step which is also the rate–determining step, the alkyl halide undergoes a dissociation process to yield a carbocation and halide ion.
- The carbocation then reacts with hydroxide ion where a C–H bond is broken to give the alkene in the second step.

On the other hand, E2 reaction is a bimolecular elementary reaction.

Using 2–bromo–2–methylpropane as an example, **Fig. 5.1** shows the overall equation for the elimination reaction of alkyl halide.

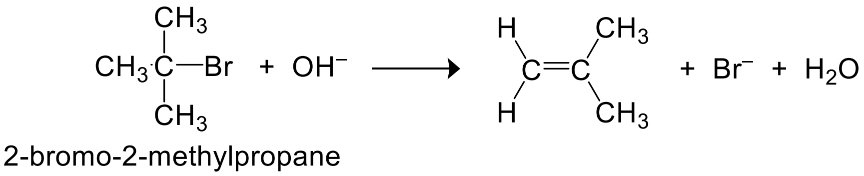


Fig. 5.1

(i) Using 2–bromo–2–methylpropane as an example, write the rate equations for the E1 reaction **and** the E2 reaction. [2]

(ii) Using the information on E1 mechanism given above, outline the E1 mechanism for 2–bromo–2–methylpropane.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(iii) Explain how the rate of E1 reaction of 2–bromo–2–methylpropane would change if $CH_3CH_2O^-$ is used as the base instead of OH^-. [2]

(c) Since both mechanisms proceed via the same carbocationic intermediate, there is usually competition between E1 reaction and S_N1 reaction.

(i) Write a balanced chemical equation for the nucleophilic reaction of 2–bromo–2–methylpropane with potassium hydroxide. [1]

(ii) Considering the equation in **Fig. 5.1** and your answer in **(c)(i)**, explain, in thermodynamic terms, why E1 reaction predominates over S_N1 reaction when a higher temperature was used. [2]

(iii) When benzyl bromide, $C_6H_5CH_2Br$, is reacted with potassium hydroxide, it was found that it does not undergo elimination reaction. Also, benzyl bromide undergoes substitution via S_N1 instead of the usual S_N2 mechanism, typical for a primary alkyl halide.

Explain the above observations. [3]

(iv) In comparing the reactivity between different alkyl halides towards nucleophilic substitution, there are two main factors at work: the strength of C–X bond and the stability of the leaving group X^-.

One way of measuring the stability of the leaving group X^- ion is to use the pK_a values of HX acids in **Table 5.2**.

Table 5.2

HX	HF	HC*l*	HBr	HI
pK_a of HX	+3	–7	–9	–10

By relating the pK_a values given in **Table 5.2** to the position of equilibrium and the stability of X^- ion, explain how the reactivity of alkyl halide towards nucleophilic substitution vary from fluorine to iodine. [3]

[Total: 20]

NAME ______________________________ CLASS **18S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2019

CHEMISTRY
9729/04

Higher 2

Paper 4 Practical

26 August 2019

2 hours 30 minutes

Candidates answer on the Question paper.

Additional Materials: As listed in the Confidential Instructions

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 23 and 24.

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 **23** printed pages and **1** blank page.

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

1 Determination of the identity of the halogen, X, in CH_2XCO_2H

Compound **W** is a halogenoethanoic acid, $CH_2\mathbf{X}CO_2H$, where **X** is a halogen.

A halogenoethanoic acid reacts with aqueous sodium hydroxide in two reactions.

The alkali neutralises the carboxylic acid.

reaction 1 $NaOH + CH_2\mathbf{X}CO_2H \rightarrow CH_2\mathbf{X}CO_2Na + H_2O$

The halogenoalkyl group then undergoes a substitution reaction.

reaction 2 $NaOH + CH_2\mathbf{X}CO_2Na \rightarrow CH_2(OH)CO_2Na + Na\mathbf{X}$

4 g of **W** were heated for one minute with 250 cm^3 of 0.40 mol dm^{-3} aqueous sodium hydroxide in a beaker. Some of the sodium hydroxide reacted with compound **W** as shown by equations 1 and 2. The solution that remained contains unreacted sodium hydroxide. This solution is **FA 1**.

In **1(a)**, you will perform a dilution and by titrating **FA 1** with the diluted sulfuric acid, you will determine the identity of **X** in $CH_2\mathbf{X}CO_2H$.

FA 1 is aqueous sodium hydroxide after reaction with **W**.

FA 2 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4.

methyl orange indicator

(a) (i) Dilution of FA 2

1. Use a pipette to transfer 10.0 cm^3 of **FA 2** into a 250 cm^3 volumetric flask.
2. Make up the contents of the flask to the 250 cm^3 mark with deionised water.
3. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times.
4. Label this diluted solution of sulfuric acid as **FA 3**.

(ii) Titration of FA 1 against FA 3

1. Fill the burette labelled **FA 3**, with **FA 3**.
2. Use a pipette to transfer 25.0 cm^3 of **FA 1** into the conical flask.
3. Add a few drops of methyl orange indicator.
4. Run **FA 3** from the burette into the conical flask. The end-point is reached when the yellow solution becomes orange.
5. Record your titration results, to an appropriate level of precision, in the space provided on Page 3.
6. Repeat points 2 to 5 as necessary until consistent results are obtained.

Titration results

[3]

(iii) From your titrations, obtain a suitable volume of **FA 3,** V_{FA3}**,** to be used in your calculations. Show clearly how you obtained this volume.

V_{FA3} = ... [3]

(b) **(i)** Calculate the concentration of sulfuric acid in **FA 3** that you have prepared.

$[H_2SO_4]$ in **FA 3** = ... [1]

(ii) Calculate the amount of sodium hydroxide present in 25.0 cm^3 of **FA 1**.

amount of NaOH in 25.0 cm^3 of **FA 1** = ... [1]

(iii) Calculate the amount of sodium hydroxide in 250 cm^3 of **FA 1** and hence, calculate the amount of sodium hydroxide that reacted with **W**.

amount of NaOH that reacted with **W** = ... [2]

(iv) Use your answer to **(b)(iii)** to calculate the M_r of **W**, $CH_2\mathbf{X}CO_2H$.

Hence, deduce the identity of **X** in $CH_2\mathbf{X}CO_2H$.
[A_r: C,12.0; O,16.0; H, 1.0; F, 19.0; C*l*, 35.5; Br, 79.9; I, 126.9]

X is .... [2]

(c) **(i)** The maximum error in any single burette reading is ±0.05 cm^3.

Calculate the maximum percentage error in the volume of **FA 3** used in **1(a)(iii)**.

maximum percentage error in the volume of **FA 3** used = ... [1]

(ii) Apart from the inaccuracies in reading the volumes of solutions, suggest a significant source of error in this experiment.

Explain how you could minimise this error.

....

.... [1]

[Total: 14]

2 An experiment to investigate the behaviour of acids and bases in aqueous solutions

FA 4 is 1.00 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$.

FA 5 is aqueous sodium hydroxide.

You will need access to the **FA 2** solution you used earlier.

According to Arrhenius theory of acids and bases, an acid produces H^+ ions and a base produces OH^- ions, in aqueous solution. An acid–base reaction involves reacting together these two ions to produce water molecules as shown in the following equation.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neutralisation} = –57.0 \text{ kJ mol}^{-1}$$

This experiment involves two different acid-base reactions.

The first reaction is between sodium hydrogencarbonate, **FA 4**, and sodium hydroxide, **FA 5**.

reaction 3 $NaHCO_3(aq) + NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ ΔH_3

The molar enthalpy change for reaction 3, ΔH_3, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

Instead of using an indicator to determine the end–point, you will perform a thermometric titration to determine the equivalence point of the reaction. You will add portions of **FA 5** progressively to a known volume of **FA 4**. You will continue adding **FA 5** until the equivalence point is reached and passed. Throughout the experiment you will note and record the temperature of the mixture after each addition.

You will then analyse your results graphically to determine the

- titration volume at the equivalence point, $V_{equivalence}$,
- maximum temperature change, ΔT_{max},
- molar enthalpy change, ΔH_3, for reaction 3.

For Examiner's Use

(a) **Determination of the enthalpy change of reaction between FA 4 and FA 5**

In this experiment you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 5** have been added. It is important that the volume of **FA 5** recorded is the total volume you have added up to that point when the temperature reading was made.

Note: If you overshoot on an addition, record the **actual** total volume of **FA 5** added up to that point.

In an appropriate format in the space provided below, record all values of temperature, *T*, and each total volume of **FA 5** added.

1. Fill a burette with **FA 5**.
2. Place a Styrofoam cup inside a second Styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer 25.0 cm^3 of **FA 4** into the first Styrofoam cup.
4. Stir the **FA 4** solution in the cup with the thermometer. Read and record its temperature. Tilt the cup if necessary to ensure the thermometer bulb is fully immersed.
5. From the burette, add 2.00 cm^3 of **FA 5** to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture, *T*, and the volume of **FA 5** added.
7. Repeat points **5** and **6** until a total of 30.00 cm^3 of **FA 5** has been added. After each addition of **FA 5**, record the maximum temperature of the mixture and the total volume of **FA 5** added up to that point.

Results

[2]

(b) **(i)** On the grid below, plot a graph of temperature, *T* on the *y*–axis against volume of **FA 5** added on the *x*–axis.

[3]

(ii) Draw **two** smooth lines of best fit.

- The first best–fit curve or straight line should be drawn using the plotted points where the temperature is **rising.**
- The second best–fit curve or straight line should be drawn using the plotted points where the temperature is **falling**.
- Extrapolate these lines until they cross.

(iii) Determine from your graph

- the maximum temperature reacted, T_{max},
- the maximum temperature change, ΔT_{max}, and
- the volume, $V_{\text{equivalence}}$, of **FA 5** needed to completely react with 25.0 cm^3 of **FA 4**.

Show on your graph how you obtained these values.
Record these values in the spaces provided below.

Maximum temperature reached, $\boldsymbol{T}_{\text{max}}$ = ...

Maximum temperature change, $\Delta\boldsymbol{T}_{\text{max}}$ = ...

Volume of **FA 5** required, $\boldsymbol{V}_{\text{equivalence}}$ = ... [3]

(iv) Calculate the concentration of sodium hydroxide, [NaOH], in **FA 5**.

[NaOH], in **FA 5** = ... [1]

(v) Calculate the heat change, *q*, for your experiment in **(a)** and hence determine a value for the molar enthalpy change for reaction 3, ΔH_3.

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}.

ΔH_3 = ... [2]

Question 2 continues on the next page.

(c) The reaction between FA 4 and FA 2

The second acid–base reaction is between sodium hydrogencarbonate, **FA 4**, and sulfuric acid, **FA 2**.

reaction 4 $NaHCO_3(aq) + ½H_2SO_4(aq) \rightarrow ½Na_2CO_3(aq) + H_2O(l) + CO_2(g)$ ΔH_4

The molar enthalpy change for reaction 4, ΔH_4, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

A student carried out an experiment to determine the molar enthalpy change for reaction 4, ΔH_4, using a known volume of **FA 4** that reacts with excess **FA 2**.

The student carried out the experiment according to the following instructions.

1. Using a measuring cylinder, transfer 40.0 cm^3 of **FA 4** into a Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
2. Stir and measure the temperature of this **FA 4**, $T_{FA\,4}$.
3. Using another measuring cylinder, measure 15.0 cm^3 of **FA 2**.
4. Stir and measure the temperature of this **FA 2**, $T_{FA\,2}$.
5. Carefully add the **FA 2** from the measuring cylinder to the **FA 4** in the Styrofoam cup in small portions to avoid too much frothing.
6. Using the thermometer, stir the mixture continuously. Measure and record the lowest temperature, T_{min}, of the mixture.

The results are shown in the table in Table 2.1.

$T_{FA\,4}$ / °C	28.6
$T_{FA\,2}$ / °C	28.9
T_{min} / °C	28.2

Table 2.1

(d) Calculate the molar enthalpy change for reaction 4, ΔH_4. For this experiment, the weighted average initial temperature, T_{average}, of **FA 4** and **FA 2** may be calculated using the formula below.

$$T_{average} = \frac{(V_{FA2} \times T_{FA2}) + (V_{FA4} \times T_{FA4})}{(V_{FA2} + V_{FA4})}$$

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}

ΔH_4 = ... [2]

(e) Ionic equations for neutralisation, reaction 3 and reaction 4 are shown below.

	$H^+ + OH^- \rightarrow H_2O$	$\Delta H_{\text{neutralisation}} = -57.0$ kJ mol^{-1}
reaction 3	$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$	ΔH_3
reaction 4	$HCO_3^- + H^+ \rightarrow H_2O + CO_2$	ΔH_4

Carbon dioxide may be removed from stale air by bubbling the air through aqueous alkali. An equation for this reaction is given below.

reaction 5 $2OH^-(aq) + CO_2(g) \rightarrow CO_3^{2-}(aq) + H_2O(l)$ ΔH_5

Use your answers to **2(b)(v)** and **2(d)**, together with the molar enthalpy change of neutralisation, $\Delta H_{\text{neutralisation}}$, to determine a value for the molar enthalpy change for this reaction, ΔH_5.

ΔH_5 = ... [4]

(g) An alternative definition of acid-base behavior was proposed by Brønsted and Lowry.

In terms of the Brønsted–Lowry theory of acids and bases, suggest the role of hydrogencarbonate ions, HCO_3^-, in reaction 3 and in reaction 4. Explain your answer.

reaction 3

role of HCO_3^- ions ....

explanation ....

reaction 4

role of HCO_3^- ions ....

explanation .... [2]

[Total: 19]

[BLANK PAGE]

3 Investigation of some reactions involving transition element ions.

Manganese containing compounds are often used in redox reactions in the laboratory.

In aqueous solution, MnO_4^-(aq) ions are stable. However, MnO_4^{2-}(aq) ions, which has a characteristic green colour, are unstable as they spontaneously undergo a redox reaction.

Both MnO_4^- and MnO_4^{2-} solid compounds are stable.

FA 6 is solid potassium manganate(VII), $KMnO_4$.

FA 8 is a hydrocarbon compound.

Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.1

		tests	observations
(a)	**(i)**	Add one spatula of **FA 6** to a hard–glass test–tube. Heat gently for about 10s and then strongly for about 20s. Leave the test–tube and residue to cool completely. Keep the residue for use in **3(a)(ii)**. **While waiting, you can start on 3(d).**	
	(ii)	Add deionised water to a small beaker until it is about half full. Place the beaker on a white tile. Pour the cooled residue from **3(a)(i)** **slowly** into the deionised water in the beaker. **Observe the solution closely.** Swirl the solution and filter a small portion of this solution into a clean test–tube. The filtrate is **FA 7**.	
	(iii)	Add 1 cm depth of **FA 7** to a test–tube. Add Fe^{2+}(aq), slowly with shaking, until no further change is seen.	

[8]

(b) Table 3.2 gives some standard electrode potential values involving manganese containing ions.

Table 3.2

electrode reaction	E / V
$MnO_4^- + 8H^+ + 5e^- \ll Mn^{2+} + 4H_2O$	+1.52
$MnO_4^- + e^- \ll MnO_4^{2-}$	+0.56
$MnO_4^{2-} + 4H^+ + 2e^- \ll MnO_2 + 2H_2O$	+2.26

Consider your observations when deionised water was added to the residue in **3(a)(ii)**, together with those you made in **3(a)(iii)** and the information in Table 3.2.

(i) Use data from Table 3.2 to explain what happens to manganese during this reaction.

....

....

.... [1]

(ii) State the type of reaction that has occurred in **3(a)(ii)**.

.... [1]

(c) The decomposition reaction in **3(a)(i)** also produces MnO_2 as one of the products.

Write a balanced equation for the decomposition reaction occurring in **3(a)(i)** using your observations in Table 3.1.

.... [1]

Question 3 continues on the next page.

(d) **Before starting this question, ensure your Bunsen burner is turned off.**

Hot water is provided for the hot water bath required in this question.

Perform the tests described in Table 3.3, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

Table 3.3

		tests	observations
	(i)	Add 2 cm depth of aqueous sodium hydroxide in a test–tube. Add 5 drops of **FA 8** to this test-tube. Add a few drops of aqueous potassium manganate(VII).	
	(ii)	Add 2 cm depth of aqueous sulfuric acid in a test–tube. Add 5 drop of **FA 8** to this test–tube. Add a few drops of aqueous potassium manganate(VII). Place the mixture in the hot water bath for a few minutes.	
	(iii)	Add 5 cm depth of deionised water in a test–tube. Add 1 drop of **FA 8** to this test–tube. Add aqueous bromine slowly, with shaking, until no further change is seen.	Yellow aqueous bromine decolourises

[1]

(e) When **FA 8** reacts with aqueous potassium managanate(VII) under alkaline conditions in **3(d)(i)**, compound **Z** is the main organic product formed.

The molecular formula of **Z** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 8**.

Explain your deduction. Your explanation should be supported by evidence from your observations in **3(d)(i)**.

molecular formula of **FA 8** .... [2]

explanation ....

....

(ii) Draw possible structures of **FA 8** and compound **Z**.

FA 8	compound **Z**

[1]

[Total: 10]

4 Planning

In acidic solution, potassium manganate(VII) undergoes a redox reaction with ethanedioate ions, $C_2O_4^{2-}$ as shown in reaction 6.

reaction 6 $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

As the initial reaction between potassium manganate(VII) and ethanedioate ions is slow, a small amount of Mn^{2+} is added to the reaction mixture to speed up the reaction. The order of the reaction with respect to the concentration of potassium manganate(VII) may be determined by performing a number of experiments and measuring the time taken, *t*, for a fixed volume of CO_2 to be produced in each of these experiments.

A teacher demonstrated one of the experiments as follows.

> She prepared a mixture containing 50 cm^3 of potassium manganate(VII), 50 cm^3 of sulfuric acid and 1 cm^3 of aqueous manganese(II) sulfate.
>
> 50 cm^3 of sodium ethandioate was added to the mixture and, 40 cm^3 of gas was collected after 12 seconds.

The order of reaction can be graphically determined by plotting the common logarithm of 1/*t*, lg(1/*t*) against the common logarithm of the volume of $KMnO_4$ used, $\lg(V_{KMnO_4})$.

(a) Write a plan for such a series of experiments.

You may assume that you are provided with:

- 0.02 mol dm^{-3} potassium manganate(VII), $KMnO_4$,
- 0.2 mol dm^{-3} sodium ethandioate, $Na_2C_2O_4$,
- 1.0 mol dm^{-3} dilute sulfuric acid, H_2SO_4,
- aqueous manganese(II) sulfate solution,
- deionised water,
- the apparatus normally found in a school or college laboratory.

Your plan should include details of:

- a clearly labelled diagram of the experimental set–up used for gas collection,
- the quantities of reactants and the apparatus to be used,
- the procedure that you would follow,
- the measurements you would make to allow a suitable graph to be drawn.

Diagram of the experimental set–*up*:

………………………………………………………………………………………………………

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For Examiner's Use

[5]

....

....

....

(b) Sketch, on Fig. 4.1, the graph you would expect to obtain.

Explain your answer.

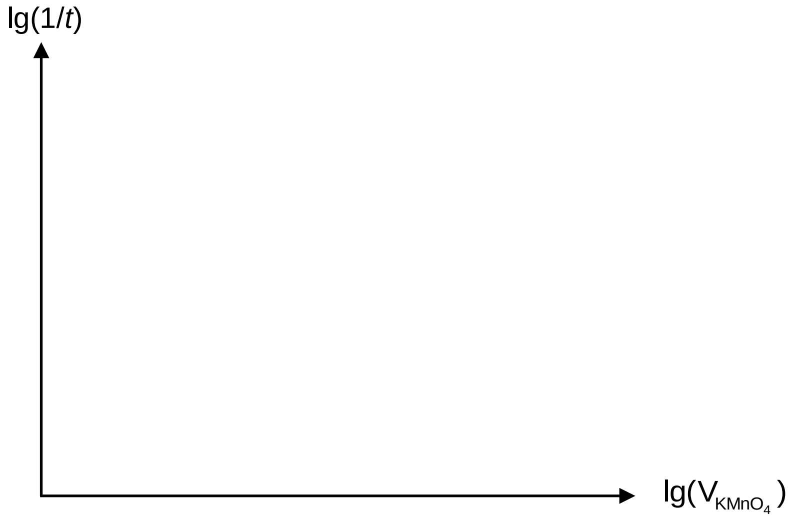


Fig 4.1

explanation ....

....

....

....

.... [3]

(c) Describe how you would use your graph to determine the order of reaction with respect to the concentration of potassium manganate(VII).

.... [1]

(d) **(i)** Suggest why the initial reaction between manganate(VII) ions and ethanedioate ions is slow.

....

.... [1]

(ii) A small amount of Mn^{2+} is added to catalyse the reaction.

State the type of catalyst involved in the reaction. Explain your answer.

.... [1]

(iii) Using the information given in **4(d)(ii)** and reaction 6, sketch, on Fig. 4.2, the graph you would expect to obtain if the experiment was conducted without the addition of Mn^{2+}(aq) solution.

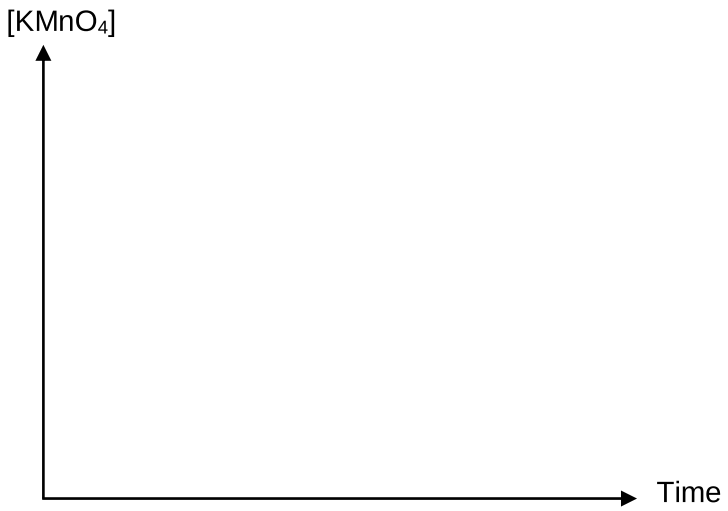


Fig 4.2

[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 Aqueous Anions

Anion	***Reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
choride, 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 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 acidified aqueous 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 PIONEER JUNIOR COLLEGE

JC2 H2 CHEMISTRY (9729) PRELIMINARY EXAM 2019

(PAPER 1) – Suggested Worked Solutions

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

JURONG PIONEER JUNIOR COLLEGE
2019 JC2 H2 CHEMISTRY (9729)
Preliminary Examination Paper 2
(Suggested Answers)

1 **(a)** **(i)** Particles: Cu^{2+} cation

Interactions: metallic bonding

(ii) Particles: I_2 molecule

Interactions: instantaneous dipole–induced dipole interactions

(b) The layers of Cu^{2+} cations can slide past each other without breaking the metallic bond (or with the mobile valence electrons holding them together).

(c) Electrical conductivity: Mobile valence electrons available to conduct electricity in copper but no mobile charge carriers available in iodine to conduct electricity.

or

Solubility in organic solvent: Iodine is able to form favourable instantaneous dipole–induced dipole interactions with the organic solvent, but copper is unable to form favourable interactions with the organic solvent.

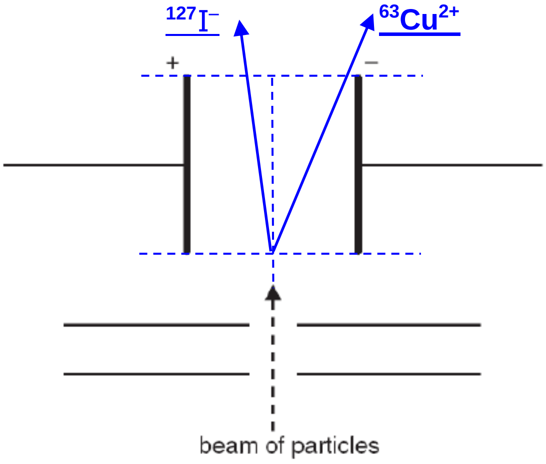
(d) **(i)** Atomic mass is the weighted average of the mass of isotopes.

(ii) Percentage abundance of the isotopes in this sample differs from what is normally obtained.

or

There are more than 2 types of isotopes of copper present in the sample.

(e)



Since angle of deflection $\propto \left|\frac{\text{charge}}{\text{mass}}\right|$,

angle of deflection of I^-

$$= \left|\frac{-1/127}{+2/63}\right| \times (7.0\ °) = \underline{1.7}\ °\ \text{(1dp)}$$

(f)

X	Cl	Br	I
E (X_2/X^-) / V	+1.36	+1.07	+0.54

Since E (X_2/X^-) becomes less positive down the group, it implies that the tendency of X_2 to be reduced to X^- decreases and hence, the oxidising power of X_2 decreases down the group.

(g) (i) [O]: $2IO_3^- + 12H^+ + 10e^- \ll I_2 + 6H_2O$ $\quad x$ V

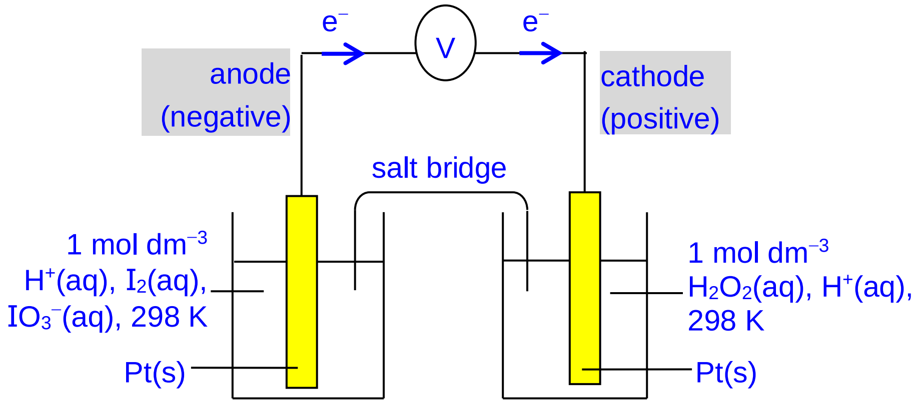
[R]: $H_2O_2 + 2H^+ + 2e^- \ll 2H_2O$ $\quad$ +1.77 V

$E_{cell} = E_{red} - E_{ox}$

$+0.57 = (+1.77) - E\ (IO_3^-/\ I_2)$

$E\ (IO_3^-/\ I_2) = +1.20$ V

(ii)



Note the E_{cell} value on the voltmeter at first instance of cell being connected.

2 (a) $$\Delta H_{soln} = \underbrace{-\underbrace{\text{LE}}_{-ve}}_{+ve} + \underbrace{\sum \Delta H_{hyd}}_{-ve}$$

Down the group, both LE of MCO_3 and ΔH_{hyd} of M^{2+} becomes less exothermic (or more endothermic or magnitude/value of LE of MCO_3 and ΔH_{hyd} of M^{2+} decreases) since the radius of M^{2+} increases down the group.

However, the decrease in LE is less than the decrease in ΔH_{hyd} since M^{2+} is smaller than CO_3^{2-}.

Hence, ΔH_{soln} becomes less exothermic and the solubility of MCO_3 decreases down the group.

(b) (i) K_{sp} of $SrCO_3$ $= [Sr^{2+}][CO_3^{2-}] = (1.05 \times 10^{-5})^2 = 1.10 \times 10^{-10}$ mol² dm⁻⁶

(ii) For precipitation to occur, ionic product $\geq K_{sp}$.

ionic product of $SrCO_3 = [Sr^{2+}]_{min}[CO_3^{2-}] \geq K_{sp}$.

$[Sr^{2+}]_{min}(0.02) = 1.1 \times 10^{-10}$

minimum $[Sr^{2+}]$ to precipitate $SrCO_3 = 5.50 \times 10^{-9}$ mol dm⁻³

ionic of $SrF_2 = [Sr^{2+}]_{min}[F^-]^2 \geq K_{sp}$.

$[Sr^{2+}]_{min}(0.1)^2 = 2.5 \times 10^{-9}$

minimum $[Sr^{2+}]$ to precipitate $SrF_2 = 2.50 \times 10^{-7}$ mol dm⁻³

$SrCO_3$ will precipitate first because a lower $[Sr^{2+}]$ is required to form the precipitate.

(c) The student's response is incorrect as $SrCO_3$ has a higher decomposition temperature than $CaCO_3$.

Thermal stability of Group 2 carbonate depends on the charge density of M^{2+}, not lattice energy.

Since Sr^{2+} has a larger radius, Sr^{2+} has a lower charge density than Ca^{2+}. Hence, Sr^{2+} polarises large CO_3^{2-} less and weaken the C–O bond to a smaller extent than that in $BaCO_3$.

Hence, $SrCO_3$ has a higher thermal stability and has a higher decomposition temperature.

(d) **(i)** Electrode **A**: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

Electrode **B**: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

Electrode **C**: $4OH^-(l) \rightarrow O_2(g) + 2H_2O(g/l) + 4e^-$

(ii) $X^{n+} + ne^- \rightarrow X$

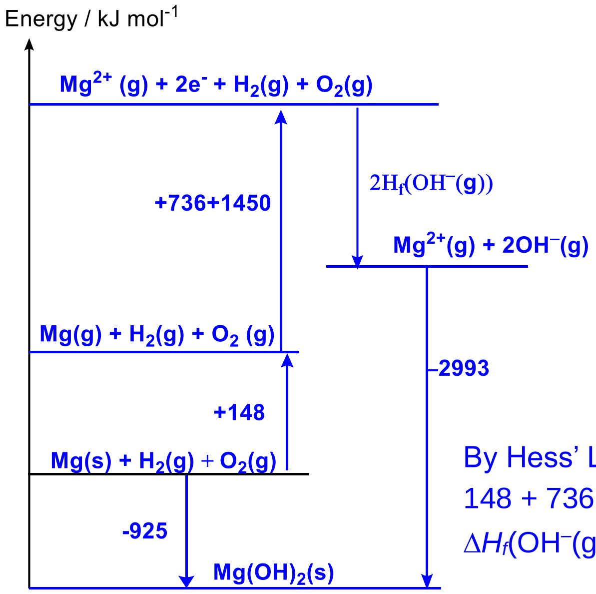
n(X) deposited = 1 ÷ 119 = 0.008403 mol

n_e passed = 3240 ÷ 96500 = 0.03358 mol

mole ratio	X	:	e^-
	0.008403	:	0.03358
	1	:	4

Hence, the value of n is 4.

(e)

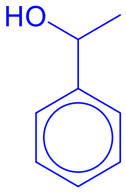
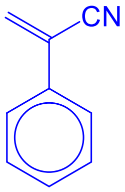


By Hess' Law,

$148 + 736 + 1450 + 2\Delta H_f(OH^-(g)) + (-2993) = -925$

$\Delta H_f(OH^-(g)) = \underline{\mathbf{-133}}$ kJ mol^{-1}

3 **(a)** **(i)**

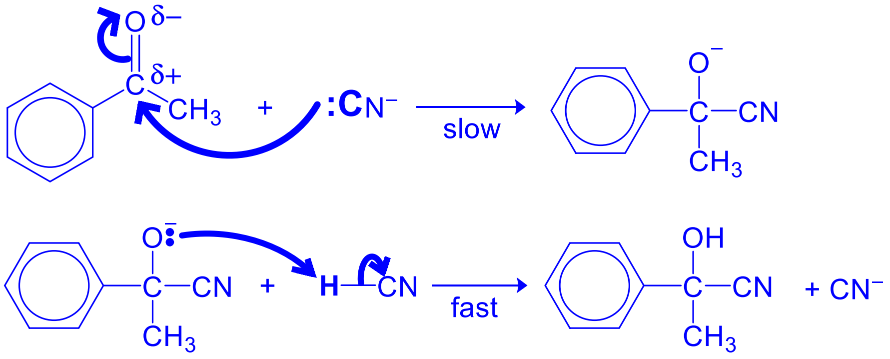
Compound **B**	Compound **C**
	

(ii) step **2** : acidified $K_2Cr_2O_7(aq)$, heat under reflux

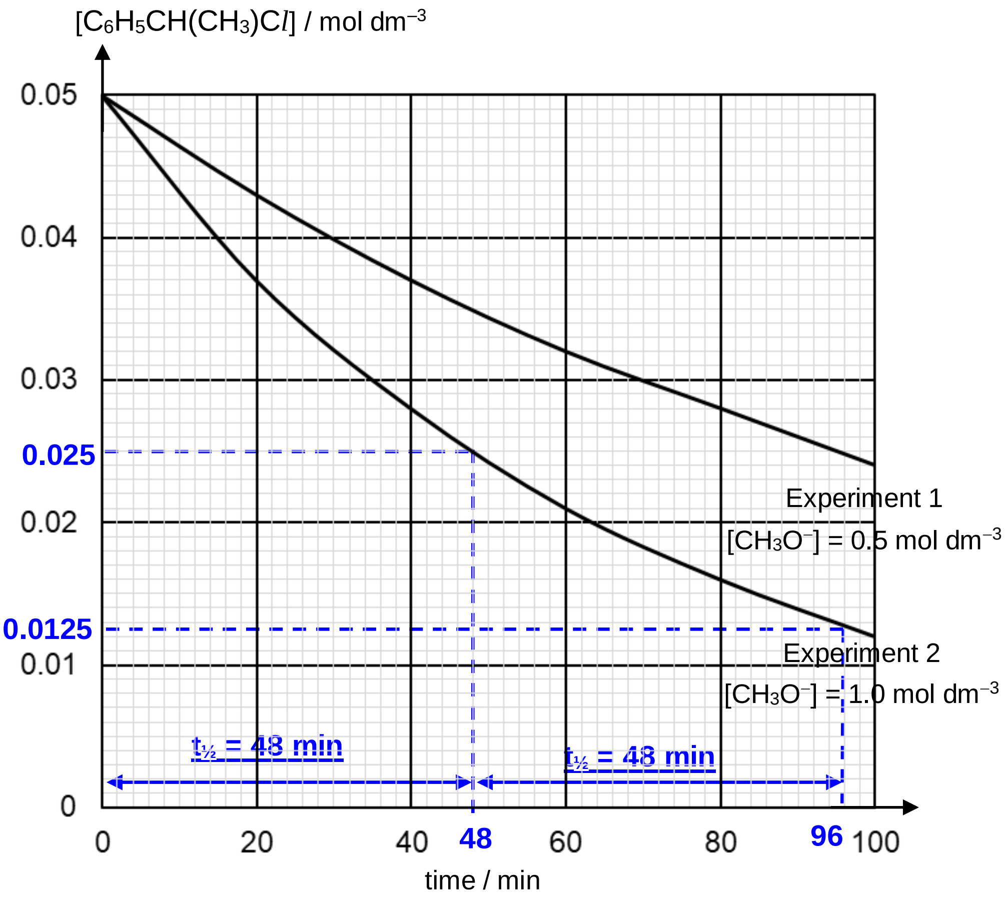
step **4** : Al_2O_3, heat (or excess conc. $H_2SO_4(l)$, heat) step **5** : $LiAlH_4$, dry ether

(iii) Type of mechanism: nucleophilic addition

$HCN \ll H^+ + CN^-$ (or $NaCN \rightarrow Na^+ + CN^-$)



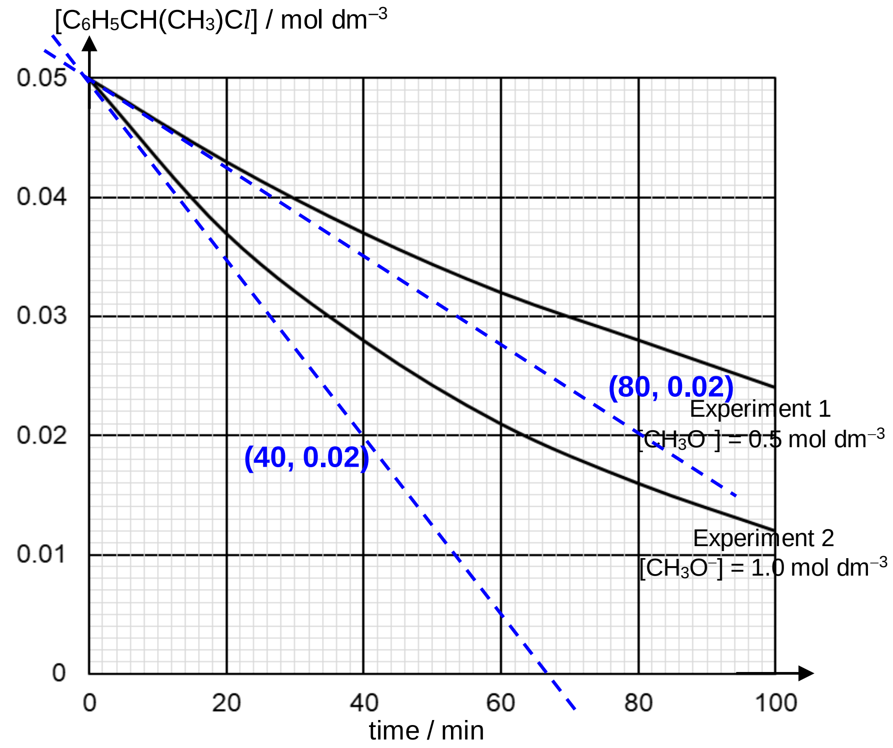
(b) **(i)**



average $t_{½}$ = ½ (48 + 48) = 48 min

Since the half–lives are constant at about 48 min, the order of reaction with respect to [$C_6H_5CH(CH_3)Cl$] is 1.

(ii)



From the graph of $[OH^-] = 1.0$ mol dm^{-3}

Initial rate $= \left|\dfrac{0.02-0.05}{40-0}\right| = 7.50 \times 10^{-4}$ mol dm^{-3} min^{-1}

From the graph of $[OH^-] = 1.0$ mol dm^{-3}

Initial rate $= \left|\dfrac{0.02-0.05}{80-0}\right| = 3.75 \text{ x } 10^{-4}$ mol dm^{-3} min^{-1}

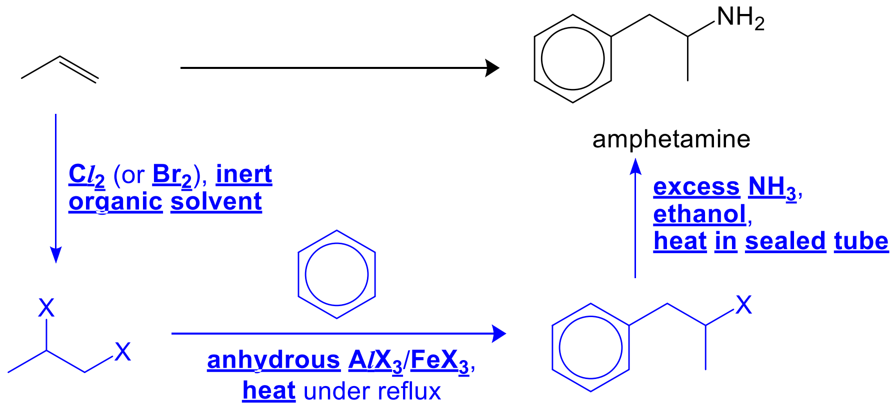
When $[CH_3O^-]$ doubles, the rate is doubled.
Hence, the order of reaction with respect to $[CH_3O^-]$ is 1.

(iii) rate = $k\,[C_6H_5CH(CH_3)Cl]\,[CH_3O^-]$

units of k = $\dfrac{\text{mol dm}^{-3}\ \text{min}^{-1}}{\left(\text{mol dm}^{-3}\right)^2} = \text{mol}^{-1}\,\text{dm}^3\,\text{min}^{-1}$

(iv) Experiment 3: $t_{½}$ of $C_6H_5CH(CH_3)Cl = \dfrac{\ln 2}{k(2.0)} = ½ \times 48 =$ <u>24 min</u>

(c)



4 **(a)** **(i)** Volume of pure methanoic acid in one ant

$= (7.5 \times 10^{-3}) \times \dfrac{50}{100} \times \dfrac{100}{80} = 4.688 \times 10^{-3}\ \text{cm}^3$

No. of ants required to produce 1 cm^3 of pure methanoic acid

$= \dfrac{1}{1000} \div (4.688 \times 10^{-3}) = 214$

(ii) volume of HCOOH injected by one ant $= (7.5 \times 10^{-3}) \times \dfrac{50}{100} = 3.75 \times 10^{-3}\ \text{dm}^3$

mass of HCOOH injected by one ant $= (3.75 \times 10^{-3}) \times 1.2 = 4.50 \text{ x } 10^{-3}$ g

no. of ants needed $= (1.8 \times 0.2) \div (4.50 \text{ x } 10^{-3}) = 80$

(iii) $2HCOOH + Na_2CO_3 \rightarrow 2HCOONa + H_2O + CO_2$

(iv) n(HCOOH) injected by one bee $= (5.4 \times 10^{-3}) \div 30.0 = 1.80 \times 10^{-4}$ mol

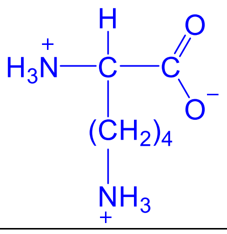
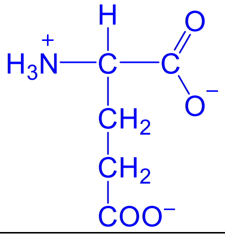
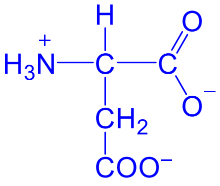
Since $1Na_2CO_3 \equiv 2HCOOH$,

$n(Na_2CO_3)$ required $= ½ \times (1.80 \times 10^{-4}) = 9.00 \times 10^{-5}$ mol

Mass of Na_2CO_3 needed to neutralise one bee sting

$= (9.00 \times 10^{-5}) \times 106.0 = 0.00954$ g

(b)

A	B	C
		

(c) **(i)** Let compound J be $C_xH_yO_z$.

$C_xH_yO_z + (x + \dfrac{y}{4} - \dfrac{z}{2})O_2 \rightarrow xCO_2 + (\dfrac{y}{2})H_2O$

$n(H_2O)$ collected $= 0.038 \div 18.0 = 0.002111$ mol

After cooling:

volume of gases = V(unreacted O_2) + V(CO_2) =140 cm^3

After reaction with NaOH:

V(CO_2) = 90 cm^3

V(unreacted O_2) = 50 cm^3

V(reacted O_2) = 150 – 50 = 100 cm^3

n(CO_2) evolved $= \dfrac{90}{1000} \div 24.0 = 0.00380$ mol

n(reacted O_2) $= \dfrac{100}{1000} \div 24.0 = 0.00417$ mol

$$\begin{array}{ccccccc} C_xH_yO_z & + & (x+\frac{y}{4}-\frac{z}{2})O_2 & \rightarrow & xCO_2 & + & (\frac{y}{2})H_2O \\ & & 0.00417 & & 0.00380 & & 0.00211 \\ & & 2 & & 1.8 & & 1 \\ & & 10 & & 9 & & 5 \end{array}$$

$x = 9$, $y = 10$ and $z =$

Hence, the molecular formula of J is $C_9H_{10}O_3$.

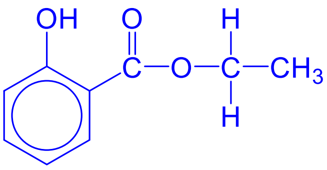
(ii) reaction **1** phenol

reaction **2** carboxylic acid

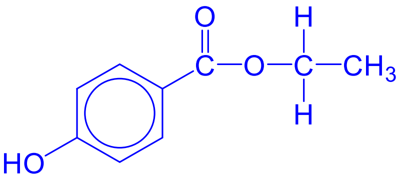
(iii) $C_7H_6O_3$

(iv) $–CH(CH_3)OH$ is present.

(v)



or



(vi) To form K (*i.e.* benzoic acid and phenol), the acid used must be a stronger acid than benzoic acid and phenol (e.g. H_2SO_4 which is a strong acid).

Since the K_a of CF_3CO_2H is higher than that of benzoic acid and phenol, CF_3CO_2H is a stronger acid and hence, it can be used as a replacement for sulfuric acid.

(vii)

- K_a of ethanoic acid is higher than that of phenol,

p–p orbital overlap results in the delocalisation of lone pair on O^- into C=O of CH_3COO^-, dispersing the negative charge over two electronegative O atoms and stabilises CH_3COO^- more than phenoxide ion. Hence, ethanoic acid is a stronger acid and has a higher K_a than phenol.

- K_a of trifluoroethanoic acid is higher than that of ethanoic acid.

The three electron–withdrawing (or electronegative) F atoms disperses the negative charge on O^- of CF_3COO^- and stabilises CF_3COO^- more than CH_3COO^-. Hence, trifluoroethanoic acid is a stronger acid and has a higher K_a than ethanoic acid.

JURONG PIONEER JUNIOR COLLEGE
2019 JC2 H2 CHEMISTRY (9729)
Preliminary Examination Paper 3
(Suggested Answers)

1 **(a)** For HI, violet fumes is observed.

E(H–Cl) = +431 kJ mol^{-1}; E(H–I) = +299 kJ mol^{-1}

Since E(H–I) < E(H–Cl), H–I bond is weaker and is more easily broken than H–Cl bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).

OR

radius of Cl = 0.099 nm; radius of I = 0.133 nm

Since I has a larger radius than Cl, H–I bond is longer and weaker so it is more easily broken than H–Cl bond. Hence, HI is less thermally stable and decomposes more readily (*i.e.* HI decomposes upon contact with the hot wire).

(b) **(i)** $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$

(ii) $E_{cell} = E_{red} - E_{ox}$ (+1.23) – (+1.36) = –0.13 V < 0 (not energetically feasible)

Overall eqn: $MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O$

$\Delta G = -zFE_{cell}$ where z = total number of electrons transferred per overall eqn

$= -(2)(96500)(-0.13) = +25090 \text{ J ol}^{-1} = +25.1 \text{ kJ mol}^{-1}$

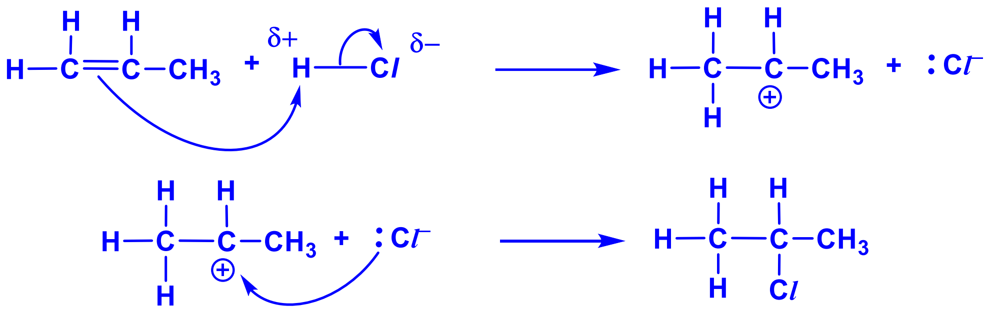
Since ΔG > 0, the reaction is not energetically feasible (or not spontaneous) and thus unlikely to occur.

(iii) When concentrated HCl is used, [H^+] is high and this causes the position of equilibrium of $MnO_2 + 4H^+ + 2e^- \ll Mn^{2+} + 2H_2O$ to shift right so as to react away some H^+ ions. This makes $E(MnO_2/Mn^{2+})$ becomes more positive than +1.23 V such that the E_{cell} becomes positive and ∴ energetically feasible.

When concentrated HCl is used, [Cl^-] is high and this causes the position of equilibrium of $Cl_2 + 2e^- \ll 2Cl^-$ to shift left so as to react away some Cl^- ions. This makes $E(Cl_2/Cl^-)$ becomes more negative (or less positive) than +1.36 V such that the E_{cell} becomes positive and ∴ energetically feasible.

The continuous removal of Cl_2 gas from the reaction mixture as it is evolved shifts the position of equilibrium of $Cl_2 + 2e^- \ll 2Cl^-$ to the left to form back some Cl_2. This makes $E(Cl_2/Cl^-)$ becomes more negative (or less positive) than +1.36 V such that the E_{cell} becomes positive and ∴ energetically feasible.

(c) **(i)** Type of mechanism: electrophilic addition

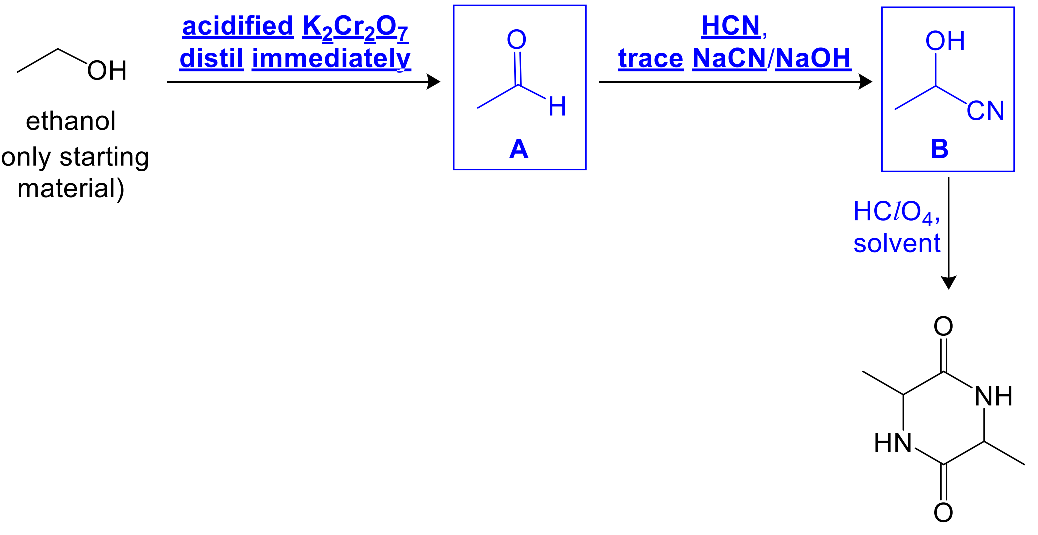


(ii) Propene can use its two π electrons to form a dative bond with H^+ (or to accept a H^+).

(iii) Nucleophilic substitution

(iv) p–p orbital overlap results in the delocalisation of lone pair on O of C–O into the π electron cloud of C=O, forming a partial double bond character in the C–O bond. This strengthens the C–O bond in $–CO_2H$, making it difficult to break. Hence, carboxylic acid is unreactive towards HCl.

(d)



compound **G**

(e) **(i)** val–ala–val–ser–gly–arg–asn–leu–gly–val

or leu–gly–val– val–ala–val–ser–gly–arg–asn

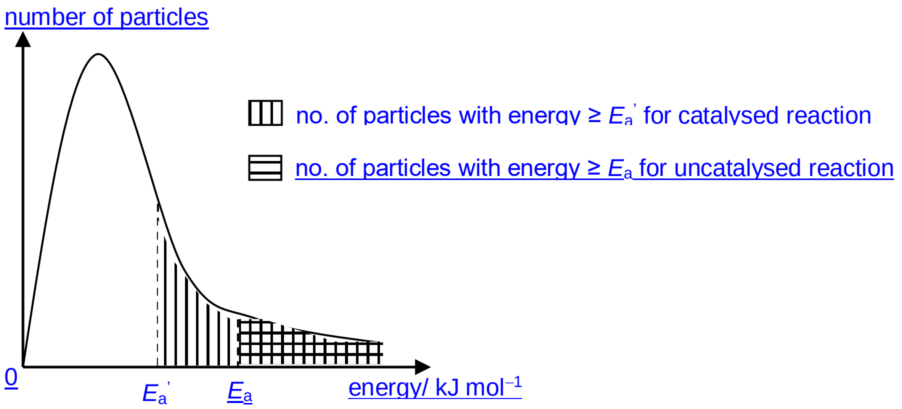
or ser–gly–arg–asn–leu–gly–val– ala–val–ser

(ii) The lone pair on N_a is in the hybridised sp^2 orbital which is perpendicular to the p–orbitals of adjacent C=C and =C–N bonds. Hence, the lone pair on N_a is not delocalised and is available for protonation.

or

The lone pair on N_b is in the unhybridised p orbital which is parallel to the p–orbitals of adjacent C=N and C=C. Hence, the lone pair on N_b is delocalised and less/not available for protonation.

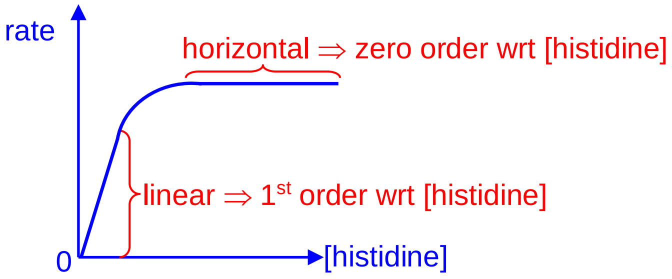
(iii)



When enzyme is used in the decarboxylation reaction, it provides an alternative reaction pathway with lower activation energy, E_a'. This increases the number of reacting particles with energy ≥ E_a'.

Hence, the frequency of effective collisions increases and the rate increases.

(iv)



2 **(a)** For ideal gas, the **volume of gas *particles* is negligible compared to the volume of gas**/**container**.

For ideal gas, there is **no**/**negligible forces of attractions between the gas *particles***.

For ideal gas, the **collision between the gas *particle* is perfectly elastic**.

(b) **(i)**

$$K_p = \frac{p_{O_3}{}^2}{p_{O_2}{}^3}$$

(ii) Using $pV = nRT$ where V is in m^3,

$$c = \frac{n}{V}\text{ mol m}^{-3} = \frac{p}{RT}\text{ mol m}^{-3} = \frac{\boldsymbol{p}}{\mathbf{1000RT}}\text{ mol dm}^{-3}$$

$$K_c = \frac{[O_2]^2}{[O_3]^3} = \left(\frac{p_{O_2}}{1000RT}\right)^2 \times \left(\frac{1000RT}{p_{O_3}}\right)^3$$

$$= K_p \times 1000RT$$

$$= (6.1 \times 10^{-62})(1000)(8.31)(273+25) = 1.5 \times 10^{-55}\text{ Pa}^{-1}\text{ (shown)}$$

(iii) Since $K_p << 1$, it implies that the position of equilibrium $3O_2 \ll 2O_3$ lies on the far left and hence, the forward reaction hardly occurs and there are much less products than reactants at equilibrium.

(iv)

	$3O_2(g)$	$\ll$	$2O_3(g)$
initial conc. / mol dm^{-3}	$10.0 \div 4 = 2.50$		0
change	$-1.5x$		$+x$
eqm conc. / mol dm^{-3}	$2.50 - 1.5x$		x

$$K_c = \frac{[O_3]^2}{[O_2]^3} = \frac{x^2}{(2.50 - 1.5x)^3}$$

Since K_c << 1, we can assume that x << 2.50 such that

$$1.5 \times 10^{-55} \approx \frac{x^2}{2.50^3}$$

equilibrium $[O_2]$, $x = 1.53 \times 10^{-27}$ mol dm^{-3}

(c) **(i)** $3SO_2 + O_3 + 3H_2O \rightarrow 3H_2SO_4$

(ii) More energy is required to remove H^+ from negatively charged ion HSO_4^- than from electrically neutral H_2SO_4 due to greater electrostatic force of attraction.

Hence, HSO_4^- is a weaker acid than H_2SO_4.

(iii)

	SO_4^{2-}	+	H^+	$\rightarrow$	HSO_4^-
initial amt	$0.200 \times \frac{10}{1000}$ $= 0.002$		$0.100 \times \frac{5}{1000}$ $= 0.0005$		0
change	-0.0005		-0.0005		$+0.0005$
final amt / mol	0.0015		0		0.0005

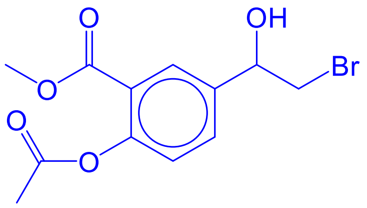
System: acidic buffer (mixture contain weak acid HSO_4^- and its salt SO_4^{2-})

$$pH = pK_a + \lg\frac{[\text{salt}]}{[\text{acid}]} = [-\lg(0.012)] + \lg\left(\frac{0.0015}{0.0005}\right) = 2.40$$

(d) p–p orbital overlap results in the delocalisation of lone pair of electrons on O of phenol into benzene ring, making the lone pair less available for donation. Hence, phenol is a weaker nucleophile than alcohol (or less reactive towards nucleophilic reaction).

Reagent and condition: (1) NaOH(aq), room temperature
(2), $CH_3COCl(l)$, room temperature

(e) **(i)**



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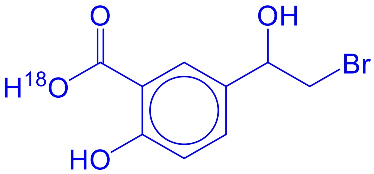
(ii)



(iii) excess $(CH_3)_3NH_2$, ethanol, heat in sealed tube

(iv) If step 2 is carried out first, the phenolic group can undergo electrophilic substitution.

(v) The N of salbutamol still possesses a lone pair and can function as a nucleophile for further substitution to occur.

3 **(a)** **(i)** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

(ii) The maximum oxidation state is determined by the total number of 4s electrons and unpaired 3d electrons.

Since the total number of 4s and unpaired 3d electrons increases from Sc to Mn and decreases from Mn to Zn, the maximum oxidation state increases from Sc to Mn then decreases from Mn to Zn.

(iii) Sc^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Iron(III) salt are usually coloured due to d–d transition.

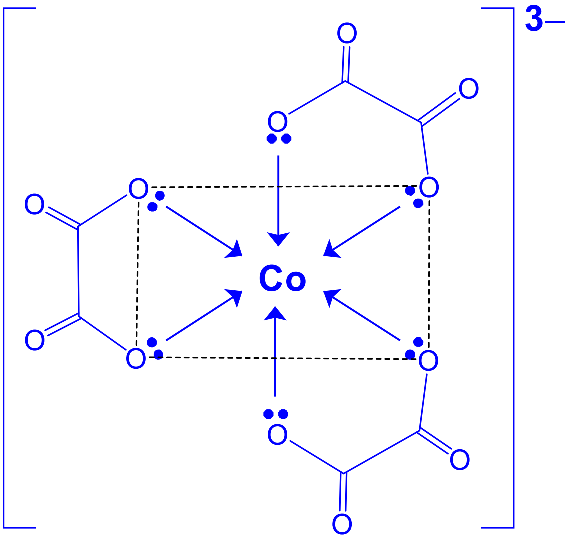
The presence of ligands causes the d orbitals to split into 2 different energy levels with relatively small energy difference, ΔE.

Radiation from the visible light region of the electromagnetic spectrum, corresponding to ΔE, is absorbed when an electron transits from a d orbital of lower energy to partially filled d orbital of higher energy.

Hence, iron(III) salts are coloured and the colour observed is the complement of the colours absorbed.

On the other hand, Sc^{3+} has no 3d electron and hence electron transition between d orbitals is not possible and radiation from visible light region is not absorbed.

(iv)



(b) **(i)**

$$Cu^{2+} + 4Cl^{-} + Cu \ll 2[CuCl_2]^{-} \text{ ---(1)}$$

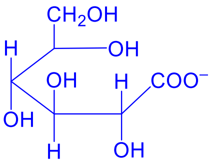
Cu^{2+} undergoes redox reaction with Cu foil to form a stable colourless $[CuCl_2]^-$ complex in the presence of Cl^- due to ligand exchange reaction.

The evaporation/removal of water due to heating causes the concentration of all aqueous species to increase while $[H_2O]$ remains relatively constant. This causes the position of equilibrium (1) to shift to the right side which has less concentration terms of aqueous species (excludes $[H_2O]$).

(ii) CuC*l*

(c) **(i)** Red-brown ppt of Cu_2O formed.

Structure of organic product:



(ii) Since glucose has chiral carbons and has no plane of symmetry, it can exhibit enantiomerism.

Since there is restricted rotation around the C–C bond of the ring structure, it can exhibit cis–trans isomerism.

(iii) Let the percentage of α–glucose in the mixture be x % and that of β–glucose is (100–x) %.

$$\left[(+113.4)\times\frac{x}{100}\right]+\left[(+19.0)\times\frac{100-x}{100}\right]=+52.2$$

% of α–glucose in the mixture, x = 35. 2 %

(iv) Disproportionation

4 **(a)** **(i)** Electronegativity increases across the period and decreases down the group. Hence, beryllium and aluminium have similar electronegativity and have similar properties.

(ii) $\mathrm{BeC}l_2$ has simple covalent/molecular structure while BeO has a giant ionic structure.

Less energy is required to overcome the weaker instantaneous dipole–induced dipole attraction between $\mathrm{BeC}l_2$ molecules than that required for the stronger ionic bonds between Be^{2+} and O^{2-}.

Hence, the boiling point of $\mathrm{BeC}l_2$ is lower than that of BeO.

(iii) $\mathrm{BeC}l_2$ dissolves in water to give $[\mathrm{Be(H_2O)_4}]^{2+}$ which hydrolyses (or react with water) to give an acidic solution. Due to the high charge density of Be^{2+}, it can polarise and weaken the O–H bond in the coordinated $\mathrm{H_2O}$ molecules, releasing H^+ into the solution.

Hence, a weakly acidic solution is formed and causes a beaker of litmus solution to change from purple to red.

Hydration: $\mathrm{BeC}l_2 + 4\mathrm{H_2O} \rightarrow [\mathrm{Be(H_2O)_4}]^{2+} + 3\mathrm{C}l^-$

Hydrolysis: $[\mathrm{Be(H_2O)_4}]^{2+} \ll [\mathrm{Be(H_2O)_3OH}]^+ + \mathrm{H}^+$

(b) **(i)** Since the A_r of Pb is 207.2, compound A can only contain 1 Pb.

% by mass of Pb in A = $\frac{207.2}{290} \times 100\ \% = 71.45\ \%$

% by mass of F in A = 100 – 71.45 – 3.08 = 25.47 %

element	Pb	Be	F
mass in 100 g / g	71.45	3.08	25.47
amount / mol	$\frac{71.45}{207.2} = 0.3448$	$\frac{3.08}{9.0} = 0.3422$	$\frac{25.47}{19.0} = 1.341$
simple ratio	1	1	4

Hence, the empirical formula of A is $\mathrm{PbBeF_4}$ and thus, $x = 1$ and $y = 4$.

or

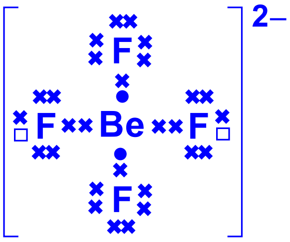
mass of Be in one mol of $\mathrm{PbBe_xF_y} = \frac{3.08}{100} \times 290 = 8.932$ g

mass of F in one mol of $\mathrm{PbBe_xF_y}$ = 290 – 207.2 – 8.932 = 73.868 g

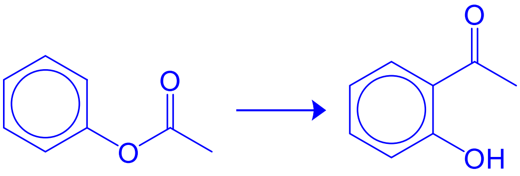
element	Pb	Be	F
mass in 100 g / g	207.2	8.932	73.868
amount / mol	$\frac{207.2}{207.2} = 1$	$\frac{8.932}{9.0} = 0.9924$	$\frac{73.868}{19.0} = 3.888$
simple ratio	1	1	4

Hence, the empirical formula of A is $\mathrm{PbBeF_4}$ and thus, $x = 1$ and $y = 4$.

(ii) $BeF_2 + 2KF \rightarrow K_2BeF_4$ (∴ anion is BeF_4^{2-})



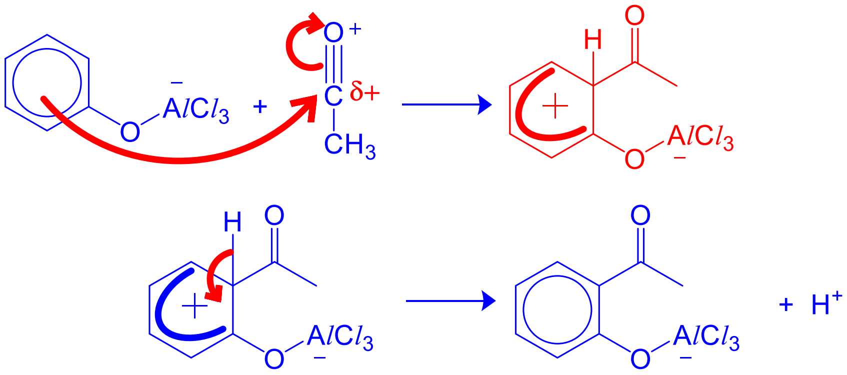
(c) **(i)**



(ii) $AlCl_3$ is acting as a catalyst since it reacted in step 1 and was regenerated in step 4.

$AlCl_3$ is also acting as a Lewis acid since it accepted a lone pair of electrons from O atom of phenyl ethanoate via dative–bond formation.

(iii)



(iv) Test: Add neutral $FeCl_3$(aq) to the reaction mixture.

Obs: If 2–hydroxyacetophenone is formed, violet coloration is formed.

or

Test: Add Br_2(aq) to the reaction mixture.

Obs: If 2–hydroxyacetophenone is formed, orange Br_2 decolourised.

or

Test: Add 2,4–DNPH to the reaction mixture.

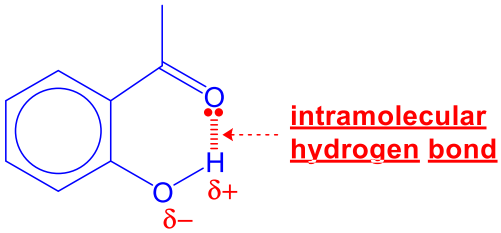
Obs: If 2–hydroxyacetophenone is formed, orange ppt is formed.

or

Test: Add alkaline I_2(aq) to the reaction mixture and heat.

Obs: If 2–hydroxyacetophenone is formed, pale yellow ppt is formed.

(v)



Checklist for hydrogen bonding:
- δ+ on H and δ– on O of O–H
- lone pair on O of C=O
- dotted line to represent hydrogen bond
- label "intramolecular hydrogen bond"

2–hydroxyacetophenone can form intramolecular hydrogen bond due to the close proximity of C=O and –OH groups, stabilising it and hence, 2–hydroxyacetophenone is likely to form in larger proportion.

(d) Electron–withdrawing $-CO_2H$ reduces the electron density of benzene and makes the benzene ring less electron–rich, causing phenyl ethanoate to be less reactive toward electrophilic attack. Hence, the rate of Fries rearrangement is slower for B compared to phenyl ethanoate.

5 **(a)** **(i)** *Bond energy* is the heat energy required when 1 mole of covalent bond in gaseous phase is broken into gaseous atoms.

(ii)

Bonds broken			Bonds formed	
C=C	+610		3C–C	3(+350)
C–N	+305			
Total	+915		Total	+1050

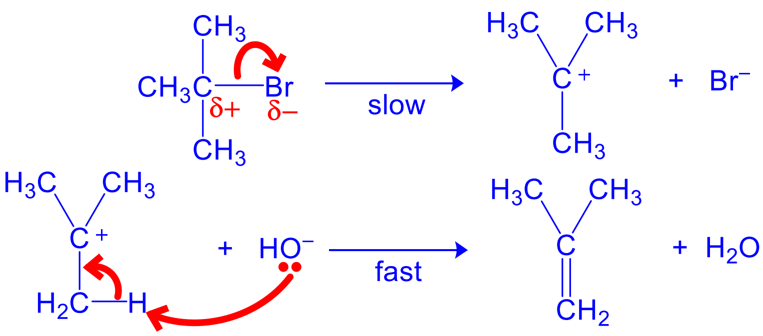
$\Delta H_r = (+915) - (+1050) = -135\ \text{kJ mol}^{-1}$

(iii) The ring strain in cyclopropane (or angle strain due to the rigid 3–membered ring structure of cyclopropane) weakens the C–C bond.

(b) **(i)** Since E1 is a unimolecular reaction, it implies that the rate–determining step involves only one unit of a chemical species. From the description of E1 given, the first step is the rate–determining step and hence, the rate equation for E1 is rate = $k[(CH_3)_3CBr]$.

Since E2 is a bimolecular elementary reaction, it implies that it is one step mechanism (*i.e.* mechanism is the same as overall equation). Hence, the rate equation for E2 is rate = $k[(CH_3)_3CBr][OH^-]$.

(ii)



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(iii) Since the rate–determining step does not involve the base (or zero order w.r.t the base or only $(CH_3)_3CBr$ is involved), changing $CH_3CH_2O^-$ to $(CH_3)_3CO^-$ would not change the rate of the E1 reaction.

(c) **(i)** $CH_3CHBr(CH_3)_2 + OH^- \rightarrow CH_3CH(OH)(CH_3)_2 + Br^-$

(ii) E1 proceeds with an increase in entropy/disorderliness in the system since the number of particles increases from 2 mol to 3 mol but no change for S_N1. Hence, ΔG of E1 becomes more negative with increasing temperature.

(iii) Benzyl chloride does not have adjacent C–H for elimination to occur.

p–p orbital overlap results in the delocalisation of the positive charge on C^+ into benzene ring, dispersing the positive charge and stabilising the carbocation.

(iv) Since the pK_a decreases from HF to HI, it implies that the position of equilibrium of $HX \ll H^+ + X^-$ lies increasingly more to the right.

Hence, the stability of leaving group X^- increases from F^- to I^- and the reactivity towards nucleophilic substitution increases from alkyl fluoride to alkyl iodide.

JURONG PIONEER JUNIOR COLLEGE
2019 JC2 H2 CHEMISTRY (9729)
Preliminary Examination Paper 4
(<u>Suggested Answers</u>)

1 Determination of the identity of the halogen, X, in CH_2XCO_2H

(a) (ii) Titration results

Titration number	1	2
Final burette reading / cm^3	24.90	34.95
Initial burette reading / cm^3	0.00	10.00
Volume of FA3 used / cm^3	24.90	24.95
	✓	✓

(iii) average volume of **FA 3** used , $V_{FA3} = \dfrac{24.90 + 24.95}{2} = 24.93$ cm^3

(b) (i) $n(H_2SO_4)$ in 10.0 cm^3 of **FA 2** $= 2.00 \times \dfrac{10.0}{1000} = 0.0200$ mol

$= n(H_2SO_4)$ in 250 cm^3 **FA 3**

$[H_2SO_4]$ in **FA 3** $= 0.020 \div \dfrac{250}{1000} = 0.0800$ mol dm^{-3}

or

Using $c_1V_1 = c_2V_2$,

$[H_2SO_4]$ in **FA 3** $= \dfrac{2.00 \times 10.0}{250} = 0.0800$ mol dm^{-3}

(ii) $n(H_2SO_4)$ reacted in titration $= \dfrac{24.93}{1000} \times 0.0800 = 0.001996$ mol

Since $1H_2SO_4 \equiv 2$ NaOH,

n(NaOH) in 25.0 cm^3 of **FA 1** $= 0.001992 \times 2 = 0.00399$ mol

(iii) n(NaOH) in 250 cm^3 of **FA 1**

$= 0.00399 \times \dfrac{250}{25.0} = 0.0399$ mol

= n(NaOH) left unreacted after reaction with **W**

n(NaOH) added to **W** = $\times 0.40 = 0.100$ mol

n(NaOH) reacted with **W** = $0.100 - 0.0399 = 0.0601$ mol

(iv) From equation 1 and 2, since 1**W** ≡ 2NaOH,

n(**W**) in 4 g = ½ × 0.0601 = 0.03004 mol

M_r of W = 4 ÷ 0.03004 = 133.2 ≈ 133 (no units)

A_r of X = 133.2 – 59 = 74.2 (no units)

X is bromine/ Br

(c) **(i)** max. % error in volume of **FA3** used = $\frac{2(\pm 0.05)}{24.95} \times 100 = \pm\, 0.401\ \%$

(ii) Error : Mass measurement of W was not precise as the mass was given to nearest g.

Modification : Use a more precise weighing balance that can measure to 3.d.p.

or

Error : Substitution of halogeno group may be incomplete.

Modification : Heat W with NaOH for a longer period of time.

or

Error : Loss of product through heating.

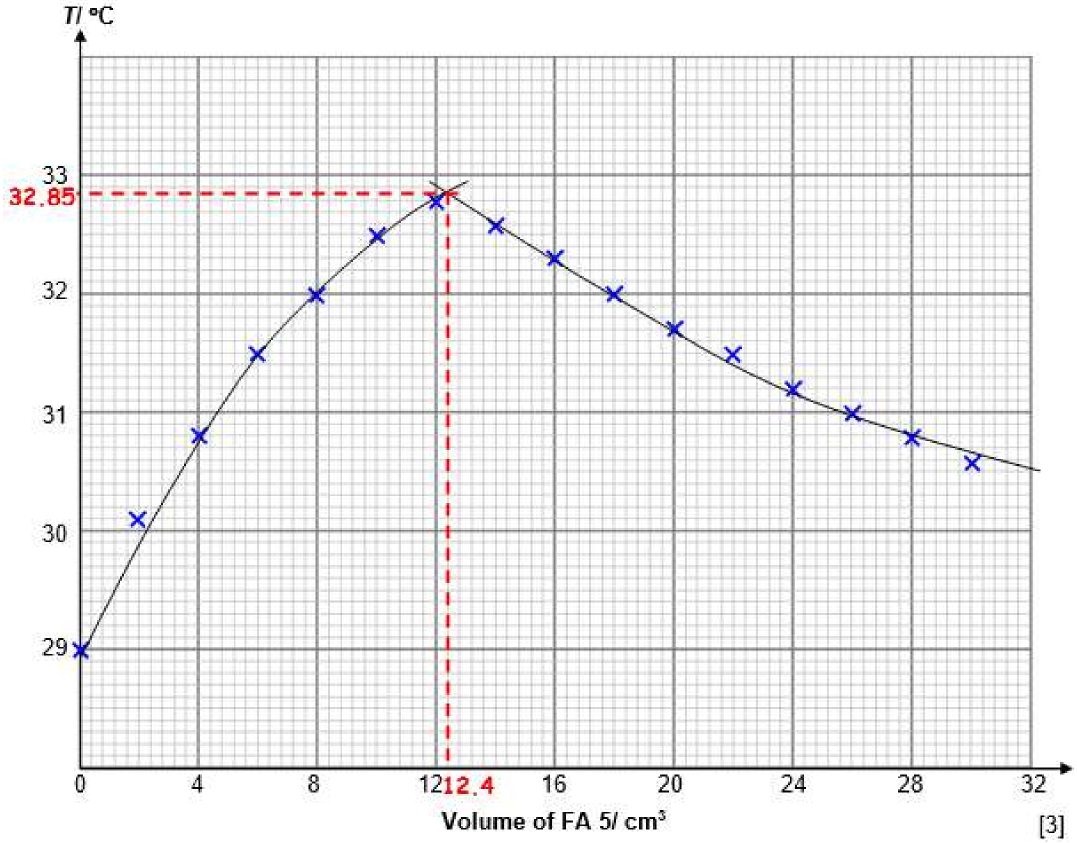
Modification : Heat the reaction mixture under reflux

2 **An experiment to investigate the behaviour of acids and bases in aqueous solutions**

(a) **Determination of the enthalpy change of reaction between FA 4 and FA 5**

Total volume of FA 5 added/ cm^3	Maximum temperature/ °C
0.00	29.0
2.00	30.1
4.00	30.8
6.00	31.5
8.00	32.0
10.00	32.5
12.00	32.8
14.00	32.6
16.00	32.3
18.00	32.0
20.00	31.7
22.00	31.5
24.00	31.2
26.00	31.0
28.00	30.8
30.00	30.6

(b) **(i)**



[3]

(ii) & (iii) correctly reads T_{max} to ±½ small square + correctly calculates ΔT_{max} + correctly reads $V_{equivalence}$ to ±½ small square.

(iv) $n(NaHCO_3)$ used = $\frac{25.0}{1000} \times 1.00$ = 0.0250 mol = n(NaOH) reacted

[NaOH] in **FA 5** = $0.0250 \div \frac{12.4}{1000} = 2.02$ mol dm^{-3}

(v) From the graph, $V_{equivalence}$ = 12.4 cm^3.

heat evolved, q = (25.0 + 12.4)(4.18)(3.85)= 603 J

$\Delta H_3 = -(603 \times 10^{-3}) \div 0.0250 = -24.1$ kJ mol^{-1}

(c) **The reaction between FA 4 and FA 2**

(d) $T_{average} = \frac{(40.0 \times 28.6) + (15.0 \times 28.9)}{(40.0 + 15.0)}$ = 28.7 °C

heat absorbed, q = (40.0 + 15.0)(4.18)(28.7 – 28.2) = 115 J

$n(NaHCO_3)$ used = $1.00 \times \frac{40.0}{1000}$ = 0.0400 mol

Since $NaHCO_3$ is the limiting reagent,

$\Delta H_4 = +(115 \times 10^{-3}) \div 0.0400 = +2.87$ kJ mol^{-1}

(e)

$H^+ + OH^- \rightarrow H_2O$	$\Delta H_{neutralisation} = -57.0$
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$	$\Delta H_3 = -24.1$
$H_2O + CO_2 \rightarrow HCO_3^- + H^+$	$-\Delta H_4 = -(+2.87)$
Overall: $2OH^-(aq) + CO_2(g) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	ΔH_5

$\Delta H_5 = (-57.0) + (-24.1) -(+2.87) = -84.0$ kJ mol^{-1}

(g) **reaction 3**

role of HCO_3^- ions Bronsted acid

explanation HCO_3^- is a proton donor (or loses a proton).

reaction 4

role of HCO_3^- ions Bronsted base

explanation HCO_3^- is a proton acceptor (or gains a proton).

3 **Investigation of some reactions involving transition element ions.**

		tests	observations
(a)	**(i)**	Add one spatula of **FA 6** to a hard-glass test-tube. Heat gently for about 10s and then strongly for about 20s. Leave the test-tube and residue to cool completely. Keep the residue for use in **3(a)(ii)**. **While waiting, you can start on 3(d).**	O_2 gas relights glowing splint. Black residue obtained.
	(ii)	Add deionised water to a small beaker until it is about half full. Place the beaker on a white tile. Pour the cooled residue from **3(a)(i)** **slowly** into the deionised water in the beaker. **Observe the solution closely.**	Solid dissolves to form green solution which then turns purple.
		Swirl the solution and filter a small portion of this solution into a clean test-tube. The filtrate is **FA 7**.	Purple filtrate obtained. Dark brown residue obtained.
	(iii)	Add 1 cm depth of **FA 7** to a test-tube. Add Fe^{2+}(aq), slowly with shaking, until no further change is seen.	Purple FA 7 turns yellow/orange/ brown and then pale green/ colourless.

(b) **(i)** The green solution obtained immediately when water is added to the residue is MnO_4^{2-}.

$E_{cell} = E_{red} - E_{ox} = (+2.26) - (+0.56)$

$= +1.70$ V > 0 (energetically feasible)

Green MnO_4^{2-} is oxidised to purple MnO_4^- and reduced to brown MnO_2 ppt.

(ii) disproportionation

(c) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

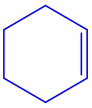
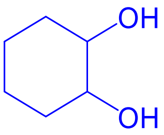
(d)

		tests	observations
	(i)	Add 2 cm depth of aqueous sodium hydroxide in a test-tube. Add 5 drops of **FA 8** to this test-tube. Add a few drops of aqueous potassium manganate(VII).	Solution turns green. Green solution then turns brown/brown ppt. formed.
	(ii)	Add 2 cm depth of aqueous sulfuric acid in a test-tube. Add 5 drop of **FA 8** to this test-tube. Add a few drops of aqueous potassium manganate(VII). Place the mixture in the hot water bath for a few minutes.	Purple FA 9 decolourises.
	(iii)	Add 5 cm depth of deionised water in a test-tube. Add 1 drop of **FA 8** to this test-tube. Add aqueous bromine slowly, with shaking, until no further change is seen.	Yellow aqueous bromine decolourises

(e) **(i)** molecular formula of **FA 8** C_6H_{10}

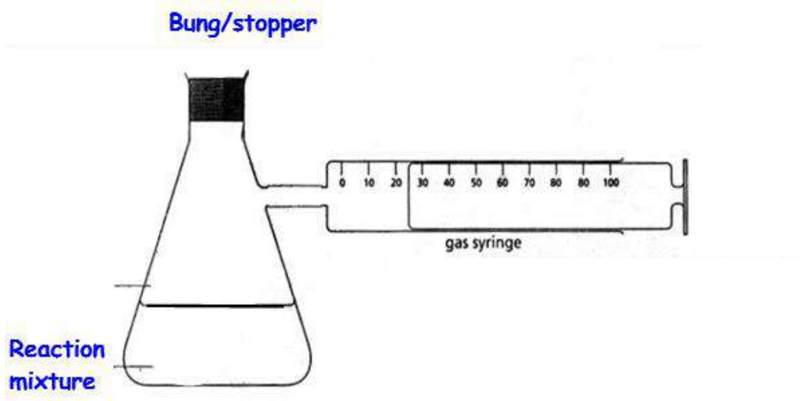
explanation **FA 8** undergoes oxidation from alkene to give diol.

(ii)

FA 8	compound **Z**
	

4 Planning

(a)



1. Use a burette to transfer 50.00 cm^3 of $KMnO_4$ into a conical flask.
2. Using a 50.0 cm^3 measuring cylinder, transfer 50.0 cm^3 of H_2SO_4 into the same conical flask. Using a dropper, add 1 cm^3 of $MnSO_4$(aq) to the conical flask.
3. Using a 50.0 cm^3 measuring cylinder, measure 50.0 cm^3 of $Na_2C_2O_4$.
4. Transfer the $Na_2C_2O_4$ to the conical flask and quickly insert the bung into the conical flask. Immediately start the stopwatch and swirl the conical flask.
5. Record time taken using stopwatch when 40 cm^3 of gas is collected in the gas syringe.
6. Repeat steps 1 to 5 for 4 other experiments, using the volumes as shown in the table below. Measure deionised water using a measuring cylinder.

Expt	Vol $KMnO_4$ /cm^3	Vol deionised water/cm^3	Vol H_2SO_4 /cm^3	Vol $Na_2C_2O_4$ /cm^3	Vol Mn^{2+} /cm^3	*t*/s
1	50.00	0.0	50.0	50.0	1	
2	40.00	10.0	50.0	50.0	1	
3	30.00	20.0	50.0	50.0	1	
4	20.00	30.0	50.0	50.0	1	
5	10.00	40.0	50.0	50.0	1	

(b)

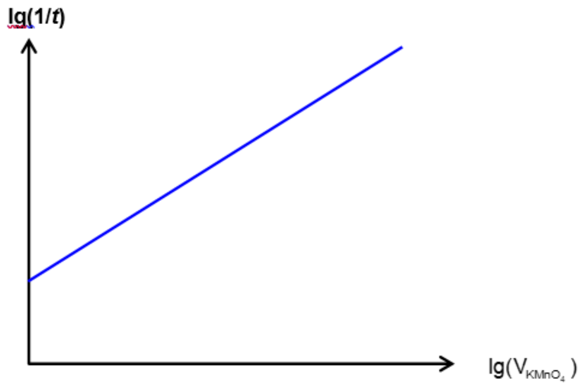


Fig 4.1

Rate = $k'[KMnO_4]^a$

Since rate $\propto$ 1/*t* and $[KMnO_4] \propto V_{KMnO4}$ since total volume is kept constant,

$1/t = k'(V_{KMnO4})^a$

$\lg(1/t) = \lg k' + a \lg(V_{KMnO4})$

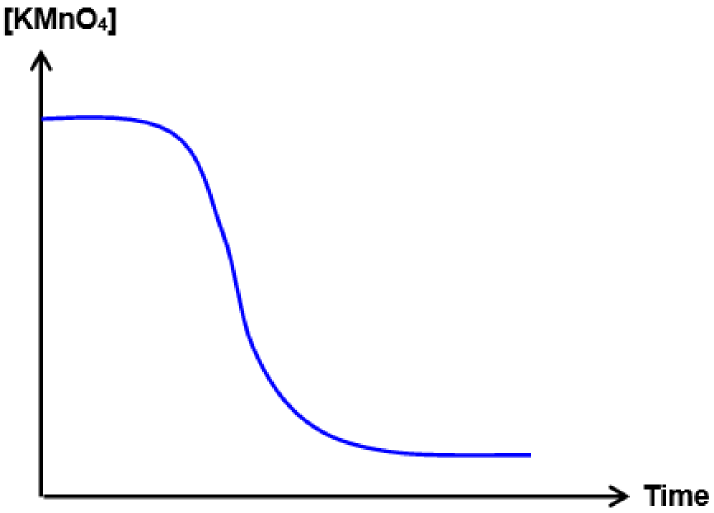
$\lg(1/t) = a \lg(V_{KMnO4}) + \lg k'$ which is similar to a y = mx + c straight line graph

(c) Gradient of the line = order of reaction

(d) **(i)** The reaction is slow as it has high activation energy due to the repulsion between both the negatively charged MnO_4^- and $C_2O_4^{2-}$.

(ii) Homogenous catalyst since Mn^{2+}(aq) is in the same phase as the reactants.

(iii)



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2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **24 Sept 2019**

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 **15** 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 Which of the following contain one mole of the stated particles?

1 H^+ ions in 1 dm^3 of 0.5 mol dm^{-3} H_2SO_4(aq)
2 atoms in 6 dm^3 of SO_3(g) at room temperature and pressure
3 electrons in 64.1 g of SO_2
4 neutrons in 1.6 g of $^{32}S_8$

A 1 and 2 only **B** 2 only **C** 1 and 3 only **D** 1, 2, 3 and 4

2 Incomplete combustion of *y* dm^3 of propanol gas yielded a mixture of carbon dioxide and carbon monoxide in the ratio of 2:1, together with water vapour.
What is the volume of oxygen consumed?

A 3.5y dm^3 **B** 4y dm^3 **C** 4.5y dm^3 **D** 5y dm^3

3 The redox reaction between potassium manganate(VII) and $MnSO_4$ gives MnO_2 as the only manganese-containing product.
How many moles of $MnSO_4$ react with one mole of potassium manganate(VII) in this reaction?

A 0.5
B 1
C 1.5
D 2

4 The ion **Z**$^{2+}$ has 12 electrons and 15 neutrons.

Which of the following statements is true?

A In an electric field, the ion **Z**$^{2+}$ will be deflected at a smaller angle than that of Mg^{2+}.

B The first ionisation energy of element **Z** is lower than that of the Group 13 element in the same period as **Z**.

C The chloride of **Z** formed is expected to have a higher melting point than $MgCl_2$.

D Element **Z** is isoelectronic with neon.

5 Consider the following four compounds.

1 $CH_3CH_2CH_2CH_3$

2 $CH_3CH_2CH_2OH$

3 CH_3CH_2Cl

4 $(CH_3)_3CH$

What is the order of increasing boiling point of the compounds?

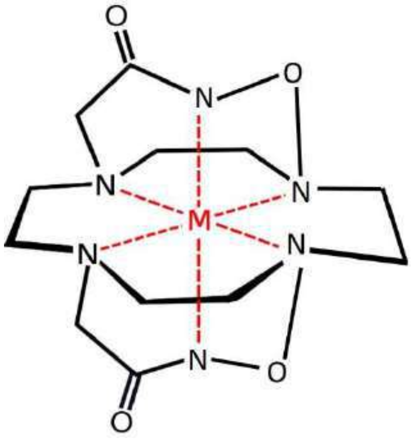
A 1 < 4 < 3 < 2

B 2 < 3 < 4 < 1

C 4 < 1 < 2 < 3

D 4 < 1 < 3 < 2

6 The research on metal complexes have achieved many international breakthrough developments, focusing on their properties and wide range of applications to tackle the challenges in human health and the environment.



Which of the following types of bonding can be found in the complex?

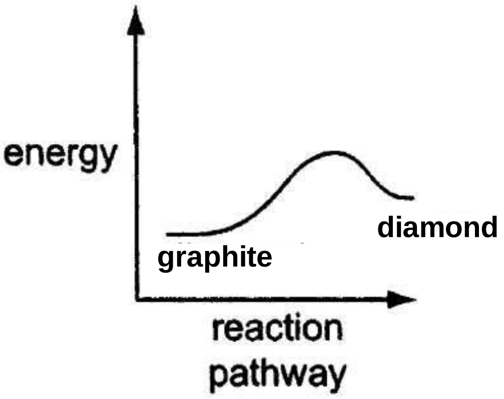
1 ionic bonding
2 dative bonding
3 hydrogen bonding
4 ion-dipole interactions

A 2 only **B** 1 and 2 only **C** 1 and 4 only **D** 2, 3 and 4 only

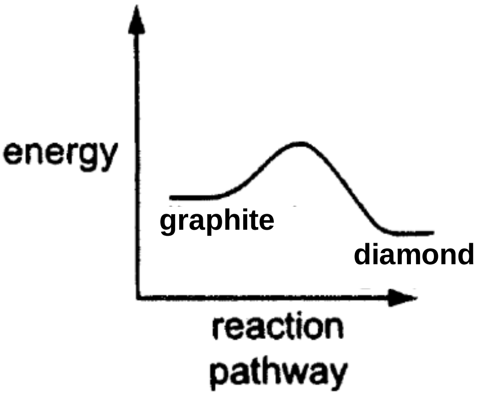
7 The conversion of graphite into diamond is endothermic and this reaction has an extremely small rate constant.

Which reaction pathway correctly represents this conversion?

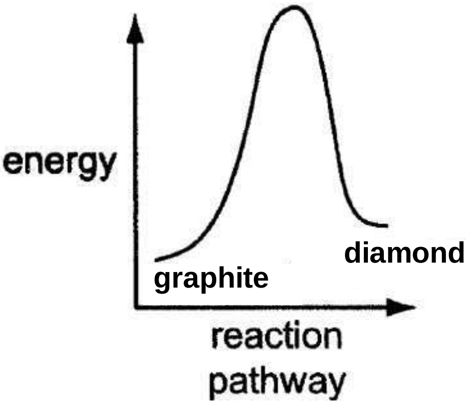
A



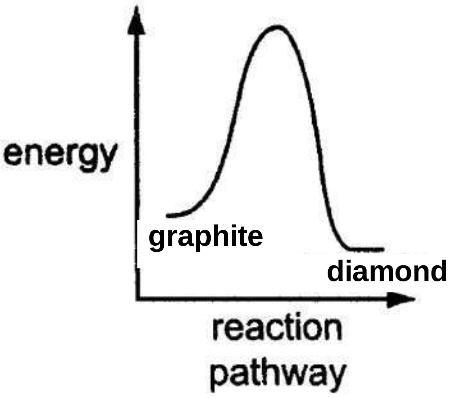
B



C



D



8

Reaction 1	Evaporation of ethanol
Reaction 2	Atomisation of magnesium
Reaction 3	Initiation step for the free radical substitution between chlorine and ethane

Which of the following statements about the reactions are correct?

1 ΔH is positive for all reactions.

2 ΔS is positive for all reactions.

3 ΔG is positive for all reactions.

A 1 only **B** 2 only **C** 1 and 2 only **D** 1,2 and 3

9 When the temperature of a closed vessel containing a gas is increased by 273 °C, the pressure was found to increase by 20%.
What is the initial temperature of the closed vessel?

A 1092 °C **B** 1092 K **C** 1365°C **D** 1365 K

10 Which of the following two species are acting as an acid and a conjugate acid respectively in the following reaction?

$$H_2O + ClO^- \rightleftharpoons HOCl + OH^-$$

A H_2O and HOC*l*

B OH^- and H_2O

C OH^- and C*l*O^-

D HOC*l* and C*l*O^-

11 The reaction for $A + 2B \rightarrow AB_2$ occurs by the following mechanism.

Step 1 $A + B \rightleftharpoons AB$ (fast)

Step 2 $AB + B \rightarrow AB_2$ (slow)

Which of the following represents the correct rate equation?

A Rate = k[A] **B** Rate = k[B] **C** Rate = k[AB][B] **D** Rate = $k[A][B]^2$

12 The following data was obtained during the first-order decomposition of the reaction:

$$2A(g) \rightarrow B(g) + C(s)$$

Time	Total pressure
10 min	300 Pa
After completion	200 Pa

Given that the reaction took place in a sealed container at constant temperature, what is the half-life of the reaction?

A 5 min

B 10 min

C 15 min

D 20 min

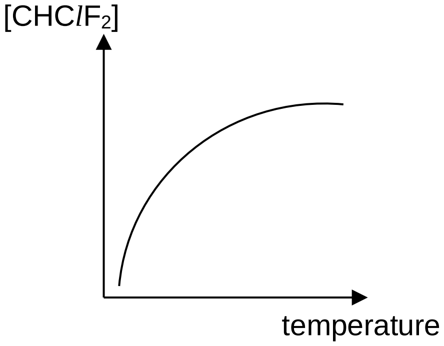
13 Chlorofluorocarbons (CFCs) are nontoxic, nonflammable chemicals containing atoms of carbon, chlorine, and fluorine. They are used in the manufacture of aerosol sprays, blowing agents for foams and packing materials, as solvents, and as refrigerants.

$$2CHClF_2\ (g) \rightleftharpoons CF_2{=}CF_2\ (g) + 2HCl\ (g)$$

Species	**Standard enthalpy change of formation / kJ mol^{-1}**
$CF_2{=}CF_2(g)$	–658.3
$HCl(g)$	–92.3
$CHClF_2(g)$	–485.2

Based on the data provided, which of the following describes how would the concentration of $CHClF_2(g)$ at equilibrium varies with temperature?

A



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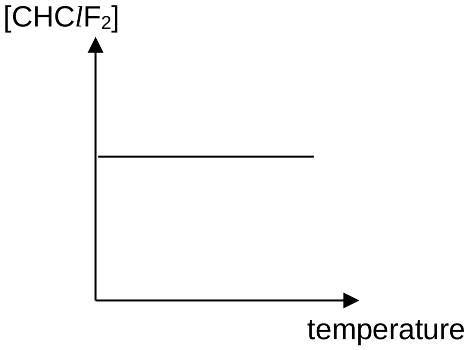
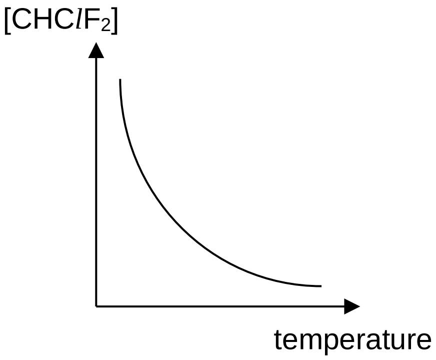
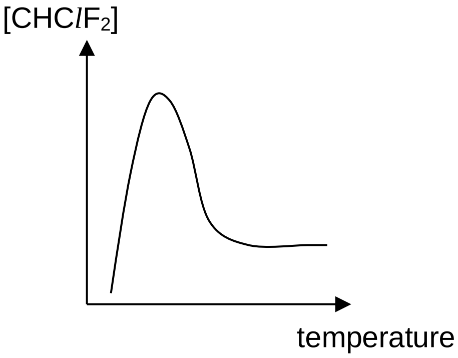


C



D



14 Which of the following mixtures will form a solution that resist pH changes when small quantites of acid or base is added?

A 500 cm^3 of 1 mol dm^{-3} aqueous $NaCl$ and 500 cm^3 of 1 mol dm^{-3} aqueous HCl

B 750 cm^3 of 1 mol dm^{-3} aqueous CH_3COOH and 250 cm^3 of 1 mol dm^{-3} aqueous NaOH

C 600 cm^3 of 1 mol dm^{-3} aqueous NH_3 and 400 cm^3 of 1 mol dm^{-3} aqueous H_2SO_4

D 400 cm^3 of 1 mol dm^{-3} aqueous NaOH and 600cm^3 of 1 mol dm^{-3} aqueous H_2SO_4

15 What is the final pH of the solution formed by mixing equal volumes of two H_2SO_4 solutions, one of pH 2.0 and the other of pH 3.0?

A 1.96 **B** 2.26 **C** 2.50 **D** 2.78

16 **Q**, **R** and **S** are three elements found in Period 3 of the Periodic Table.

Among the elements in Period 3,

- the melting point of the oxide of **R** is the highest.
- the electrical conductivity of **Q** is the highest.
- the melting point of **S** is the lowest.

Which of the following elements is **not** represented by **Q**, **R** or **S**?

A Na **B** Mg **C** A*l* **D** Ar

17 Fluorine has anomalous properties in Group 17.

Which of the following statements is correct?

A HF is a strong acid.

B Fluorine is intensely coloured.

C The melting point of fluorine is high.

D The F–F bond is unusually weak.

18 *Use of the Data Booklet is relevant to this question.*

Each galvanic cell is made up of two half-cells. E_1, E_2 and E_3 are the cell potentials of the three galvanic cells respectively.

Half-cell 1	Half-cell 2	E_{cell}
1 mol dm^{-3} Zn^{2+}(aq) and Zn	0.1 mol dm^{-3} Cu^{2+}(aq) and Cu(s)	E_1
1 mol dm^{-3} Zn^{2+}(aq) and Zn	1 mol dm^{-3} Cu^{2+}(aq)and Cu(s)	E_2
0.1 mol dm^{-3} Zn^{2+}(aq) and Zn	1 mol dm^{-3} Cu^{2+}(aq) and Cu(s)	E_3

Which of the following shows the correct sequence of E_{cell} arranged in decreasing order?

A $E_2 > E_3 > E_1$

B $E_3 > E_2 > E_1$

C $E_1 > E_2 > E_3$

D $E_1 > E_3 > E_2$

19 Electrolysis of a dilute aqueous Na*Cl* solution was carried out by passing 0.1 A current through it.

What is the time required to liberate 0.01 mol of H_2 gas at the cathode?

A 9.65×10^3 s

B 1.93×10^4 s

C 2.90×10^4 s

D 3.86×10^4 s

20 *Use of the Data Booklet is relevant to this question.*

In research laboratories, the standard calomel reference electrode and the AgC*l* / Ag reference electrodes are often used in place of the standard hydrogen electrode (SHE). Their standard reduction potentials with respect to the SHE are shown below.

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$ $E^\ominus = +0.27$ V

AgC*l* / Ag electrode: $AgCl + e^- \rightleftharpoons Ag + Cl^-$ $E^\ominus = +0.22$ V

A half–cell containing Au^+/Au has a reduction potential of +1.61 V with respect to AgC*l* / Ag electrode.

Which of the following statements is correct?

A The reduction potential of the Au^+/Au half–cell with respect to the SHE is +1.83 V.

B The reduction potential of the Au^+/Au half–cell with respect to the calomel electrode is +1.88 V.

C Ag is a stronger reducing agent than H_2.

D Hg_2Cl_2 is a weaker oxidising agent than AgC*l*.

21 Which of the following statements is **not** correct?

A Both Fe^{2+} and Fe^{3+} can catalyse the reaction between I^- and $S_2O_8^{2-}$.

B $[Fe(C_2O_4)_3]^{4-}$ has a coordination number of 6.

C $[Fe(H_2O)_6]^{3+}$ has a lower pK_a than $[Fe(H_2O)_6]^{2+}$.

D Aqueous solutions of Fe^{2+} appear green due to the absorption of green light.

22 Which of the following ions does **not** form coloured solutions?

A Co^{3+} **B** Cu^+ **C** Mn^{3+} **D** Ti^{2+}

23 Four different complexes can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Different proportions of chloride are precipitated when each complex is treated with aqueous silver nitrate.

	empirical formula	colour of solid	number of moles of AgC*l* precipitated per mole of complex
I	$CoCl_3(NH_3)_6$	orange	3
II	$CoCl_3(NH_3)_5$	violet	2
III	$CoCl_3(NH_3)_4$	violet	1
IV	$CoCl_3(NH_3)_4$	green	1

Which of the following statements are correct regarding the four different complexes?

1 Complex **I** is the only complex that is made up of only one type of ligand.
2 The cations of the four complexes have the same charge.
3 Complexes **III** and **IV** are stereoisomers.
4 All four complexes have the coordination number of 6.

A 1 and 2 only **B** 3 and 4 only **C** 1, 2 and 4 only **D** 1, 3 and 4 only

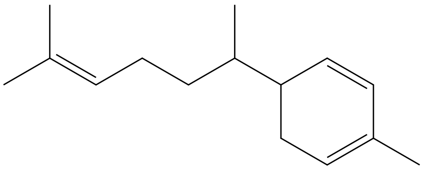
24 Which of the following compounds are arranged in increasing order of their solubility in water?

A $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2Cl$
B $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$
C $CH_3CH_2CH_2Cl$, $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2OH$
D $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$, $CH_3CH_2CH_2Cl$

25 How many isomeric esters have the molecular formula $C_4H_8O_2$?

A 2 **B** 3 **C** 4 **D** 5

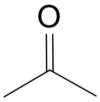
26 The flavour of ginger comes from zingiberene.



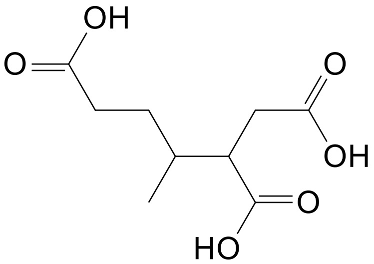
zingiberene

Which of the following compounds are produced from the reaction between zingiberene and hot concentrated acidified $KMnO_4$?

1

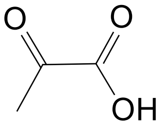


2



3 CO_2

4



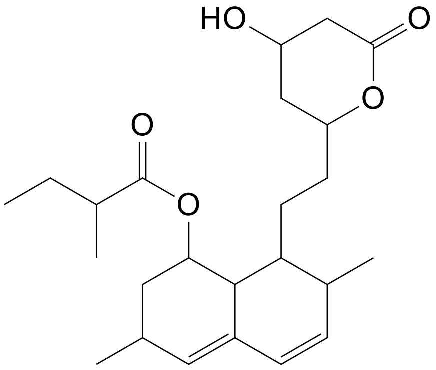
A 1 and 3 only **B** 2 and 4 only **C** 1, 2 and 4 only **D** 1, 3 and 4 only

27 Which of the following reactions would result in the formation of racemic mixture?

1 1-chloropropane ⟶ propan-1-ol
2 ethanal ⟶ cyanoethanol
3 but-2-ene ⟶ 2-chlorobutane

A 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

28 Statin is a class of lipid-lowering medication which is effective in lowering cholesterol and used for primary prevention in people at high risk of cardiovascular disease.



Statin

Which statement about statin is **not** correct?

A When statin reacts with aqueous Br_2, the product contains chiral centres.

B When heated with ethanoic acid and concentrated sulfuric acid, statin forms an ester.

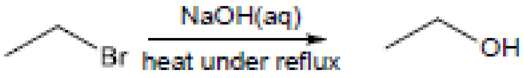
C When statin reacts with hot acidified $K_2Cr_2O_7$, one of the products contains three ketone groups.

D When 2,4-dinitrophenylhydrazine is added to statin, an orange precipitate is observed.

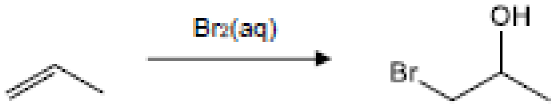
29 Which of the following reactions involves an organic intermediate which has a different charge from the other three reactions?

A

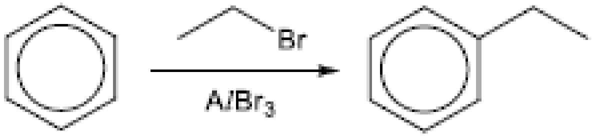
B



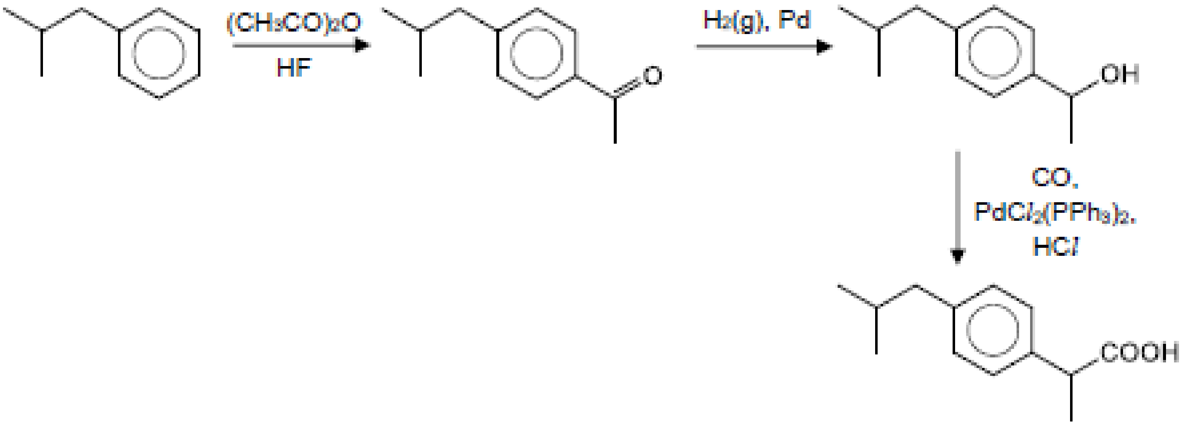
C



D



30 Ibuprofen is used to relieve pain from headache and to reduce fever. The synthesis of ibuprofen is shown below.



Ibuprofen

Which of the following type of reactions can be found in the synthetic route?

1 reduction
2 elimination
3 acidic hydrolysis
4 electrophilic substitution

A 1 only **B** 1 and 4 only **C** 1, 2 and 3 only **D** 1, 2, 3 and 4

END OF PAPER 1

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Class	Adm No

Candidate Name: ____________________

H

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

16 Sept 2019

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	**7**	**23**	**16**	**14**	**15**	**75**

This question paper consists of **16** printed pages and **2** blank pages.

1 **(a)** Zinc-air batteries worked by oxidising zinc with oxygen from the air. At the cathode, oxygen converts to hydroxide ions. At the anode, zinc reacts with the hydroxide ions to form zincate, $[Zn(OH)_4]^{2-}$.

(i) Construct an ion-electron equation for the reaction that takes place at each electrode under alkaline conditions. [2]

Cathode: ……………………………………………………………………………………

Anode: ………………………………………………………………………………………

(ii) At 298K, the standard electrode potential of the $[Zn(OH)_4]^{2-}(aq)|Zn(s)$ half-cell is -1.25 V. Calculate the cell voltage using relevant data from the *Data Booklet*. [1]

(iii) Using relevant data from the *Data Booklet*, deduce if oxygen gas can be replaced with chlorine gas. [2]

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(b) Another type of battery known as the nickel-cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The electrode reaction equations for the **discharging** process under alkaline conditions is given below.

Cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
Anode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$

(i) Construct the overall equation for the reaction that takes place during **charging**. [1]

…………………………………………………………………………………………………

(ii) Suggest a disadvantage of using nickel-cadmium battery. [1]

………

………

[Total: 7]

2 Paramagnetism and diamagnetism are different forms of magnetism. Paramagnetic materials are weakly attracted by an externally applied magnetic field and form magnetic fields in the direction of the applied magnetic field. In contrast, diamagnetic materials are repelled from magnetic fields and form magnetic fields in the direction opposite to that of the applied magnetic field.

Transition metals are mostly paramagnetic or diamagnetic. The magnetic property is characterised by the presence of unpaired electrons in paramagnetic compounds and absence of unpaired electrons in diamagnetic compounds.

The table below shows the magnetic property of metal complexes.

Formula of complex	**Magnetic property of complex**
$Fe(CO)_5$	Paramagnetic
$[Fe(H_2O)_6]^{2+}$	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Paramagnetic
$[ZnCl_4]^{2-}$	Diamagnetic
$[V(H_2O)_6]^{3+}$	
$[Sc(H_2O)_3(OH)_3]$	

(a) **(i)** Write the electronic configurations of V in $[V(H_2O)_6]^{3+}$ and Sc in $[Sc(H_2O)_3(OH)_3]$. [2]

V in $[V(H_2O)_6]^{3+}$: ……………………………………………………………………………………

Sc in $[Sc(H_2O)_3(OH)_3]$: ………………………………………………………………………………

(ii) State the magnetic property of $[V(H_2O)_6]^{3+}$ and $[Sc(H_2O)_3(OH)_3]$ in the above table. [1]

(iii) Draw labelled diagrams to show the shapes of the d orbitals of the metal ion in $[V(H_2O)_6]^{3+}$. Include the relative energy of the d-orbitals in the complex. [3]

d-orbitals of lower energy:……………………………………………………………………..

d-orbitals of higher energy: ……………………………………………………………………..

(iv) Explain why transition metal can show variable oxidation states. [1]

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(b) Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate, $Na_2Fe(CO)_4$.

$$2Na + Fe(CO)_5 \longrightarrow Na_2Fe(CO)_4 + CO \quad \text{------- eqn (1)}$$

(i) Explain what is meant by the coordination number of a complex using $Fe(CO)_5$ as an example. [1]

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(ii) Draw the structure of $Fe(CO)_5$ and state its shape. [2]

Shape: ……………………………………………………………………………………………

(iii) Deduce the oxidising and reducing agent in eqn (1). [2]

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(iv) Explain why carbon monoxide, CO, is poisonous. [2]

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(v) The tetracarbonylferrate dianion acts as a nucleophile and react with alkyl halide by the S_N2 mechanism to form a new C-Fe bond.

$$[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow [Fe(CH_3)(CO)_4]^{-} + Br^{-} \text{ ------- eqn (2)}$$

Suggest a mechanism between $Fe(CO)_4^{2-}$ and CH_3Br. State clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs. [3]

(vi) State the rate equation for the reaction in eqn (2). [1]

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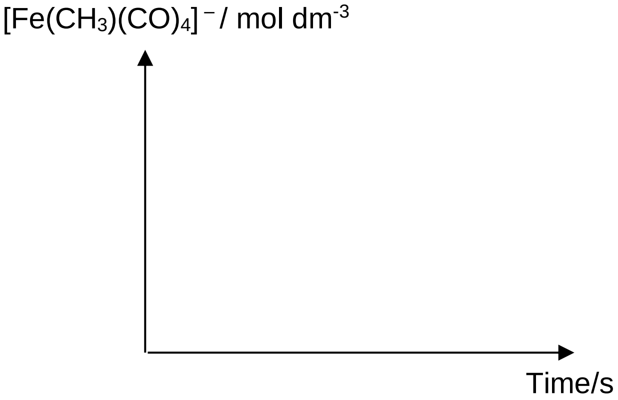
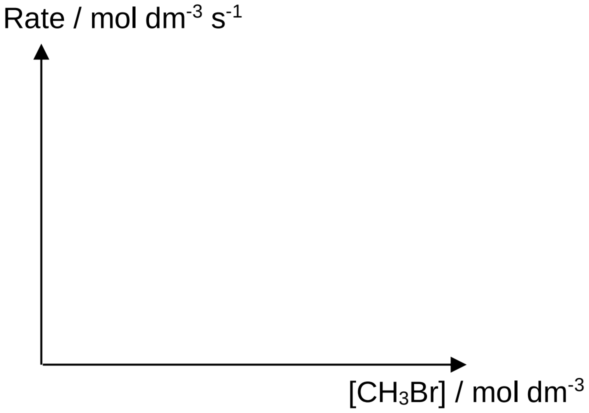
(vii) **I** Sketch the graph of $[Fe(CH_3)(CO)_4]^-$ against time.



II Sketch the graph of rate against $[CH_3Br]$ given that $[Fe(CO)_4]^{2-}$ is in excess.



[2]

(c) The melting point of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$ is lower than that of sodium oxide. With reference to the structure and bonding, explain the difference in melting point.[3]

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[Total: 23]

3 **(a)** Phosgene, $COCl_2$, is essential in the manufacturing of everyday products, including medical products and footwear. Phosgene is produced by combining carbon monoxide and chlorine with a catalyst.

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

(i) Draw a 'dot-and-cross' diagram of $COCl_2$ and state the bond angle about the central atom. [2]

Bond angle: ………………………..

(ii) Using relevant data from the *Data Booklet*, construct a fully labelled energy level diagram to calculate the enthalpy change of the above reaction. [3]

(iii) Explain what is meant by the term entropy of a chemical system. [1]

……………………………………………………………………………………………………

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(iv) Predict, with reasons, the sign of the entropy change of the reaction between CO(g) and Cl_2(g) to form $COCl_2$. [2]

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(v) Hence, state and explain the significance of the sign of the standard Gibbs free energy change when temperature is low. [2]

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(b) Above 200°C, a 2.0 dm^3 cylinder containing gaseous phosgene decomposes to carbon monoxide and chlorine in a dynamic equilibrium according to the following equation:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

(i) Predict and explain the effect of a catalyst on the position of the above equilibrium. [1]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(ii) At 350°C, the percentage dissociation of $COCl_2$ is found to be 45% and the total pressure at equilibrium is 3.5 atm. Calculate the value of K_p at 350 °C. [3]

(iii) Calculate the mass of the carbon monoxide gas that exists inside the cylinder at 350°C. [2]

[Total: 16]

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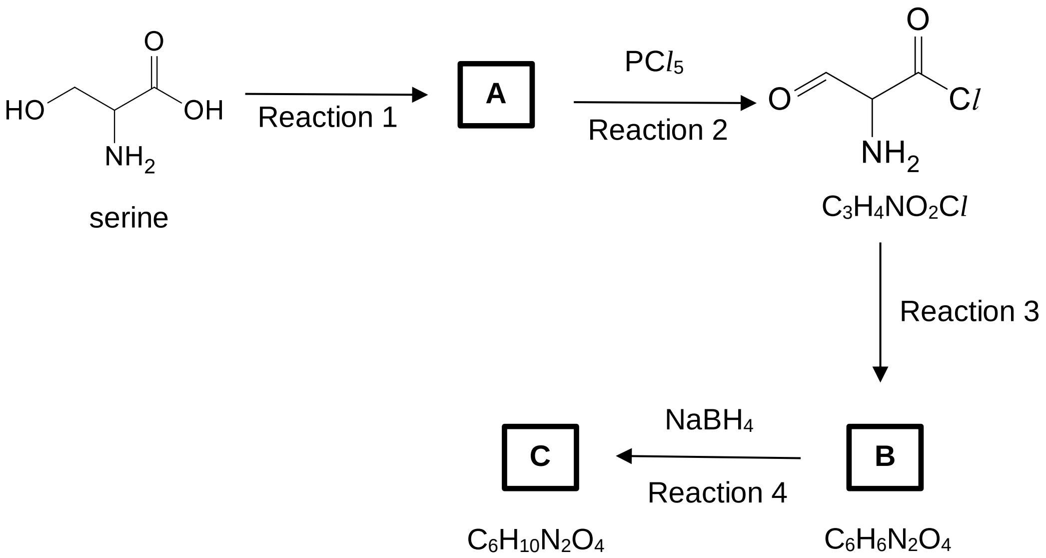
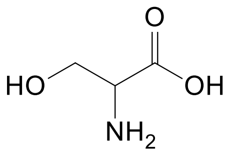
4 Spider silk is a protein fibre. Major amino acids in the silk protein are alanine, serine and glycine.

The following reaction scheme involves serine as a starting material.



(a) Explain what is meant by a chiral centre.

Label with an asterisk (*) for any chiral centre that is present in serine. [2]



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(b) Name the functional group common to compounds **B** and **C**. [1]

....

(c) Draw the structure of compound **A** and state the reagents and conditions for reaction 1. [2]

A

Reagent and conditions: …………………………………………………………………………..

(d) Name the type of reaction for reactions 2, 3 and 4. [3]

Reaction 2: ………………………………………………………………………………………...

Reaction 3: ………………………………………………………………………………………...

Reaction 4: ………………………………………………………………………………………...

(e) Draw the structures of compound **B** and **C**. [2]

B

C

(f) The following table contains the pK_a values of different compounds.

Compound	**pK_a**
Serine	2.21
Propanoic acid	4.87
Phenol	9.95

(i) Suggest a reason why pK_a of propanoic acid is higher than serine. [2]

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(ii) Suggest a reason why pK_a of propanoic acid is lower than phenol. [2]

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[Total: 14]

5 **(a)** **X** and **Y** are two different elements in Period 3. The following are some of their properties:

- Oxide of **X** is insoluble in water while the aqueous solution of chloride of **X** is weakly acidic.
- Element **Y** conducts electricity and has a lower melting point than element **X**.
- The first ionisation energy of element **X** is lower than that of element **Y**.

(i) Identify the elements, **X** and **Y**. [2]

X: ……………………………………………………………………………………………

Y: ……………………………………………………………………………………………

(ii) Write the balanced equation(s) for the reaction when chloride of **X** dissolves in water and state the pH of the solution. [2]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(iii) Explain why oxide of **X** is insoluble in water. [1]

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……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(iv) Explain why element **Y** has a lower melting point than element **X**. [2]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(v) Explain why the first ionisation energy of element **X** is lower than that of element **Y**. [2]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(b) Sulfur is another period 3 element with a relative atomic mass of 32.09.

There are three naturally occurring isotopes. The relative abundances of the isotopes of sulfur are found to be the following.

Isotope	**% Abundance**
^{32}S	95.0
^{33}S	*a*
^{34}S	*b*

(i) Define the term *relative atomic mass*. [1]

……………………………………………………………………………………………………

……………………………………………………………………………………………………

(ii) Calculate the percentage abundances of isotopes ^{33}S and ^{34}S. [2]

(c) A 2.00 g sample of food additive containing magnesium carbonate is allowed to react with 50 cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid. The excess acid required 19.30 cm^3 of 0.100 mol dm^{-3} aqueous potassium hydroxide for complete reaction.

Calculate the percentage of magnesium carbonate that is present in the food additive. [3]

[Total: 15]

END OF PAPER 2

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Class	Adm No

Candidate Name: ____________________

H

millennia institute

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **20 Sept 2019**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph 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.

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	**19**	**19**	**22**	**20**	**20**	**80**

This question paper consists of **9** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** 3–chloropropanoic acid, $CH_2ClCH_2CO_2H$, is a weak Brønsted acid. A 0.100 mol dm^{-3} solution of $CH_2ClCH_2CO_2H$ has a pH of 2.49.

(i) Calculate the pK_a of 3–chloropropanoic acid. [3]

(ii) State and explain the differences in the relative acid strength between 3–chloropropanoic acid and propanoic acid. [2]

(iii) 3-chloropropanoyl bromide is the acid derivative of 3–chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]

(b) A student investigated the rate of reaction between 3–chloropropanoic acid and aqueous sodium carbonate. The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3–chloropropanoic acid and sodium carbonate. The following results were obtained.

Experiment Number	Volume / cm^3			Time / s
	3–chloropropanoic acid	Na_2CO_3	H_2O	
1	20.0	40.0	40.0	78
2	20.0	30.0	50.0	100
3	5.0	20.0	25.0	75

(i) Write an equation, including state symbols, for the reaction between sodium carbonate and 3–chloropropanoic acid. [1]

(ii) State the relationship between time and rate. [1]

(iii) Determine the order of the reaction with respect to 3–chloropropanoic acid and sodium carbonate. [2]

(iv) Hence, write the rate equation, stating the units of k. [2]

(v) With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3–chloropropanoic acid and sodium carbonate. [3]

[Total: 19]

2 **(a)** Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom, with an oxidation state of 0 and +2 respectively. [2]

(b) A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute NaOH(aq) produces a colourless, pungent gas that turns moist red litmus paper blue.

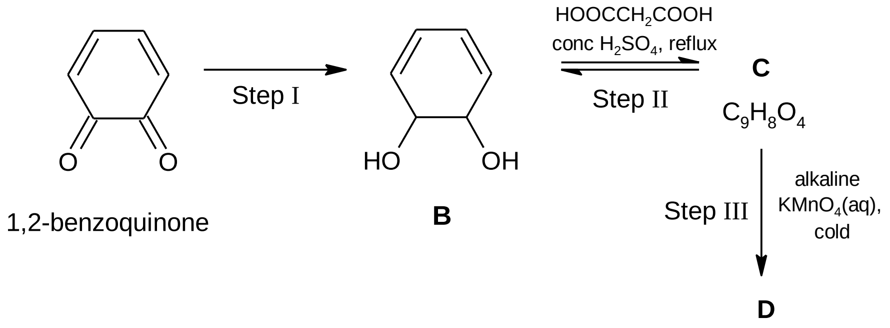
(i) Draw the structure of compound **A** and state the functional group present. [2]

(ii) The functional group present in compound **A** can be reduced by lithium aluminium hydride, $LiAlH_4$. Draw the dot-and-cross diagram for $LiAlH_4$. [1]

(iii) Other than $LiAlH_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. $LiAlH_4$ is able to produce hydride ion, H^- more readily than $NaBH_4$. Suggest why $LiAlH_4$ is a more powerful reducing agent than $NaBH_4$. [1]

(c) Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

The following scheme involves 1, 2-benzoquinone, where step I involves the use of $LiAlH_4$.

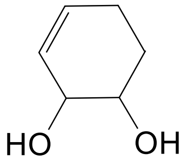


(i) Draw the structures of **C** and **D**. [2]

(ii) Identify the chiral centres on **B**. Hence, explain why it does not display optical activity. [2]

(iii) Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

(iv) When compound **B** undergoes partial hydrogenation, it forms compound **E**.



E

Describe the mechanism of the reaction when compound **E** reacts with Br_2 in CCl_4 in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

(d) $K_2Cr_2O_7$ and $KMnO_4$ are common oxidising agents used in organic synthesis where $KMnO_4$ is the more powerful of the two. Compound **F**, C_4H_8O, reacted with $K_2Cr_2O_7$ and $KMnO_4$ separately to yield different products as shown in the reactions below.

$$\underset{\mathbf{F}}{C_4H_8O} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \underset{\mathbf{G}}{C_4H_6O_2}$$

$$\underset{\mathbf{F}}{C_4H_8O} \xrightarrow[KMnO_4/H_2SO_4]{} \underset{\mathbf{H}}{C_2H_4O_2}$$

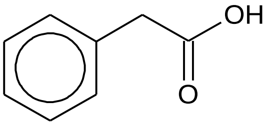
Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with Na_2CO_3, but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

[Total: 19]

3 **(a)** Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.



phenylethanoic acid

(i) In an experiment, 60 cm^3 of 0.10 mol dm^{-3} of sodium hydroxide was added to 20 cm^3 of 0.20 mol dm^{-3} of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 cm^3 of sodium hydroxide was added to the flask. [3]

(ii) 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.

Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]

(iii) Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]

(iv) Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]

(b) **(i)** Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]

(ii) Given that phenylethanoyl chloride has a boiling point of 95 °C and phenylethanoic acid has a boiling point of 266 °C, explain this difference in terms of structure and bonding. [2]

(iii) State the number of sp^2 and sp^3 hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]

(iv) State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

(c) Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

First stage

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the π bond of the C=O bond to break.

Second stage

- The carbon-oxygen double bond reforms and a chloride ion is released.
- As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.

(i) Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]

(ii) State the type of reaction occurring in the first stage of the mechanism. [1]

(d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when heated with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

[Total: 22]

Section B

Answer **one** question from this section.

4 **(a)** Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to Ni^{2+}.

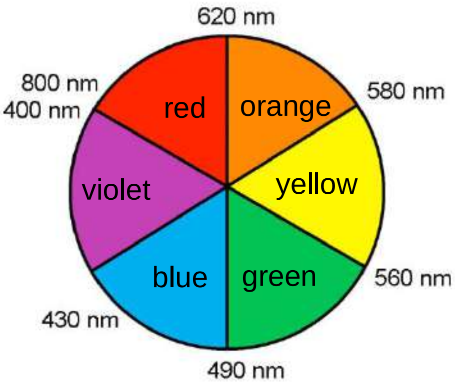
(i) Define the term *standard electrode potential*. [1]

(ii) Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of Ni^{2+}/Ni under standard conditions. [3]

(iii) Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part **(ii)**. [1]

(iv) An electrolytic cell contains $Ni(NO_3)_2$ and $Mn(NO_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]

(b) Aqueous nickel salts are coloured. $[Ni(NH_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[NiCl_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.



(i) State the oxidation number of nickel in $[NiCl_4]^{2-}$. [1]

(ii) Suggest the colour of:

I: $[Ni(NH_3)_6]^{2+}$

II: $[NiCl_4]^{2-}$ [2]

(iii) Explain why the two complexes are coloured. [3]

(c) The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$. The stability constant, K_{stab}, is given by

$$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6}$$

Complex	Stability constant
$Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$	4.8×10^7
$Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$	2.0×10^{18}

State and explain if the en ligand will replace the NH_3 ligand for the nickel complexes. [2]

(d) **(i)** The coordination compound $NiCl_2(H_2O)_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]

(ii) Explain why $[Ni(en)_3]Cl_2$ can dissolve in water. [2]

[Total: 20]

5 **(a)** **(i)** State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

(ii) Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

Thermochemical term	**ΔH / kJ mol^{-1}**
Lattice energy of $NaCl(s)$	-788
Enthalpy change of atomisation of Na(s)	+108
First electron affinity of Cl(g)	-349

(iii) Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

(b) The reactions of different halogens with hydrogen differ due to their reactivity.
Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

(c) The iodine clock reaction involves 2 reactions.
First reaction involves peroxydisulfate ($S_2O_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($S_2O_3^{2-}$) ion reacting with the iodine produced.

(i) Write the equations for the two reactions of the clock reaction. [2]

(ii) If 30 cm^3 of 0.002 mol dm^{-3} of $S_2O_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

(iii) Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in speeding up the rate of reaction.

[2]

(d) Iron is also used in other reactions, such as the Haber Process.
State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

[Total: 20]

END OF PAPER 3

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Class	Adm No

Candidate Name: ____________________

H

Shift
Laboratory

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY

9729/04

Paper 4 Practical

4th Sept 2019

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	18	22	9	6	55

1 Determination of titration value at equivalence point

The reaction between acid and carbonates is well known. In the presence of excess acid, the following reaction occurs:

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \qquad pK_a(HCO_3^-) = 10.32 \qquad \textbf{equation 1}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq) \qquad pK_a(H_2CO_3) = 6.37 \qquad \textbf{equation 2}$$

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l) \qquad \textbf{equation 3}$$

$CO_2(aq)$ is then released from the solution as $CO_2(g)$, which is observed as effervescence. The entire reaction is known to release heat.

FA 1 is 1.8 mol dm^{-3} of aqueous potassium carbonate, K_2CO_3.
FA 2 is nitric acid, HNO_3, of concentration between 1.9–2.1 mol dm^{-3}.

Assuming that the first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with the HCO_3^- produced, the reaction between **FA 1** and the first equivalent of **FA 2** can be simplified as:

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

And the reaction between **FA 1** and the second equivalent of **FA 2** can be simplified as:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

As the precise concentration of **FA 2** is unknown, determination of ΔH_{rxn} can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as ΔH_{rxn}. 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 an acid-carbonate thermometric titration. The data from this titration will be used to determine:

- the titration value at the first equivalence point, V_{eq1},
- the precise concentration of **FA 2**, [HNO_3],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of reaction, ΔH_{rxn}.

(a) **(i)** 25.0 cm^3 of **FA 1** is reacted with **FA 2**.

Calculate the **theoretical volume of** FA 2 needed for the first equivalence point, V_{eq1}', and the second equivalence point, V_{eq2}', of the reaction between **FA 1** and **FA 2**. Assume [HNO_3] to be 2.0 mol dm^{-3}.

V_{eq1}' = ... cm^3 **M1**

V_{eq2}' = ... cm^3 **M2**

[2]

For Examiners' Use

Determination of V_{eq1} and ΔH_{rxn} using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 2** have been added to **FA 1**.

In an appropriate format in the space provided below, prepare a table to record your results. Record all values of temperature, T, to 0.1°C, and each total volume of **FA 2** added.

Note: You should aim to perform each subsequent addition of **FA 2** quickly.

1. Fill a burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** 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 1**. Record this temperature.
4. Add 4.00 cm^3 of **FA 2** from the burette to the **FA 1** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 2** added.
6. Repeat steps **4** and **5** until a total volume of 48.00 cm^3 of **FA 2** has been added.

Results

[2]

(ii) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 2** added, on the *x*-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.0 °C greater than the maximum temperature recorded.

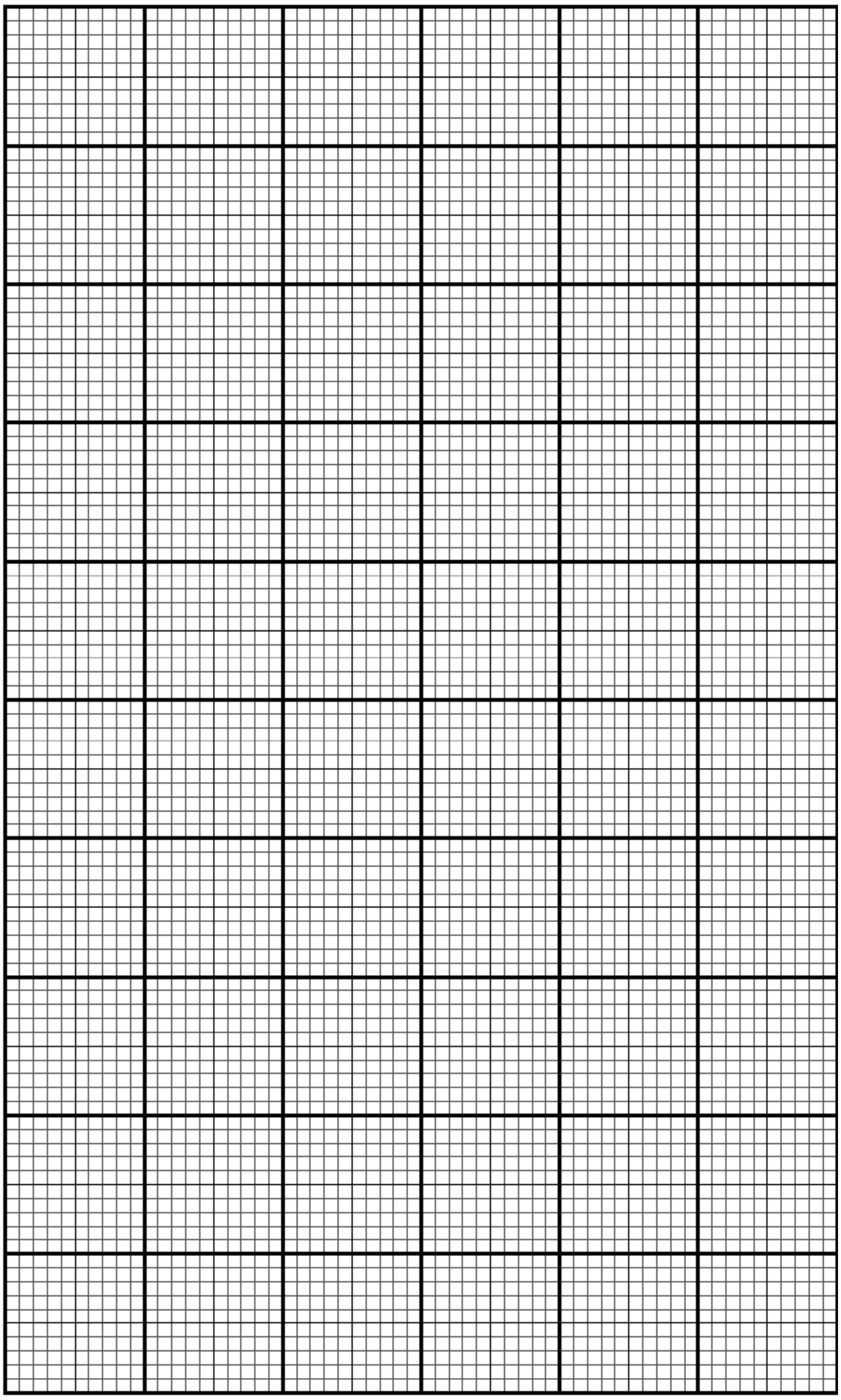

Fig. 1.1

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]

(iii) 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_{eq1} = ... cm^3

T_{max} = ... °C

ΔT_{max} = ... °C

[3]

(iv) Determine the concentration of HNO_3, $[HNO_3]$, in **FA 2**.

$[HNO_3]$ in **FA 2** = ... [1]

(v) Determine the enthalpy change of reaction, ΔH_{rxn}.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

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}.

ΔH_{rxn} = ... [3]

(b) **(i)** With reference to your graph in **Fig. 1.1**, explain why the titre at second equivalence point, V_{eq2}, cannot be determined from this experiment.

……………………………………………………………………………………………….

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……………………………………………………………………………………………….

[1]

(ii) Suggest, using chemistry concepts, a possible explanation for the observation in **(b)(i)**.

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……………………………………………………………………………………………….

……………………………………………………………………………………………….

[1]

(iii) The value of V_{eq1} could also have been determined via a regular acid-base titration with a suitable indicator.

Suggest which titration method is likely to give a more accurate value of V_{eq1} and give two reasons for why this is so.

Method:

I. ……………………………………………………………………………………

……………………………………………………………………………………

II. ……………………………………………………………………………………

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[2]

[Total: 18]

2 Investigation of the kinetics of an acid-carbonate reaction via gravimetric analysis

FA 1 is 1.8 mol dm^{-3} of K_2CO_3.
FA 3 is dilute nitric acid, HNO_3, of concentration 1.0 mol dm^{-3}.

$$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$$

The rate equation of the reaction between **FA 1** and **FA 3** is expressed as such:

$$\text{Rate} = k[K_2CO_3]^a[H^+]$$

where *a* represents the order of reaction with respect to K_2CO_3, and is an integer value of either 0, 1, or 2.

The acid-carbonate reaction results in the release of $CO_2(g)$, which escapes the reaction vessel as effervescence. To determine the kinetics of a reaction involving the loss of a gas, gravimetric analysis can be used, where the change in mass of the reaction vessel is monitored over time.

In this experiment, you will use gravimetric analysis to determine the value of *a*.

(a) Determination of orders of reaction via the 'continuous method'

The orders of reaction can be determined via either the 'continuous method' or the 'initial rates method'. In the 'continuous method', a single reaction is carried out and a measurement (e.g. concentration; mass) is monitored over time.

You will be using the 'continuous method' in this part of the experiment, monitoring the change in mass over time.

1. Weigh and record the mass of an empty 100 cm^3 measuring cylinder.
2. Measure out 80 cm^3 of **FA 3** into this measuring cylinder and record the mass of the measuring cylinder with **FA 3**.
3. Measure out 20 cm^3 of **FA 1** using a 25 cm^3 measuring cylinder into an empty 250 cm^3 conical flask. Weigh and record the mass of the conical flask with **FA 1**.
4. Place the conical flask with **FA 1** on the mass balance provided individually.
5. Start the stopwatch and **simultaneously** pour the **FA 3** in the measuring cylinder into the conical flask. **Do not swirl the flask**.
6. Record the mass readings at 10s intervals until 90s has elapsed, then at 30s intervals. Continue taking readings **until it is appropriate to stop**.

   Given that:
   initial mass of conical flask with **FA 1** and **FA 3**
   = initial mass of **FA 3** + initial mass of conical flask with **FA 1**

In an appropriate form in the space on the next page, record all your time values, balance readings, and mass of $CO_2(g)$ evolved.

Results

[6]

(i) Plot a graph of mass of $CO_2(g)$ evolved, *m*, on the *y*-axis, against time of reaction, *t*, on the *x*-axis on the grid in **Fig. 2.1**.

Fig. 2.1

[3]

(ii) By means of a suitable extrapolation drawn on your graph in **Fig. 2.1**, determine a value for the mass of $CO_2(g)$ evolved when the reaction is complete.

mass of $CO_2(g)$ evolved = ... g [1]

(iii) The observed half-life ($t_{1/2}$) of a reaction would be constant if the reaction proceeds with an overall order of 1. The table below shows the percentage of reactants and products in the reaction vessel at different instances of time elapsed:

time elapsed	**% of reactants**	**% of products**
0	100	0
$t_{1/2}$ x 1	50	50
$t_{1/2}$ x 2	25	75
$t_{1/2}$ x 3	12.5	87.5
	⋮	
$t_{1/2}$ x ∞	0	100

Assume that the reaction proceeds with an overall order of 1.

Using your answer from **(a)(ii)**, calculate the theoretical total mass of CO_2(g) evolved after the first half-life has elapsed, and then after the second half-life has elapsed.

total mass of CO_2(g) evolved after first half-life = ... g

total mass of CO_2(g) evolved after second half-life = ... g [1]

(iv) Hence, determine from your experiment whether the acid-carbonate reaction has a consistent half-life, and state if the reaction has an overall order of 1.

Show your working clearly on your graph in **Fig. 2.1** and in the space below.

[2]

(v) Rate = $k[K_2CO_3]^a[H^+]$, where *a* is an integer value of either 0, 1, or 2.

Identify a possible value of *a*.

[1]

(b) Planning

The 'initial rates method' can also be used to determine the orders of reaction. Unlike the 'continuous method', multiple reactions have to be carried out, each time varying the concentrations of certain solutions.

Although the initial rate of a single reaction can be determined from the gradient of the tangent to a graph plotted at $t = 0$ (such as in **Fig 2.1**), the process is tedious as the graphs for multiple experiments have to be plotted.

A simplified 'initial rates method' experiment would involve determining the time elapsed for a certain *condition* to be met, then simply taking the reciprocal of time elapsed as the initial rate. A common example of such an experiment is iodine-clock reaction, whereby the time taken for the colouration formed to obscure text is measured.

It is important to keep the measured durations of time elapsed for the reactions short (maximum 120s), or the reciprocal becomes a poor approximation of rate.

(i) Plan an experiment using the simplified "initial rates method" by carrying out multiple reactions to determine the order of reaction with respect to K_2CO_3, *a*, for the reaction between K_2CO_3 and HNO_3.

You may assume that you are provided with

- **FA 1**,
- the same apparatus used in **Experiment 2(a)**,
- 4.0 mol dm^{-3} of nitric acid, HNO_3(aq),
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the quantities you would choose for the experiment and why,
- the procedure for the multiple reactions carried out,
- the measurements you would take,
- an outline of how you would use your results to determine the value of *a* non-graphically.

You may wish to consider the best mode of presentation for your answers.

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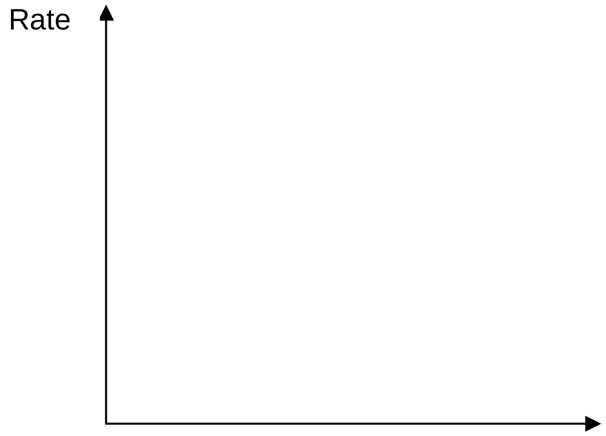
[6]

(ii) The orders of reaction can also be determined graphically.

Assuming that HNO_3 is in large excess, and *a* = 2, label the x-axis and sketch the expected rate-concentration graph that you would expect to obtain from **(b)(i)**.

Explain your answer briefly.



explanation ……………………………………………………………………………………..

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……………………………………………………………………………………………... [2]

[Total: 22]

3 Qualitative Analysis of an unknown salt mixture

FA 4 is a salt mixture comprising of an insoluble salt and a soluble salt. It contains **two cations** and **two anions**.

(a) Transfer 1 spatula of **FA 4** into a test tube and observe its appearance.

State, with explanation, a possible deduction that can be made about the identity of (at least) one of the ions present in **FA 4**.

…………………………………………………………………………………………………

…………………………………………………………………………………………………. [1]

(b) 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.	To the test tube from **(a)**, add 2 cm depth of HNO_3, then dropwise until all the **FA 4** dissolves. The resulting solution will be known as '**FA 5 solution**'.	
2.	Add about 1 cm depth of **FA 5 solution** to a fresh boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	
3.	Add about 1 cm depth of **FA 5 solution** into a test-tube. To this test-tube, add silver nitrate dropwise.	

[4]

(c) Based on your observations, deduce the identities of the ions present in **FA 5**.

cation 1: ……....   cation 2: ……....   anion 1: ……....   anion 2: ……....

[2]

(d) Explain in detail, the observations in **(b)(2.)**.

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……………………………………………………………………………………………………….. [2]

[Total: 9]

4 Planning

Consider the following organic compounds.

butanal but-3-enol 1-hydroxypropan-2-one propanone

Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

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. [6]

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[Total: 6]

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 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) 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

Q1 Option 1: Amount of H_2SO_4 = 0.5 x 1 = 0.5 mol

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Amount of H^+ = 0.5 x 2 = 1 mol

Option 2: Amount of SO_3 molecules = 6 / 24 = 0.25 mol

1 SO_3 molecule has 4 atoms (1 S and 3 O atoms)

Amount of atoms = 0.25 x 4 = 1 mol

Option 3: Amount of SO_2 molecule = 64.1 / (32.1 + 16.0 x 2) = 1 mol

1 SO_2 molecule has 16 + 8 x 2 = 32 electrons

Amount of electrons = 1 x 32 = 32 mol

Option 4: Amount of S_8 molecule = 1.6 /(32.1 x 8) = 0.00623 mol

1 S_8 molecule has 16 x 8 = 128 neutrons

Amount of neutrons = 0.798 mol

Ans: 1 and 2 are correct => A

Q2 $CH_3CH_2CH_2OH + 4O_2 \rightarrow 2CO_2 + CO + 4H_2O$

Since mole ratio = volume ratio of gases,

Vol of O_2 consumed = 4y

Ans: B

Q3 [R] $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2\ H_2O$

[O] $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$

$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 2MnO_2 + 3MnO_2 + 4H^+$

2 mol of MnO_4^- reacts with 3 mol of Mn^{2+}

1 mol of MnO_4^- reacts with 1.5 mol of Mn^{2+}

Ans: C

Q4 Z^{2+} has 12 electrons and 15 neutrons

Z has 14 electrons, 14 protons and 15 neutrons=> $A_r = 14 + 25 = 39$

Option A: angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

$\frac{\textbf{charge}}{\textbf{mass}}$ **for** $Z^{2+} = \frac{+2}{14+15} = \frac{+2}{29}$

$\frac{\textbf{charge}}{\textbf{mass}}$ **for** $Mg^{2+} = \frac{+2}{24.3}$

$\frac{\textbf{charge}}{\textbf{mass}}$ **for** $Mg^{2+} > \frac{\textbf{charge}}{\textbf{mass}}$ **for** Z^{2+}

Angle of deflection for Mg^{2+} > Angle of deflection for Z^{2+}

Option A is correct

Option B: Based on the proton number, **Z** is referring to Silicon.

Si has a higher IE than Al (Group 13 element in the same period as Z) => You can check from Data Booklet or recall from the trend across the period.

Option C: $SiCl_4$ has a lower melting point than $MgCl_2$ as $SiCl_4$ has a simple molecular structure while $MgCl_2$ has a giant ionic structure. Larger amount of energy is needed to overcome the stronger electrostatic forces of attraction between Mg^{2+} and Cl^- than the weaker instantaneous dipole-induced dipole forces of attraction between $SiCl_4$ molecules.

Option D: Element **Z** has 14 electrons while neon has 10 electrons. Hence, they are not isoelectronic.

Q5 All options have simple molecular structures.

Option 1 and 4 have instantaneous dipole-induced dipole forces of attraction between molecules

Option 2 has hydrogen bonding between molecule

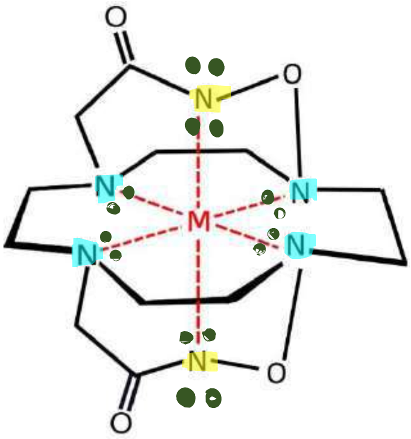
Option 3 has permanent dipole-permanent dipole forces of attraction between molecules.

Hence option 2 will be the highest followed by option 3

For option 1 and 4, the two molecules are isomers of each other. Thus, the surface area determines the boiling point. Since option 1 is a straight-chained molecule, it has a larger surface area between molecules which results in stronger instantaneous dipole-induced dipole forces of attraction than that of option 4 since option 4 is a branched-chain molecule. Hence option 4 as the lowest boiling point.

Boiling point: 4 < 1 < 3 < 2 => Option D is correct

Q6



The N highlighted in yellow has 6 electrons from N hence this N has a charge of -1.

The N highlighted in turquoise has 5 electrons from N hence thus N has no charge.

Since the complex has no overall charge, M has a charge of +2.

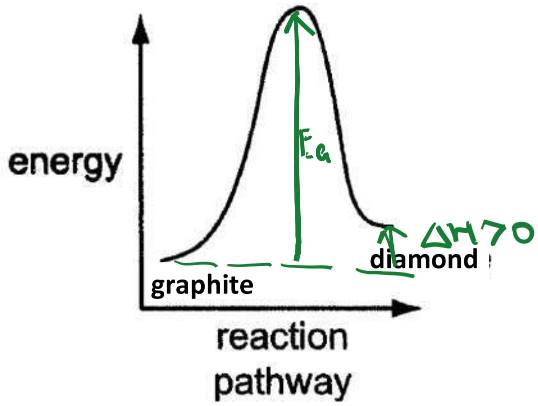
Bond between M^{2+} and N (in turquoise) is due to dative bond.

Bond between M^{2+} and N (in yellow) is due to ionic bond.

Ans: 1 and 2 => B is correct

Q7 Converting from graphite to diamond has $\Delta H > 0$ and k is small refers to large E_a.

Thus C is the answer.



Q8 Reaction 1: Evaporation of ethanol: $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

$\Delta H > 0$ => energy is taken in to overcome the hydrogen bonding between the molecules to convert liquid to gas.
Recall: Liquid is more closely packed than gas

$\Delta S > 0$ => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

$\Delta G = 0$ as it is an equilibrium reaction

Reaction 2: Atomisation of magnesium: $Mg(s) \rightarrow Mg(g)$
$\Delta H > 0$ => energy is taken in to overcome the forces of attraction to convert solid to gas.
Recall: solid is more closely packed than gas

$\Delta S > 0$ => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

Reaction 3: Initiation step for the free radical substitution between chlorine and ethane

$$Cl_2(g) \xrightarrow[uv]{} 2Cl\bullet_{(g)}$$

$\Delta H > 0$ => energy is taken in to break the covalent bond between the Cl atoms

$\Delta S > 0$ => increase in number of gas molecules from zero to one.
More ways of arranging the particels. Entropy increases.

$\Delta G > 0$ as it is not a spontaneous reaction since uv light is supplied for the reaction to occur.
Option 1 and 2 are correct=> C

Q9 $pV = nRT$

Since nR and V are constant, p=kT

$\frac{p}{T} = k$

$\frac{p_1}{T_1} = \frac{p_2}{T_2}$

$\frac{p_1}{T_1} = \frac{1.2p_1}{T_1+273}$

$\frac{T_1+273}{T_1} = 1.2$

$0.2T_1 = 273$

$T_1 = 1365$ K

Ans: D

Q10 $H_2O + ClO^- \rightleftharpoons HOCl + OH^-$

Acid and its conjugate base is a difference of H^+

Hence H_2O is the acid and OH^- is its conjugate base

ClO^- is the base and HOCl is the conjugate acid.

Hence, option A is the correct answer

Q11 rate equation depends on the slow step and it **cannot include intermediate**.

To determine if the species is an intermediate, write the overall equation by summing up the steps in the mechanism. If the species appear on either side of the overall equation, it is not an intermediate.

Overall equation: $A + 2B \rightarrow AB_2$

Based on slow step, rate= k[AB][B]

Since AB is an intermediate, it has to be re-expressed by using K_C.

$K_c = \frac{[AB]}{[A][B]}$ => $[AB] = K_c[A][B]$

rate= $k[AB][B] = k\{K_c[A][B]\}[B] = k'[A][B]^2$

Ans: D

Q 12 [Rxt] 100% → 50% → 25% …

[Pdt] 0% → 50% → 25% …

	2A(g)	→	B(g)	+	C(s)
I	x		0		0
C	-x		$+\frac{1}{2}x$		-
F	0		$\frac{1}{2}x$		-

This is based on completion of reaction, hence A will be completely used up.

Hence $\frac{1}{2}x = 200$ Pa $x = 400$ Pa

Note: pressure only applies to gas, hence carbon solid is ignored.

At the 1st half-life, 50% of A will be used up.

	2A(g)	→	B(g)	+	C(s)
I	x		0		0
C	$-\frac{1}{2}x$		$+\frac{1}{4}x$		-
F	$\frac{1}{2}x$		$\frac{1}{4}x$		-
	=200		=100		

At the 1st half-life, the total pressure = 200 + 100 = 300Pa

$t_{1/2}$ = 10 min => B is correct

13 $\Delta H_{rxn} = [-685.3 + 2(-92.3)] - [2(-485.3)] = +127.5$ kJ mol^{-1}

As temperature increases, the system is disturbed. By LCP, the system will oppose the change by decreasing the temperature and favours the endothermic reaction to absorb the heat. Position of equilibrium shifts right and produces more products. Hence, [$CHClF_2$] decreases with increasing temperature.

Ans: C

14 Consider if there is a reaction from the mixtures and determine the resultant species left in the solution to decide if it is a buffer.

Recall that a buffer must contain either:

a weak acid and its conjugate base OR a weak base and its conjugate acid.

Option A is made up of a salt and acid which does not react.

resultant species: NaC*l* and HC*l* => not a buffer as it contains a strong acid

Option B: a reaction will take place

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

I	0.75	0.25	0	0
C	-0.25	-0.25	+0.25	+0.25
F	0.50	0	0.25	0.25

resultant species: CH_3COOH and CH_3COONa => a buffer since it contains a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-)

Option B is correct

Option C: a reaction will take place

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

I	0.6	0.4	0
C	-0.6	-0.3	+0.3
F	0	0.1	0.3

resultant species: H_2SO_4 and $(NH_4)_2SO_4$ => not a buffer as it contains a strong acid

Option D: a reaction will take place.

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

I	0.4	0.6	0	0
C	- 0.4	-0.2	+0.2	+0.4
F	0	0.4	0.2	0.4

resultant species: H_2SO_4 and Na_2SO_4 => not a buffer as it contains a strong acid

Q15 $[H^+]$ from pH 2 = 10^{-2}

$[H^+]$ from pH 3 = 10^{-3}

When equal volumes are mixed, each concentration is halved.

$[H^+]_{\text{total after mixing}} = \frac{1}{2}[10^{-2} + 10^{-3}] = 0.00550$ mol dm^{-3}

pH = -log 0.00550 = 2.26

Ans: B

Q16 MgO has the highest melting point across Period 3 oxides. => **R** is Mg

Al has the highest electrical conductivity => **Q** is Al

Ar has the lowest melting point => **S** is Ar

Ans: Na is not represented. Option A is the answer.

Q17 HF is a weak acid

Fluorine is a pale yellow gas => not intensely coloured.

Melting point of fluorine is low as it has simple molecular structure.

F – F bond is unusually weak as observed from the trend. General trend of X –X bond decreases down the group due to increasing bond length. However, F –F bond is the weakest as seen from the values in Data Booklet. This is due to the repulsion as a result of the small atomic radius of F.

Bond	Bond energy
F-F	+158
Cl-Cl	+244
Br-Br	+193
I-I	+151

Ans: D

18 $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\theta = -0.76$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\theta = +0.34$V

Based on the standard electrode potential, Zn is the anode while Cu is the cathode.

[O] $Zn \rightarrow Zn^{2+} + 2e^-$ –(1)

[R] $Cu^{2+} + 2e^- \rightarrow Cu$ –(2)

E_2 is the reaction that happens at standard condition since the ions are 1 mol dm^{-3}

$E_2 = +0.34 - (-0.76) = + 1.10$ V

For E_1 and E_3, the reactions are not at standard conditions.

For the reaction that is represented by E_1, $[Cu^{2+}]$ is lower than that of the standard condition. By LCP, the system will oppose the change by shifting the position of equilibrium (2) to the left to replenish the Cu^{2+}. This results in oxidation to be preferred and makes $E_{Cu2+/Cu}$ less positive.

$E_1 = E_{cathode} - E_{anode} = E_{Cu2+/Cu} - E_{Zn2+/Zn}$ => E_1 will be less positive than E_2

For the reaction that is represented by E_3, $[Zn^{2+}]$ is lower than that of the standard condition. By LCP, the system will oppose the change by shifting the position of equilibrium to the right (1) to replenish the Zn^{2+}. This results in oxidation to be preferred and makes $E_{Zn2+/Zn}$ less positive.

$E_1 = E_{cathode} - E_{anode} = E_{Cu2+/Cu} - E_{Zn2+/Zn}$ => E_3 will be more positive than E_2

Hence $E_3 > E_2 > E_1$ => Ans: B

19 [R] $2H_2O + 2e^- \rightarrow H_2 + OH^-$

$n_e = 0.01 \times 2 = 0.02$

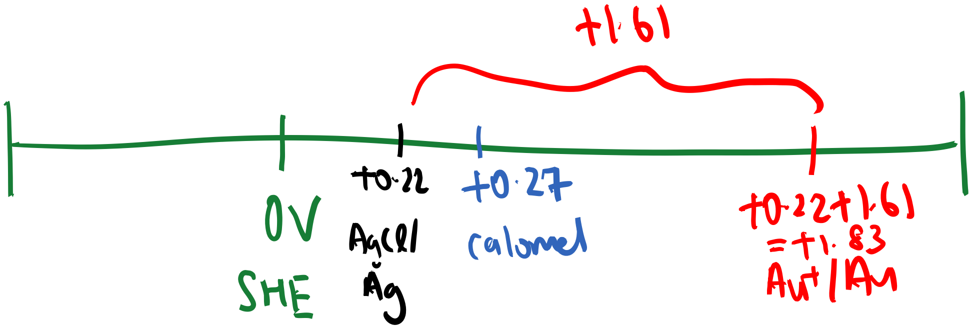
$Q = n_eF = It$

$0.02 \times 96500 = 0.1t$

$t = 19300$ s

Ans: B

20



Option A is correct as observed from the number line. Hence E(Au^+/Au) is +1.83 V wrt SHE

Option B: E(Au^+/Au) wrt calomel = +1.83 – (+0.27) = +1.56V

Option C: $E_{AgCl/Ag}$ is more positive than $E_{H+/H2}$ => Hence H_2 is more likely to be oxidised than Ag. Thus, H_2 is a stronger reducing agent.

Option D: $E_{HgCl2/Hg}$ is more positive than $E_{AgCl/Ag}$ => Hence $HgCl_2$ is more likely to be reduced than AgCl. Thus, $HgCl_2$ is a stronger oxidising agent.

21 Option A is correct:

When Fe^{2+} is the catalyst,

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

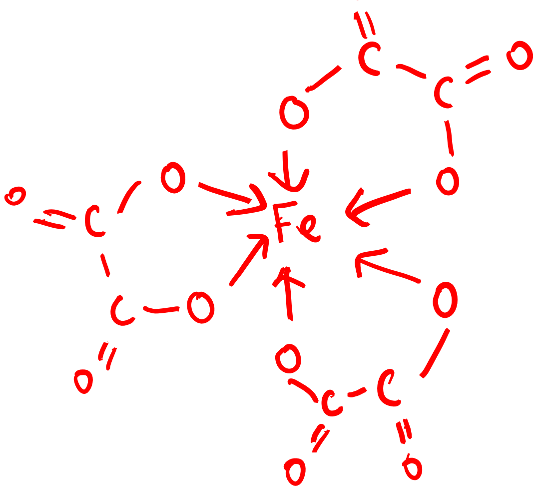
$2Fe^{3+} + 2I^{-} \rightarrow I_2 + 2Fe^{2+}$

When Fe^{3+} is the catalyst,

$2Fe^{3+} + 2I^{-} \rightarrow I_2 + 2Fe^{2+}$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

Option B: coordination number is denoted by the number of dative bonds formed around the central metal and not via the number of ligands. Coordination no = 6



Option C: $[Fe(H_2O)_6]^{3+}$ forms a more acidic solution than $[Fe(H_2O)_6]^{2+}$ due to the higher charge density of Fe^{3+} which has a stronger polarizing power and thus distorts the O-H bond to a larger extent, releasing H^+. Thus, $[Fe(H_2O)_6]^{3+}$ has a lower pK_a.

Option D: The appearance of the colour of solution is complementary to the colour absorbed. Thus the green solution observed is due to the absorption of red light. This statement is not correct.

22 Co^{3+}: $[Ar]3d^6$

Cu^+: $[Ar]3d^{10}$

Mn^{3+}: $[Ar]3d^4$

Ti^{2+}: $[Ar]3d^2$

Ans: B since there is no d-d transition which can take place as the d-orbitals are fully filled. The other options have partially filled d-orbitals which result in d-d transition.

23 The number of moles of AgCl represents the no of free Cl^- found outside of the complex.

Complex **I**: Since there are 3 moles of AgCl, there are 3 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_6]^{3+}$

Complex **II**: Since there are 2 moles of AgCl, there are 2 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_5Cl]^{2+}\ 2Cl^- \bullet NH_3$

Complex **III**: Since there is 1 mole of AgCl, there is 1 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_4Cl_2]^+\ Cl^- \bullet 2NH_3$

Complex **IV**: Since there is 1 mole of AgCl, there is 1 free Cl^- outside of the complex. Complex formula: $[Co(NH_3)_4Cl_2]^+\ Cl^- \bullet 2NH_3$

Option 1 is correct as complex **I** only contains NH_3 ligand.

Option 2 is incorrect as the charge are different for the complexes.

Option 3 is correct as complexes **III** and **IV** can form cis-trans isomers.

Option 4 is correct.

Ans: D

24 $CH_3CH_2CO_2Na$: forms ion-dipole interaction with water

$CH_3CH_2CH_2OH$: forms hydrogen bonding with water

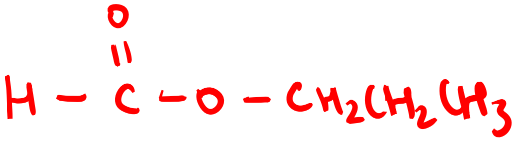
$CH_3CH_2CH_2Cl$: forms permanent dipole- permanent dipole with water

Strength: ion-dipole interaction> hydrogen bonding > permanent dipole- permanent dipole

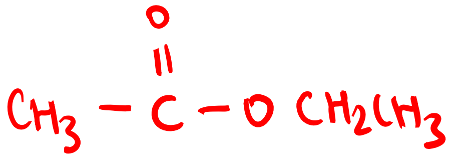
Increasing order: $CH_3CH_2CH_2Cl$, $CH_3CH_2CH_2OH$, $CH_3CH_2CO_2Na$,

Ans: B

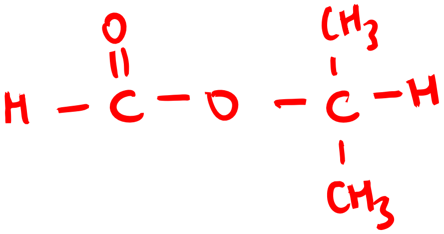
25



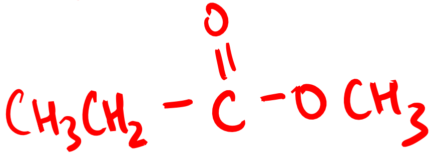
$$H-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2CH_3$$



$$CH_3-\overset{O}{\overset{\|}{C}}-O\,CH_2CH_3$$

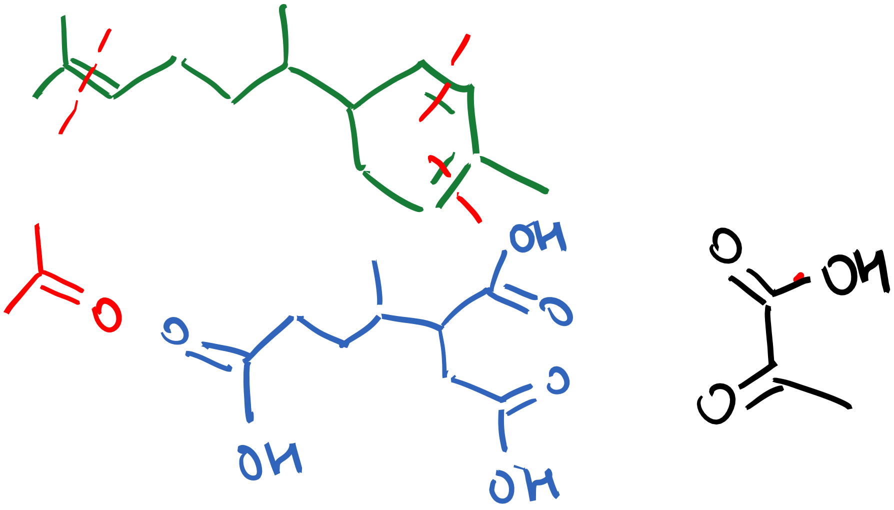


$$H-\overset{O}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{CH_3}{C}}-H$$



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-O\,CH_3$$

26

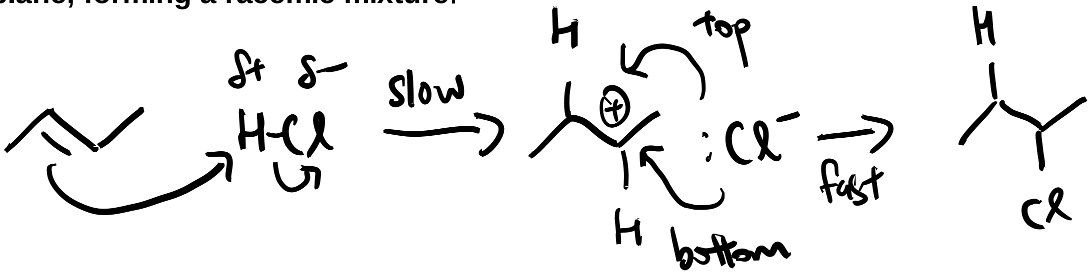


Ans: 1,2 and 4=> Option C

27 Option 1: 1-chloropropane undergoes S_N2 nucleophilic substitution to form propan-1-ol which will result in the inversion of configuration.

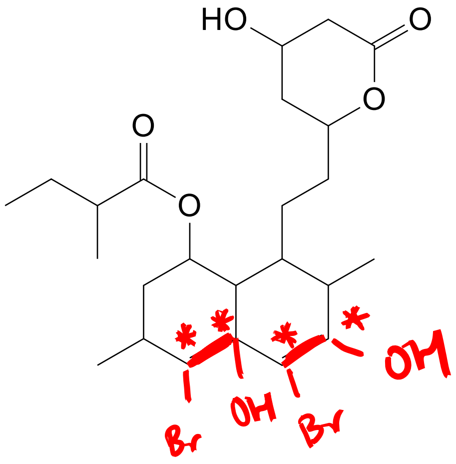
Option 2: A racemic mixture is formed as the reactive C in ethanal is trigonal planar in shape, hence the CN^- nucleophile can attack from the top or bottom of the plane, forming a racemic mixture.

Option 3: A racemic mixture is formed as the intermediate is trigonal planar in shape, hence the nucleophile can attack from the top or bottom of the plane, forming a racemic mixture.



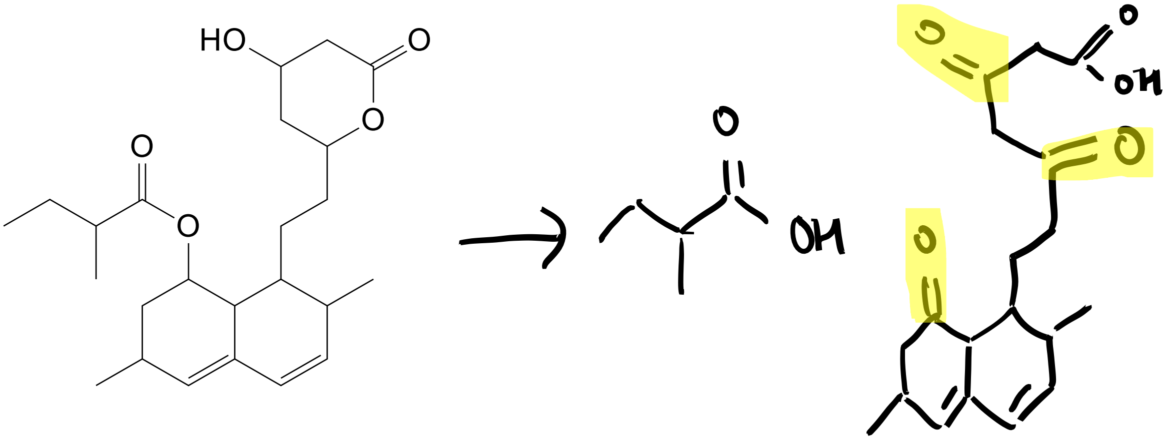
Ans: C

28 Option A is correct:



Option B is correct as the secondary alcohol will react with ethanoic acid to form ester in the presence of conc H_2SO_4.

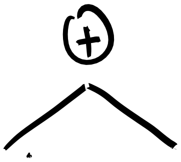
Option C is correct as secondary alcohol undergoes oxidation and acidic hydrolysis takes place for ester.



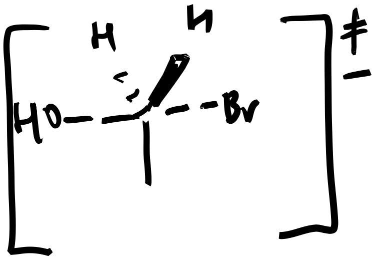
Option D: There is no carbonyl group present, thus no orange precipitate will be observed.

29

A

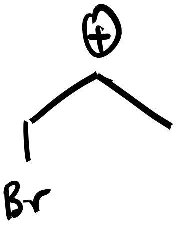


B

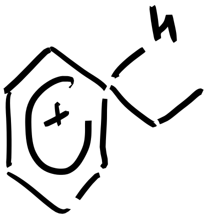


(no intermediate)

C

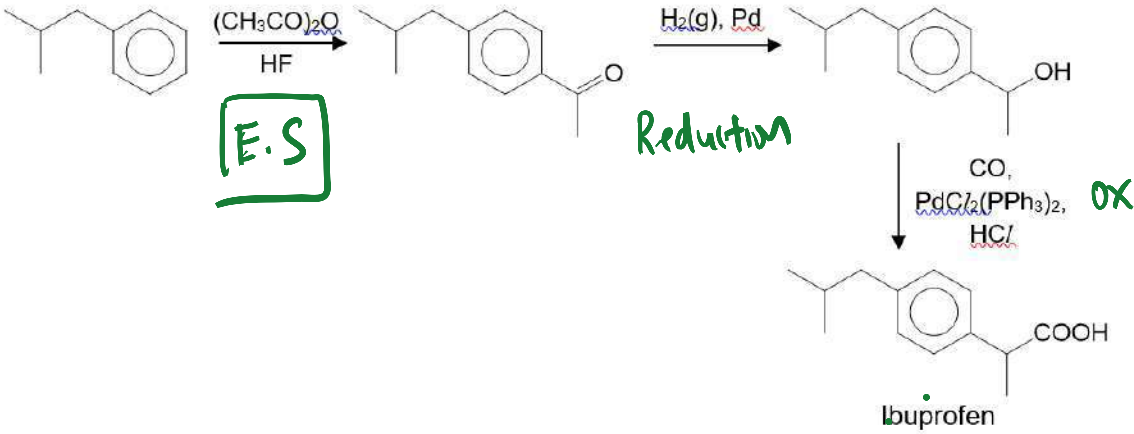


D



Ans: B

30



E.S

Reduction

oxidation

Ans: B

	Class	Adm No
Candidate Name: ____________________		

H

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **16 Sept 2019**

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	7	23	16	14	15	75

1	**(a)**	Zinc-air batteries worked by oxidising zinc with oxygen from the air. At the cathode, oxygen converts to hydroxide ions. At the anode, zinc reacts with the hydroxide ions to form zincate, $[Zn(OH)_4]^{2-}$.		
		(i)	Construct an ion-electron equation for the reaction that takes place at each electrode under alkaline conditions. [2]	
			Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ Anode: $Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$	
		(ii)	At 298K, the standard electrode potential of the $[Zn(OH)_4]^{2-}(aq)\|Zn(s)$ half-cell is -1.25 V. Calculate the cell voltage using relevant data from the *Data Booklet*. [1]	
			$E_{cell} = 0.40 – (-1.25) = +1.65$ V	
		(iii)	Using relevant data from the *Data Booklet*, deduce if oxygen gas can be replaced with chlorine gas. [2]	
			$E_{cell} = 1.36 – (-1.25) = +2.61$ V Since the E_{cell} value is more positive when oxygen gas is replaced with chlorine gas, the reaction is feasible.	
	(b)	Another type of battery known as the nickel-cadmium battery is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes. The electrode reaction equations for the **discharging** process under alkaline conditions is given below. Cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ Anode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$		
		(i)	Construct the overall equation for the reaction that takes place during **charging**. [1]	
			$2Ni(OH)_2 + Cd(OH)_2 \rightarrow 2NiO(OH) + Cd + 2H_2O$	
		(ii)	Suggest a disadvantage of using nickel-cadmium battery. [1]	
			Cadmium is a toxic heavy metal which can result in pollution if discarded in landfill or incinerated.	
			[Total: 7]	

2 Paramagnetism and diamagnetism are different forms of magnetism. Paramagnetic materials are weakly attracted by an externally applied magnetic field and form magnetic fields in the direction of the applied magnetic field. In contrast, diamagnetic materials are repelled from magnetic fields and form magnetic fields in the direction opposite to that of the applied magnetic field.

Transition metals are mostly paramagnetic or diamagnetic. The magnetic property is characterised by the presence of unpaired electrons in paramagnetic compounds and absence of unpaired electrons in diamagnetic compounds.

The table below shows the magnetic property of metal complexes.

Formula of complex	**Magnetic property of complex**
$Fe(CO)_5$	Paramagnetic
$[Fe(H_2O)_6]^{2+}$	Paramagnetic
$[Fe(H_2O)_6]^{3+}$	Paramagnetic
$[ZnCl_4]^{2-}$	Diamagnetic
$[V(H_2O)_6]^{3+}$	
$[Sc(H_2O)_3(OH)_3]$	

(a) **(i)** Write the electronic configurations of V in $[V(H_2O)_6]^{3+}$ and Sc in $[Sc(H_2O)_3(OH)_3]$. [2]

Sc^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

V^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

(ii) State the magnetic property of $[V(H_2O)_6]^{3+}$ and $[Sc(H_2O)_3(OH)_3]$ in the above table. [1]

$[V(H_2O)_6]^{3+}$: paramagnetic

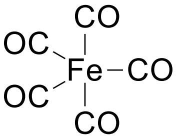
$[Sc(H_2O)_3(OH)_3]$: diamagnetic

(iii) Draw labelled diagrams to show the shapes of the d orbitals of the metal ion in $[V(H_2O)_6]^{3+}$. Include the relative energy of the d-orbitals in the complex. [3]

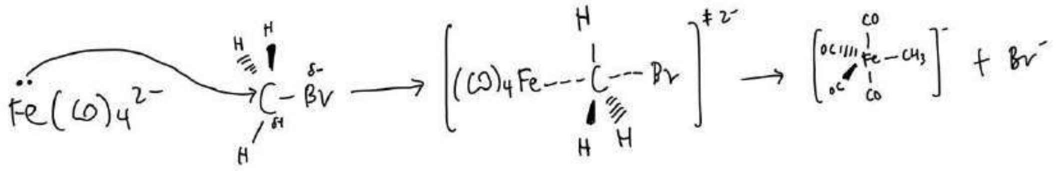
Draw d_{xy}, d_{xz} and d_{yz}, stating that it is of lower energy and $d_{x^2-y^2}$ and d_{z^2} at higher energy

(iv) Explain why transition metal can show variable oxidation states. [1]

The electrons in the 3d and 4s subshells are similar in energy, 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.

	(b)	Sodium reacts with iron pentacarbonyl to produce a salt known as sodium tetracarbonylferrate, $Na_2Fe(CO)_4$. $2Na + Fe(CO)_5 \longrightarrow Na_2Fe(CO)_4 + CO$ ------- eqn (1)	
		(i)	Explain what is meant by the coordination number of a complex using $Fe(CO)_5$ as an example. [1]
			Co–ordination number is the number of dative bonds attached to the central atom or ion in a complex. In the case of $Fe(CO)_5$, there are 5 dative bonds formed between Fe atom and C of CO, thus, the coordination number of $Fe(CO)_5$ is 5.
		(ii)	Draw the structure of $Fe(CO)_5$ and state its shape. [2]
			 Shape: trigonal bipyramidal
		(iii)	Deduce the oxidising and reducing agent in eqn (1). [2]
			Na is the reducing agent since itself is oxidised from Na to Na^+ in $Na_2Fe(CO)_4$, with an increase in oxidation number from 0 to +1. $Fe(CO)_5$ is the oxidising agent since Fe is reduced with a decrease in oxidation number from 0 in $Fe(CO)_5$ to -2 in $Na_2Fe(CO)_4$.
		(iv)	Explain why carbon monoxide, CO, is poisonous. [2]
			CO competes with O_2 for bonding with haemoglobin as it enters into the bloodstream. Being a stronger ligand than O_2, CO will displace the weaker O_2 ligand in oxyhaemoglobin by forming a stronger dative bond with iron in haemoglobin, resulting in a more stable carboxyhaemoglobin complex. The formation of carboxyhaemoglobin complex is not readily reversible due to its stability, and this reduces the availability of haemoglobin for oxygen transport. Deprivation of oxygen causes damage to living organs and tissues, resulting in death. Hence, Co is poisonous.
		(v)	The tetracarbonylferrate dianion acts as a nucleophile and react with alkyl halide by the S_N2 mechanism to form a new C-Fe bond. $[Fe(CO)_4]^{2-} + CH_3Br \longrightarrow [Fe(CH_3)(CO)_4]^- + Br^-$ ------- eqn (2) Suggest a mechanism between $Fe(CO)_4{}^{2-}$ and CH_3Br. State clearly any intermediates that may be formed and use curly arrows to indicate the movement of electron pairs. [3]

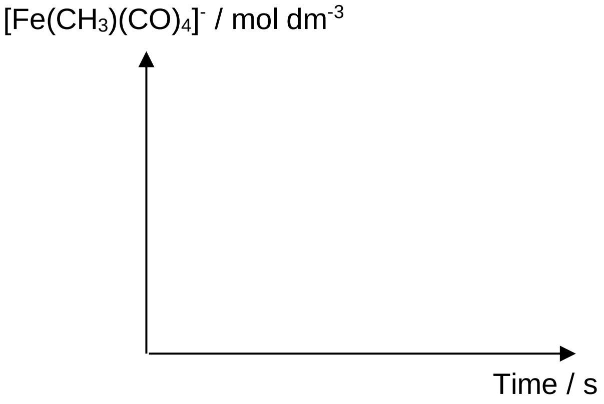
S_N2 Nucleophilic Substitution (not included in marking point as question already states S_N2)



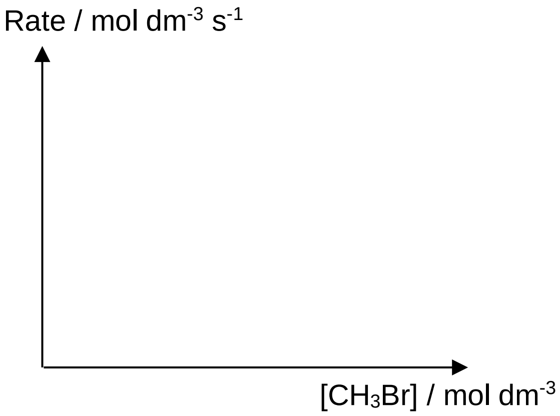
(vi) State the rate equation for the reaction in eqn 2. [1]

Rate = k $[CH_3Br][Fe(CO)_4^{2-}]$

(vii) **I** Sketch the graph of $[Fe(CH_3)(CO)_4]^-$ against time.

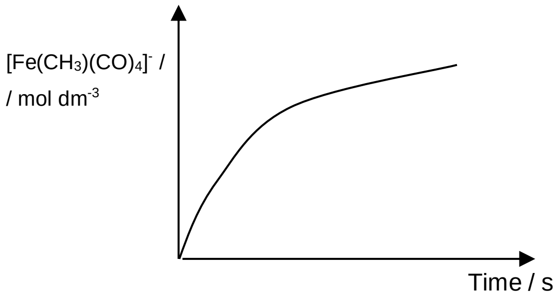


II Sketch the graph of rate against $[CH_3Br]$ given that $[Fe(CO)_4]^{2-}$ is in excess.

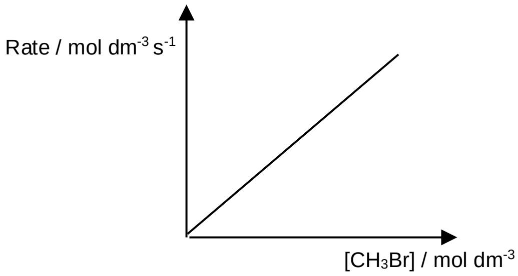


[2]

I:



II:



(c) The melting point of sodium tetracarbonylferrate, $Na_2Fe(CO)_4$ is lower than that of sodium oxide. With reference to the structure and bonding, explain the difference in melting point.[3]

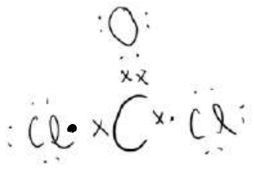
Both sodium oxide and $Na_2Fe(CO)_4$ have giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged ions. Both compounds have Na^+ as the cation. Since L.E$\propto\left|\frac{q^+q^-}{r^++r^-}\right|$ and $[Fe(CO)_4]^{2-}$ anion is larger than O^{2-} anion, the lattice energy of Na_2O is more exothermic than that of $Na_2Fe(CO)_4$. Thus, more energy is needed to overcome the stronger ionic bonds in Na_2O than $Na_2Fe(CO)_4$, thus $Na_2Fe(CO)_4$ has a lower melting point.

[Total: 23]

3 **(a)** Phosgene, $COCl_2$, is essential in the manufacturing of everyday products, including medical products and footwear. Phosgene is produced by combining carbon monoxide and chlorine with a catalyst.

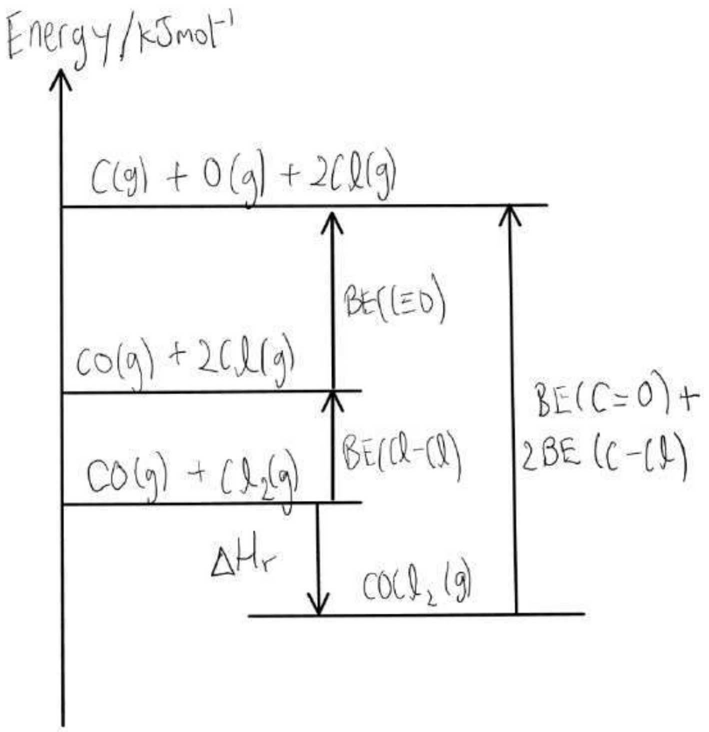
$$CO(g) + Cl_2(g) \rightarrow COCl_2(g)$$

(i) Draw a 'dot-and-cross' diagram of $COCl_2$ and state the bond angle about the central atom. [2]



Bond angle: 120°

(ii) Using relevant data from the *Data Booklet*, construct a fully labelled energy level diagram to calculate the enthalpy change of the above reaction. [3]



$\Delta H_r = 244 + 1077 - (740 + 2(340)) = -99$ kJ mol^{-1}

(iii) Explain what is meant by the term entropy of a chemical system. [1]

Entropy measures the amount of disorderliness in a system.

(iv) Predict, with reasons, the sign of the entropy change of the reaction between CO(g) and Cl_2(g) to form $COCl_2$. [2]

Entropy change of the reaction should be negative, as the number of moles of gas decreases from 2 moles to 1 mole, there are less ways of arranging the particles, hence the system decreases in disorderness.

(v) Hence, state and explain the significance of the sign of the standard Gibbs free energy change when temperature is low. [2]

$\Delta G = \Delta H - T\Delta S$, standard Gibbs free energy change should be negative at low temperature, since the enthalpy change is negative, and entropy change is negative. $|T\Delta S| < |\Delta H|$. Thus, the reaction is spontaneous at low temperature.

(b) Above 200°C, a 2.0 dm^3 cylinder containing gaseous phosgene decomposes to carbon monoxide and chlorine in a dynamic equilibrium according to the following equation:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

(i) Predict and explain the effect of a catalyst on the position of the above equilibrium. [1]

No change in the position of equilibrium since the catalyst increases the rate of both the forward and backward reaction to the same extent.

(ii) At 350°C, the percentage dissociation of $COCl_2$ is found to be 45% and the total pressure at equilibrium is 3.5 atm. Calculate the value of K_p at 350 °C. [3]

	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
Initial pressure/ atm	a		0		0
Change in pressure / atm	-0.45a		+0.45a		+0.45a
Equilibrium pressure / atm	0.55a		0.45a		0.45a

0.55a + 0.45a + 0.45a = 3.5 atm

a = 2.414

$K_p = \frac{(2.414\times0.45)^2}{(2.414\times0.55)} = 0.889$ atm

(iii) Calculate the mass of the carbon monoxide gas that exists inside the cylinder at 350°C. [2]

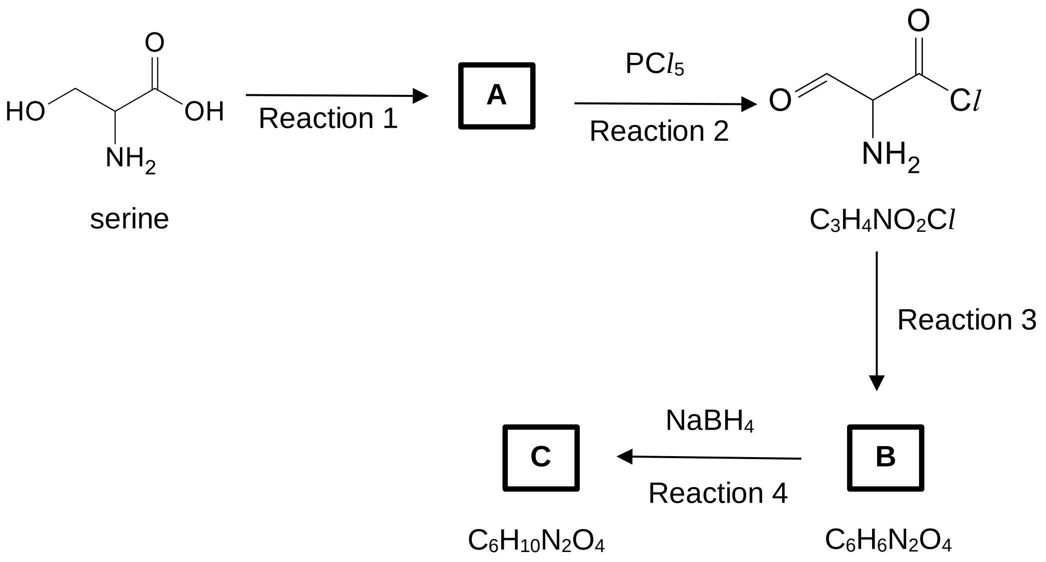
pV = m/Mr RT

$(2.41 \times 0.45) \times 101325 \times 2.0 \times 10^{-3} = (m / 28)(8.31)(350 + 273)$

M = 1.19 g

[Total: 16]

4 Spider silk is a protein fibre. Major amino acids in the silk protein are alanine, serine and glycine. The following reaction scheme involves serine as a starting material.

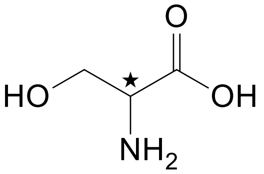


(a) Explain what is meant by a chiral centre.

Label with an asterisk (*) for any chiral centre that is present in serine. [2]

A chiral centre exists when a molecule has at least one asymmetric carbon atom where the carbon atom is bonded to 4 different substituents.

Serine has a chiral carbon.

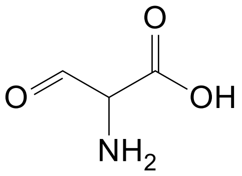


(b) Name the functional group common to compounds **B** and **C**. [1]

Secondary Amide

(c) Draw the structure of compound **A** in the box and state the reagents and conditions for reaction 1. [2]

A:



Dilute $K_2Cr_2O_7$, H_2SO_4(aq), heat with immediate distillation

(d) Name the type of reaction for reactions 2, 3 and 4. [3]

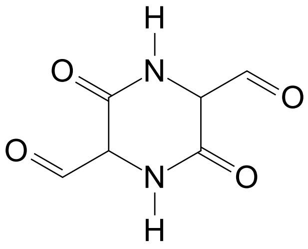
Reaction 2: nucleophilic substitution

Reaction 3: condensation / nucleophilic substitution

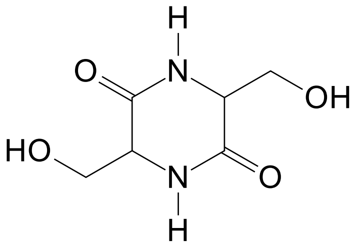
Reaction 4: Reduction

(e) Draw the structures of compound **B** and **C** in the box. [2]

B:



C:



(f) The following table contains the pK_a values of different compounds.

Compound	**pK_a**
Serine	2.21
Propanoic acid	4.87
Phenol	9.95

(i) Suggest a reason why pK_a of propanoic acid is higher than serine. [2]

The NH_2 group in serine exerts an electron-withdrawing effect, pulling electrons away from the O atom of the carboxylate salt, dispersing the negative charge and making the carboxylate ion more stable. Thus, serine is more acidic than propanoic acid and has a lower pK_a value.

(ii) Suggest a reason why pK_a of propanoic acid is lower than phenol. [2]

For the propanoate ion, there is a delocalisation of the negative charge over the two oxygen atoms. This disperses the negative charge and stabilises the anion. For the phenoxide ion, the p-orbital of oxygen overlaps with the π orbital of the benzene ring and this delocalises the negative charge on the oxygen atom into the benzene ring. However, this delocalisation is not as effective as that of the carboxylate ion as the carbon atoms are not very electronegative compared to oxygen atoms. Hence phenol is less acidic than propanoic acid.

[Total: 14]

5	**(a)**	**X** and **Y** are two different elements in Period 3. The following are some of their properties: - Oxide of **X** is insoluble in water while the aqueous solution of chloride of **X** is weakly acidic. - Element **Y** conducts electricity and has a lower melting point than element **X**. - The first ionisation energy of element **X** is lower than that of element **Y**.	
		(i)	Identify the elements, **X** and **Y**. [2]
			X: aluminium **Y**: Magnesium
		(ii)	Write the balanced equation(s) for the reaction when chloride of **X** dissolves in water and state the pH of the solution. [2]
			$AlCl_3 (s) + 6 H_2O(l) \rightarrow [Al(H_2O)_6]^{3+} (aq) + 3Cl^- (aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightarrow [Al(H_2O)_5(OH)]^{2+} (aq) + H^+ (aq)$ pH = 3
		(iii)	Explain why oxide of **X** is insoluble in water. [1]
			Energy released from the ion-dipole interaction between Al^{3+} and O^{2-} and water is insufficient to overcome the high strong electrostatic forces of attraction between oppositely charged ions in Al_2O_3.
		(iv)	Explain why element **Y** has a lower melting point than element **X**. [2]
			Both X and Y has giant metallic lattice structure with strong electrostatic forces of attraction between the positively charged ions and sea of delocalised electrons. Since Al has more delocalised electrons than Mg (or Al^{3+} has a higher charge density than Mg^{2+}), more energy is needed to overome the stronger electrostatic forces of attraction in Al than in Mg. Thus, Mg (element Y) has a lower melting point.
		(v)	Explain why the first ionisation energy of element **X** is lower than that of element **Y**. [2]
			Less energy is required to remove an electron from the 3p orbital in Al than to remove an electron from the 3s orbital in Mg as the 3p electron is further away from the nucleus and experiences greater screening than 3s electron.

(b) Sulfur is another period 3 element with a relative atomic mass of 32.09.

There are three naturally occurring isotopes. The relative abundances of the isotopes of sulfur are found to be the following.

Isotope	**% Abundance**
^{32}S	95.0
^{33}S	*a*
^{34}S	*b*

(i) Define the term *relative atomic mass*. [1]

Relative atomic mass (A_r) is defined as the weighted average mass of the isotopes of an element compared to $\frac{1}{12}$ of the mass of one atom of ^{12}C.

(ii) Calculate the percentage abundances of isotopes ^{33}S and ^{34}S. [2]

32.09 = 0.95(32) + 33(a/100) + 34(100-95-a/100)

a = 1.0 %

b = 4.0 %

(c) A 2.00 g sample of food additive containing magnesium carbonate is allowed to react with 50 cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid. The excess acid required 19.30 cm^3 of 0.100 mol dm^{-3} aqueous potassium hydroxide for complete reaction.

Calculate the percentage of magnesium carbonate that is present in the food additive. [3]

$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2$

$KOH + HCl \rightarrow NaCl + H_2O$

Amount of initial HCl = 50/1000 x 0.2 = 0.01 mol

Amount of HCl in excess = 19.3/1000 x 0.1 = 0.00193 mol

Amount of reacted HCl = 0.01 - 0.00193 = 0.00807 mol

Amount of $MgCO_3$ = 0.00807/2 = 0.004035 mol

Mass of $MgCO_3$ = 0.004035 x (24.3 + 12 + 48) = 0.340 g

Percentage of magnesium carbonate = 0.34/2 x 100 = 17.0 %

[Total: 15]

END OF PAPER 2

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Class Adm No

Candidate Name: ____________________

H

2019 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **20 Sept 2019**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph 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.

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	**19**	**19**	**22**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** 3–chloropropanoic acid, $CH_2ClCH_2CO_2H$, is a weak Brønsted acid. A 0.100 mol dm^{-3} solution of $CH_2ClCH_2CO_2H$ has a pH of 2.49.

(i) Calculate the pK_a of 3–chloropropanoic acid. [3]

Since pH = 2.49, $[H^+] = 10^{-2.49}$

$$K_a = \frac{[CH_2ClCH_2CO_2^-][H^+]}{[CH_2ClCH_2CO_2H]}$$

$$= \frac{[10^{-2.49}][10^{-2.49}]}{[0.100]}$$

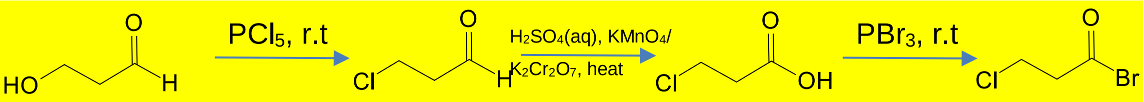
$$= 1.05 \times 10^{-4}$$

$pK_a = -\lg(1.05 \times 10^{-4}) = 3.98$

(ii) State and explain the differences in the relative acid strength between 3–chloropropanoic acid and propanoic acid. [2]

3–chloropropanoic acid is a stronger acid than propanoic acid. Due to the presence of the electron withdrawing group, C*l*, the negative charge of O on the carboxylate anion is dispersed. ; This causes the conjugate base of 3–chloropropanoic acid to be more stable. Hence, acidity increases. ;

(iii) 3-chloropropanoyl bromide is the acid derivative of 3–chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]



1m x 3 reagents and conditions

1m x 2 correct intermediates

(b) A student investigated the rate of reaction between 3–chloropropanoic acid and aqueous sodium carbonate.

The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3–chloropropanoic acid and sodium carbonate. The following results were obtained.

Experiment Number	Volume / cm^3			Time / s
	3–chloropropanoic acid	Na_2CO_3	H_2O	
1	20.0	40.0	40.0	78
2	20.0	30.0	50.0	100
3	5.0	20.0	25.0	75

(i) Write an equation, including state symbols, for the reaction between sodium carbonate and 3–chloropropanoic acid. [1]

$2CH_2ClCH_2CO_2H(aq) + Na_2CO_3(aq) \rightarrow 2CH_2ClCH_2CO_2^-Na^+(aq) + CO_2(g) + H_2O(l)$

(ii) State the relationship between time and rate. [1]

Inverse relationship

(iii) Determine the order of the reaction with respect to 3–chloropropanoic acid and sodium carbonate. [2]

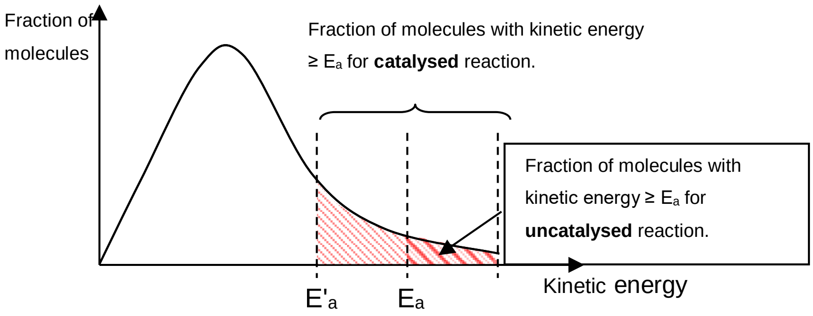
Comparing Expt 1 and 2, while volume of 3–chloropropanoic acid is kept constant and volume of Na_2CO_3 is 4/3 times, rate is 100/78 times. Order with respect to Na_2CO_3 is 1.

Comparing Expt 1 and 3, while volume of Na_2CO_3 is kept constant after multiplying the volume by two, volume of 3–chloropropanoic acid is halved, rate stays relatively constant. Order with respect to 3–chloropropanoic acid is 0.

(iv) Hence, write the rate equation, stating the units of k. [2]

Rate = k[Na_2CO_3]
k = s^{-1}

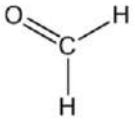
(v) With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3–chloropropanoic acid and sodium carbonate. [3]



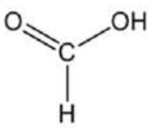
A catalyst provides an alternative pathway for the reaction, lowering the activation energy required. Hence, there is a greater fraction of molecules with energy greater than activation energy. Frequency of effective collisions increases, leading to increase rate of reaction. (2m for diagram, 1m for explanation)

[Total: 19]

2 **(a)** Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom with an oxidation state of 0 and +2 respectively. [2]



O.S. = 0



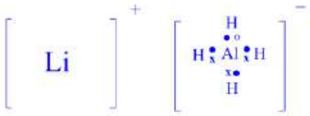
O.S. = +2

(b) A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute NaOH(aq) produces a colourless, pungent gas that turns moist red litmus paper blue.

(i) Draw the structure of compound **A** and state the functional group present. [2]

$(CONH_2)_2$, amide

(ii) The functional group present in compound **A** can be reduced by lithium aluminium hydride, $\mathrm{LiA}\mathit{l}\mathrm{H}_4$. Draw the dot-and-cross diagram for $\mathrm{LiA}\mathit{l}\mathrm{H}_4$. [1]



(iii) Other than $\mathrm{LiA}\mathit{l}\mathrm{H}_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. $\mathrm{LiA}\mathit{l}\mathrm{H}_4$ is able to produce hydride ion, H^- more readily than $NaBH_4$. Suggest why $\mathrm{LiA}\mathit{l}\mathrm{H}_4$ is a more powerful reducing agent than $NaBH_4$. [1]

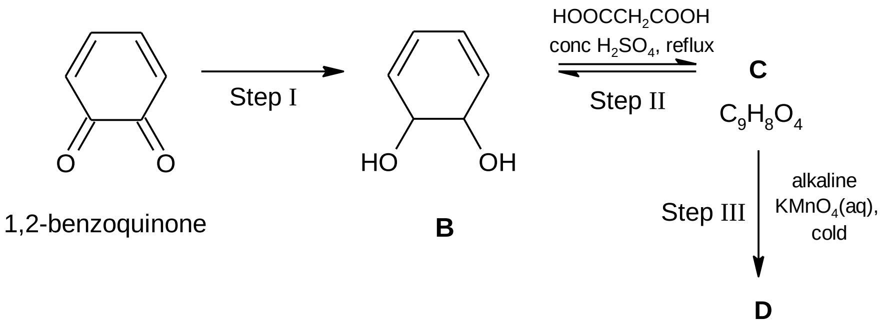
The electronegativity of Al is lesser than that of B. Hence, H bonded to Al can produce H^- more readily than H bonded to B. Thus, reduction occurs more readily for $LiAlH_4$, proving that it is a stronger reducing agent.

OR

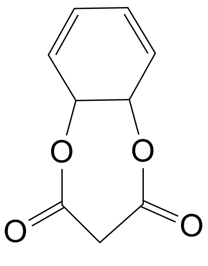
The size of A*l* atom is larger compared to B, thus the orbital overlap between A*l* and H is less effective. Therefore the bond length of A*l*–H bond is longer than that of B–H bond. ; Less energy is required to break the weaker A*l*–H bond, resulting in a greater ease of generating H^- for the reduction process.

(c) Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

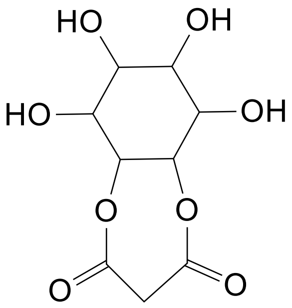
The following scheme involves 1, 2-benzoquinone, where step I involves the use of LiA*l*H$_4$.



(i) Draw the structures of **C** and **D**. [2]

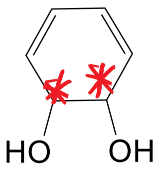


C



D

(ii) Identify the chiral centres on **B**. Hence, explain why it does not display optical activity.[2]



It does not display optical activity as there is a plane of symmetry in the compound.

(iii) Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

2,4-DNPH, warm.

Orange ppt observed for 1,2-benzoquinone, no orange ppt observed for **B**.

OR

PC*l*$_5$, r.t.

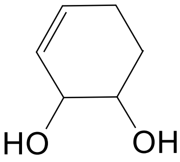
White fumes observed for **B**, no white fumes observed for 1,2-benzoquinone.

OR

$K_2Cr_2O_7/H_2SO_4(aq)$, heat.

Orange $K_2Cr_2O_7$ turns green for **B**, orange $K_2Cr_2O_7$ remains orange for 1,2-benzoquinone.

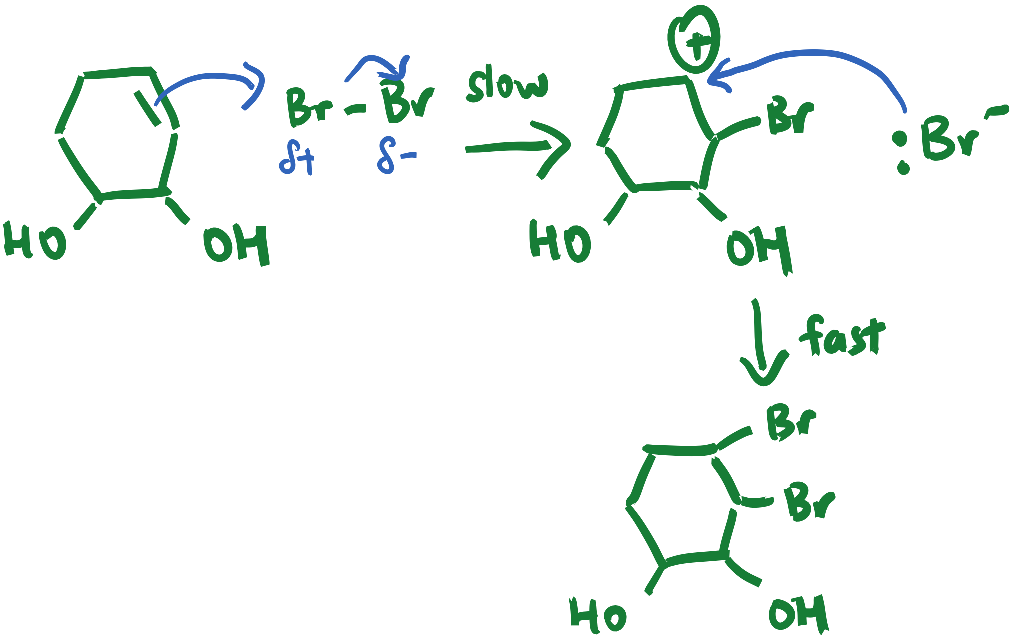
(iv) When compound **B** undergoes partial hydrogenation, it forms compound **E**.



E

Describe the mechanism of the reaction when compound **E** reacts with Br_2 in CCl_4 in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

Electrophilic addition



1m for correct intermediate, 1m for name of mechanism, 1m for correct movement of electrons

(d) $K_2Cr_2O_7$ and $KMnO_4$ are common oxidising agents used in organic synthesis where $KMnO_4$ is the more powerful of the two. Compound **F**, C_4H_8O, reacted with $K_2Cr_2O_7$ and $KMnO_4$ separately to yield different products as shown in the reactions below.

$$\underset{\mathbf{F}}{C_4H_8O} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \underset{\mathbf{G}}{C_4H_6O_2}$$

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[KMnO_4/H_2SO_4]{} \underset{\textbf{H}}{C_2H_4O_2}$$

Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with Na_2CO_3, but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

F: $CH_3CH=CHCH_2OH$;

G: $CH_3CH=CHCOOH$;

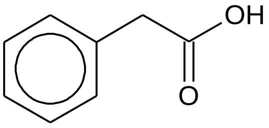
H: CH_3COOH ;

1m for explanation

All three compounds, **F**, **G** and **H** react with sodium metal	All 3 compounds contain the -OH functional group
G and **H** react with Na_2CO_3, but **F** does not	Presence of carboxylic acid in C and D
F and **G** decolourise aqueous bromine.	Presence of alkene

[Total: 19]

3 **(a)** Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.



phenylethanoic acid

(i) In a titration experiment, 60 cm^3 of 0.10 mol dm^{-3} of sodium hydroxide was added to 20 cm^3 of 0.20 mol dm^{-3} of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 cm^3 of sodium hydroxide was added to the flask. [3]

Amount of acid present = 20/1000 x 0.2 = 0.004 mol
Volume of NaOH required at equivalence point = 0.004 / 0.1 = 40 cm^3 ;

When 60 cm^3 of NaOH is added:

$$[OH^-] = [NaOH] = \frac{\text{moles of excess NaOH}}{\text{new volume of solution}} = \frac{[(60-40)/1000] \times 0.10}{(20+60)/1000}$$

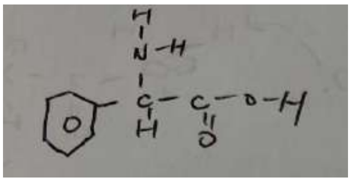
$$= 0.0250 \text{ mol dm}^{-3} \quad ;$$

$$pOH = -\log_{10} 0.0250 = 1.60$$

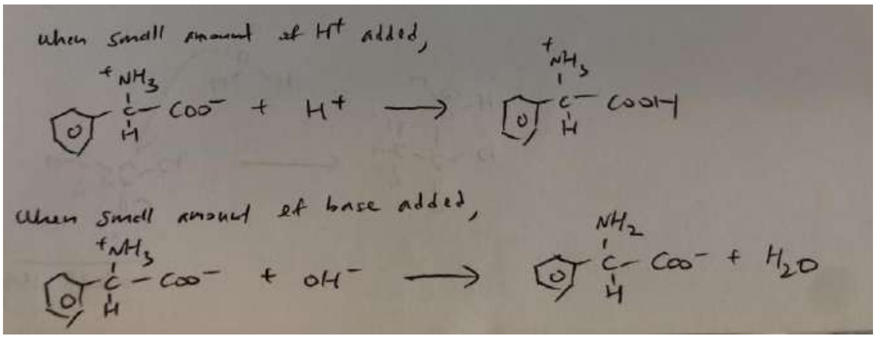
$$pH = 14 - pOH = 14 - 1.60 = 12.4 \quad ;$$

(ii) 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.

Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]



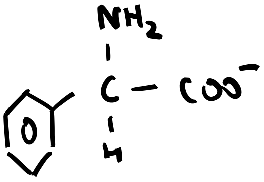
(iii) Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]



when small amount of H+ added,

when small amount of base added,

(iv) Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]



(b) **(i)** Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]

Phenylethanoyl chloride is more reactive as the reactive carbon is more electron deficient since it is attached to two highly electronegative atoms (Cl and O) which results in the nucleophiles to attack it more readily.

(ii) Given that phenylethanoyl chloride has a boiling point of 95 °C and phenylethanoic acid has a boiling point of 266 °C, explain this difference in terms of structure and bonding. [2]

Phenylethanoic acid will have a higher boiling point ; due to the presence of strong intermolecular hydrogen bonding between its molecules, compared to the weaker permanent dipole-permanent dipole forces of attraction between molecules of phenylethanoyl chloride. ; More energy is required to overcome the stronger H-bonding between phenylethanoic acid, resulting in a higher boiling point.

(iii) State the number of sp^2 and sp^3 hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]

7 sp^2 and 1 sp^3 C

(iv) State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

18 sigma and 4 pi

(c) Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

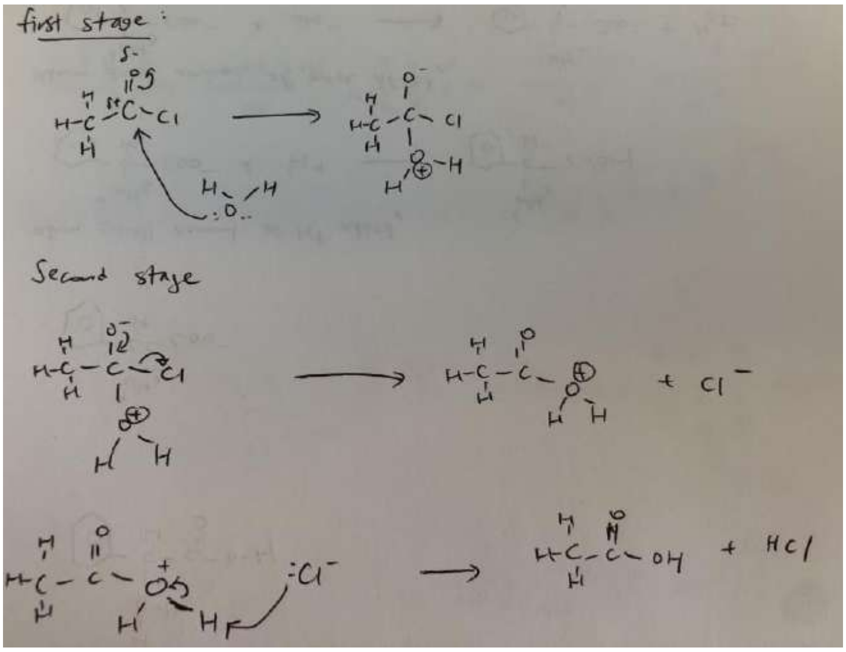
First stage

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the π bond of the C=O bond to break.

Second stage

- The carbon-oxygen double bond reforms and a chloride ion is released.
- As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.

(i) Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]



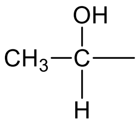
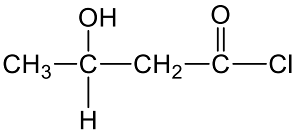
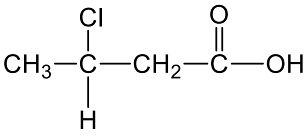
1m for each step

(ii) State the type of reaction occurring in the first stage of the mechanism. [1]

Nucleophilic addition

(d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when heated with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

- Compound Y is an acyl chloride that undergoes hydrolysis in water, giving a solution of lower pH value since HC*l* is formed. ;
- White precipitate of AgC*l* is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride. No white precipitate of AgC*l* is formed when Z is added to aqueous silver nitrate, Z contains a chloroalkane. ;
- Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of H^+ ions in water. ;
- Both Z and Y contains  $CH_3-\overset{OH}{\underset{H}{C}}-$.
- Y is  $CH_3-\overset{OH}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Cl$;
- Z is  $CH_3-\overset{Cl}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OH$;

[Total: 22]

Section B

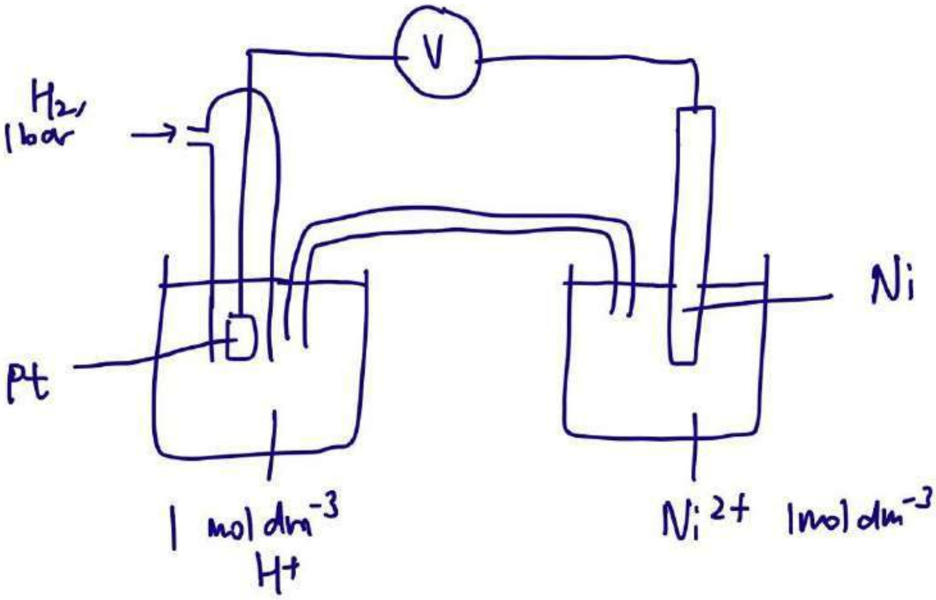
Answer **one** question from this section.

4 **(a)** Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to Ni^{2+}.

(i) Define the term standard electrode potential. [1]

The **Standard electrode potential, $E^\ominus$,** of an electrode, is the relative potential of this electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.

(ii) Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of Ni^{2+}/Ni under standard conditions. [3]



(iii) Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part **(ii)**. [1]

The reading will become less positive.

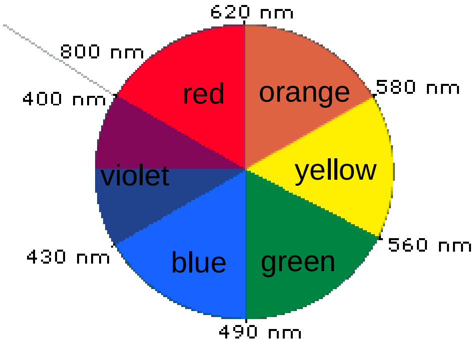
(iv) An electrolytic cell contains $Ni(NO_3)_2$ and $Mn(NO_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]

Cathode: Ni discharged, $Ni^{2+} + 2e \longrightarrow Ni$

Anode: O_2 discharged, $2H_2O \longrightarrow O_2 + 4H^+ + 4e$

Overall: $2Ni^{2+} + 2H_2O \longrightarrow 2Ni + O_2 + 4H^+$

(b) Aqueous nickel salts are coloured. $[Ni(NH_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[NiCl_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.



(i) State the oxidation number of nickel in $[NiCl_4]^{2-}$. [1]

+2

(ii) Suggest the colour of:

I: $[Ni(NH_3)_6]^{2+}$

II: $[NiCl_4]^{2-}$ [2]

$[Ni(NH_3)_6]^{2+}$ is blue, while $[NiCl_4]^{2-}$ is yellow

(iii) Explain why the two complexes are coloured. [3]

In the presence of an octahedral ligand field, the degenerate d-orbitals will split into two energy levels. In the partially-filled d orbitals (d4), electrons are able to promote from the lower to the higher level by absorbing energy in the visible spectrum (blue-green). The colour shown is the complementary colour (orange-red or yellow).

(c) The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$. The stability constant, K_{stab}, is given by

$$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6}$$

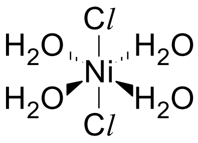
Complex	Stability constant
$Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$	4.8×10^7
$Ni(H_2O)_6]^{2+} + 3\text{ en} \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$	2.0×10^{18}

State and explain if the en ligand will replace the NH_3 ligand for the nickel complexes. [2]

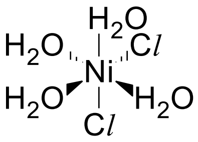
Yes, ligand exchange will take place as the stability constant for $[Ni(en)_3]^{2+}$ is higher than that of $[Ni(NH_3)_6]^{2+}$. Hence this implies that $[Ni(en)_3]^{2+}$ is more stable and will tend to be formed more.

(d) **(i)** The coordination compound $NiCl_2(H_2O)_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]

Cis-trans isomerism



Trans



cis

(ii) Explain why $[Ni(en)_3]Cl_2$ can dissolve in water. [2]

$[Ni(en)_3]Cl_2$ is ionic in nature. The energy evolved in the formation of ion-dipole interaction is sufficient to overcome the ionic bonds between the oppositely charged ion and hence it is soluble in water.

[Total: 20]

5 **(a)** **(i)** State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

Sodium chloride – giant ionic structure with strong electrostatic forces of attraction between the opposite charged ions ;

Aluminium chloride – simple covalent structure with id-id between the molecules and covalent bonds between Al and Cl atoms;

(ii) Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

Thermochemical term	**ΔH / kJ mol^{-1}**
Lattice energy of NaCl(s)	-788
Enthalpy change of atomisation of Na(s)	+108
First electron affinity of Cl(g)	-349

ΔH_f = (+108) + (+494) + (+122) + (-349) + (-788) = -413 kJ mol^{-1} ;

2m for correct energy level diagram

(iii) Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$;

$AlCl_3$ undergoes partial hydrolysis to produce a pH 3 solution which appears red in the presence of universal indicator. ;

$SiCl_4 (l) + 2H_2O (l) \rightarrow SiO_2 (s) + 4HCl (aq)$;

$SiCl_4$ undergoes complete hydrolysis to produce a pH 2 solution which appears red in the presence of universal indicator.;

(b) The reactions of different halogens with hydrogen differ due to their reactivity. Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

As the **size of the Halogen increases down the Group;** , **the H–X bond becomes longer and weaker due to the less effective overlap of the orbitals** ; and so it is easily broken. Thus, the thermal stability of the hydrides decreases down the Group, due to the decrease in strength of the H–**X** bond.

Bond	**Bond energy / kJ mol^{-1}**
H–F	568
H–C*l*	431
H–Br	366
H–I	299

(c) The iodine clock reaction involves 2 reactions.

First reaction involves peroxydisulfate ($S_2O_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($S_2O_3^{2-}$) ion reacting with the iodine produced.

(i) Write the equations for the two reactions of the clock reaction. [2]

$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

(ii) If 30 cm^3 of 0.002 mol dm^{-3} of $S_2O_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

Amount of $S_2O_3^{2-}$ = 0.00006 mol

Amount of $K_2S_2O_8$ = 0.00003 mol

Mass of $K_2S_2O_8$ = 0.00003 mol x 270.4 = 0.00811g

(iii) Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in the speeding up the rate of reaction.

[2]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$

(d) Iron is also used in other reactions, such as the Haber Process. State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

It acts as a heterogenous catalyst. It has partially-filled d-orbitals that can accept electron pairs from reactant particles.

[Total: 20]

Class	Adm No

Candidate Name: ____________________

Shift
Laboratory

H

millennia institute

2019 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical **4th Sept 2019**

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	18	22	9	6	55

1 Determination of titration value at equivalence point

The reaction between acid and carbonates is well known. In the presence of excess acid, the following reaction occurs:

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq) \qquad pK_a(HCO_3^-) = 10.32 \qquad \textbf{equation 1}$$

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq) \qquad pK_a(H_2CO_3) = 6.37 \qquad \textbf{equation 2}$$

$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(l) \qquad \textbf{equation 3}$$

CO_2(aq) is then released from the solution as CO_2(g), which is observed as effervescence. The entire reaction is known to release heat.

FA 1 is 1.8 mol dm^{-3} of aqueous potassium carbonate, K_2CO_3.
FA 2 is nitric acid, HNO_3, of concentration between 1.9–2.1 mol dm^{-3}.

Assuming that the first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with the HCO_3^- produced, the reaction between **FA 1** and the first equivalent of **FA 2** can be simplified as:

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

And the reaction between **FA 1** and the second equivalent of **FA 2** can be simplified as:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

As the precise concentration of **FA 2** is unknown, determination of ΔH_{rxn} can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as ΔH_{rxn}. 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 an acid-carbonate thermometric titration. The data from this titration will be used to determine:

- the titration value at the first equivalence point, V_{eq1},
- the precise concentration of **FA 2**, [HNO_3],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of reaction, ΔH_{rxn}.

(a) **(i)** 25.0 cm^3 of **FA 1** is reacted with **FA 2**.

Calculate the **theoretical volume of** FA 2 needed for the first equivalence point, V_{eq1}', and the second equivalence point, V_{eq2}', of the reaction between **FA 1** and **FA 2**. Assume [HNO_3] to be 2.0 mol dm^{-3}.

Amount of K_2CO_3 reacted = 1.8 x 25.0 x 10^{-3} = 0.045 mol
Amount of H^+ for first equivalence point = 0.045 mol
$V_{eq1}' = \frac{0.045}{2.0}$ = 0.0225 dm^3 = 22.5 cm^3 **M1**
V_{eq2}' = 22.5 x 2 = 45.0 cm^3 **M2**

V_{eq1}' = ... cm^3

V_{eq2}' = ... cm^3

[2]

Determination of V_{eq1} and ΔH_{rxn} using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 2** have been added to **FA 1**.

In an appropriate format in the space provided below, prepare a table to record your results. Record all values of temperature, *T*, to 0.1°C, and each total volume of **FA 2** added.

Note: You should aim to perform each subsequent addition of **FA 2** quickly.

1. Fill a burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 1** 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 1**. Record this temperature.
4. Add 4.00 cm^3 of **FA 2** from the burette to the **FA 1** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 2** added.
6. Repeat steps **4** and **5** until a total volume of 48.00 cm^3 of **FA 2** has been added.

Results

Vol of **FA 2** added / cm^3	Maximum T / °C
0.00	32.7
4.00	33.7
8.00	34.5
12.00	35.0
16.00	35.4
20.00	35.6
24.00	35.6
28.00	35.4
32.00	35.2
36.00	35.0
40.00	34.7
44.00	34.5
48.00	34.2

[2]

(ii) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 2** added, on the *x*-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.0 °C greater than the maximum temperature recorded.

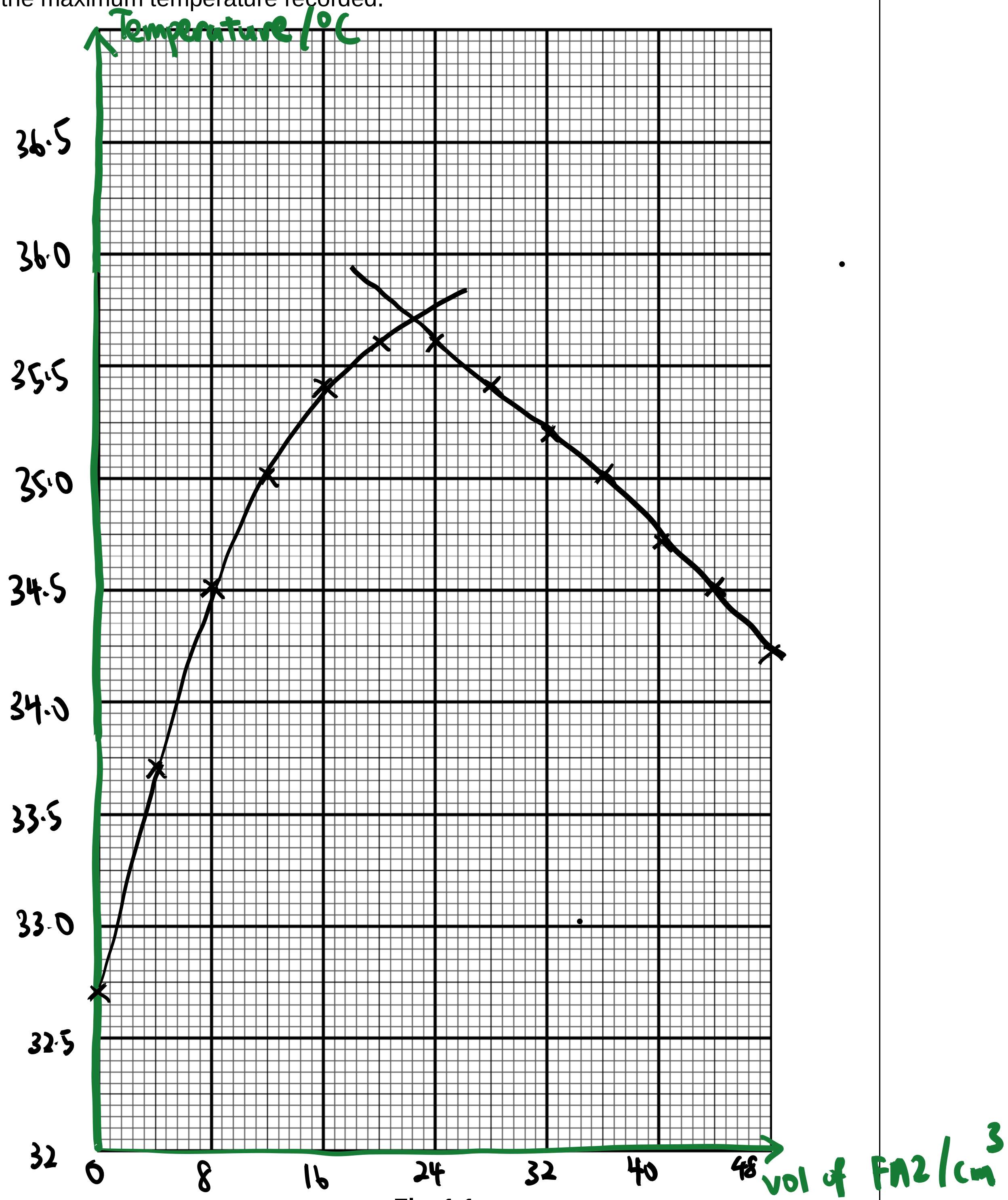


Fig. 1.1

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]

(iii) 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.

ΔT_{max} = 35.7 – 32.7 = 3.0 °C

V_{eq1} = 22.40 cm^3

T_{max} = 35.7 °C

ΔT_{max} = 3.0 °C

[3]

(iv) Determine the concentration of HNO_3, [HNO_3], in **FA 2**.

Amount of K_2CO_3 reacted = 1.8 x 25.0 x 10^{-3} = 0.045 mol

Amount of HNO_3 reacted at V_{eq1} = 0.045 mol

[NaOH] = $\frac{0.045}{22.40\times10^{-3}}$ = 2.01 mol dm^{-3} (3sf)

[HNO_3] in **FA 2** = …………… [1]

(v) Determine the enthalpy change of reaction, ΔH_{rxn}.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq) \qquad \Delta H_{rxn}$$

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 + 22.40 = 47.4 g

q = mcΔT = (47.4)(4.18)(3) = 594.4 J

$\Delta H_{rxn} = -\frac{q}{n_{LR}} \times \text{CLR} = -\frac{594.4}{0.045} \times 1$ = –13.2 kJ mol^{-1} (3 sf)

ΔH_{rxn} = …………… [3]

(b) **(i)** With reference to your graph in **Fig. 1.1**, explain why the titre at second equivalence point, V_{eq2}, cannot be determined from this experiment.

The temperature does not increase / reaction is not exothermic for **equation 2**.

OR There is only one intersection point

OWTTE

[1]

(ii) Suggest, using chemistry concepts, a possible explanation for the observation in **(b)(i)**.

Equation 2 is not exothermic / the temperature does not increase as **equation 3** could be endothermic.

or

pK_a(H_2CO_3) is small compared to pK_a(HCO_3^-) and the energy released from the reaction is used to complete the reaction.

[1]

(iii) The value of V_{eq1} could also have been determined via a regular acid-base titration with a suitable indicator.

Suggest which titration method is likely to give a more accurate value of V_{eq1} and give two reasons for why this is so.

Method:

Accept any reasonable answer for both

Regular titration: heat loss to surroundings does not affect value of V_{eq1} unlike thermometric method; The first equivalent of H^+ fully reacts with CO_3^{2-} before reacting with HCO_3^- may not be true.

Thermometric titration: does not require use of indicator which may affect pH of solution and end point may not match exactly with equivalence point [2]

[Total: 18]

2 Investigation of the kinetics of an acid-carbonate reaction via gravimetric analysis

FA 1 is 1.8 mol dm^{-3} of K_2CO_3.
FA 3 is dilute nitric acid, HNO_3, of concentration 1.0 mol dm^{-3}.

$$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + CO_2 + H_2O$$

The rate equation of the reaction between **FA 1** and **FA 3** is expressed as such:

$$\text{Rate} = k[K_2CO_3]^a[H^+]$$

where *a* represents the order of reaction with respect to K_2CO_3, and is an integer value of either 0, 1, or 2.

The acid-carbonate reaction results in the release of CO_2(g), which escapes the reaction vessel as effervescence. To determine the kinetics of a reaction involving the loss of a gas, gravimetric analysis can be used, where the change in mass of the reaction vessel is monitored over time.

In this experiment, you will use gravimetric analysis to determine the value of *a*.

(a) Determination of orders of reaction via the 'continuous method'

The orders of reaction can be determined via either the 'continuous method' or the 'initial rates method'. In the 'continuous method', a single reaction is carried out and a measurement (e.g. concentration; mass) is monitored over time.

You will be using the 'continuous method' in this part of the experiment, monitoring the change in mass over time.

1. Weigh and record the mass of an empty 100 cm^3 measuring cylinder.
2. Measure out 80 cm^3 of **FA 3** into this measuring cylinder and record the mass of the measuring cylinder with **FA 3**.
3. Measure out 20 cm^3 of **FA 1** using a 25 cm^3 measuring cylinder into an empty 250 cm^3 conical flask. Weigh and record the mass of the conical flask with **FA 1**.
4. Place the conical flask with **FA 1** on the mass balance provided individually.
5. Start the stopwatch and **simultaneously** pour the **FA 3** in the measuring cylinder into the conical flask. **Do not swirl the flask**.
6. Record the mass readings at 10s intervals until 90s has elapsed, then at 30s intervals. Continue taking readings **until it is appropriate to stop**.

   Given that:
   initial mass of conical flask with **FA 1** and **FA 3**
   = initial mass of **FA 3** + initial mass of conical flask with **FA 1**

In an appropriate form in the space on the next page, record all your time values, balance readings, and mass of CO_2(g) evolved.

Results

Mass of empty measuring cylinder / g	
Mass of measuring cylinder + **FA 3** / g	
Mass of **FA 3** added / g	
Mass of conical flask + **FA 1** / g	
Total mass of conical flask + **FA 1** + **FA 3** before reaction / g	213.82

time / s	total mass / g	total mass of CO_2 evolved / g
0	213.82	0.00
10	213.02	0.80
20	212.91	0.91
30	212.84	0.98
40	212.77	1.05
50	212.72	1.10
60	212.68	1.14
70	212.64	1.18
80	212.61	1.21
90	212.59	1.23
120	212.53	1.29
150	212.49	1.33
180	212.47	1.35
210	212.47	1.35
240	212.47	1.35

[6]

(i) Plot a graph of mass of CO_2(g) evolved, *m*, on the *y*-axis, against time of reaction, *t*, on the *x*-axis on the grid in **Fig. 2.1**.

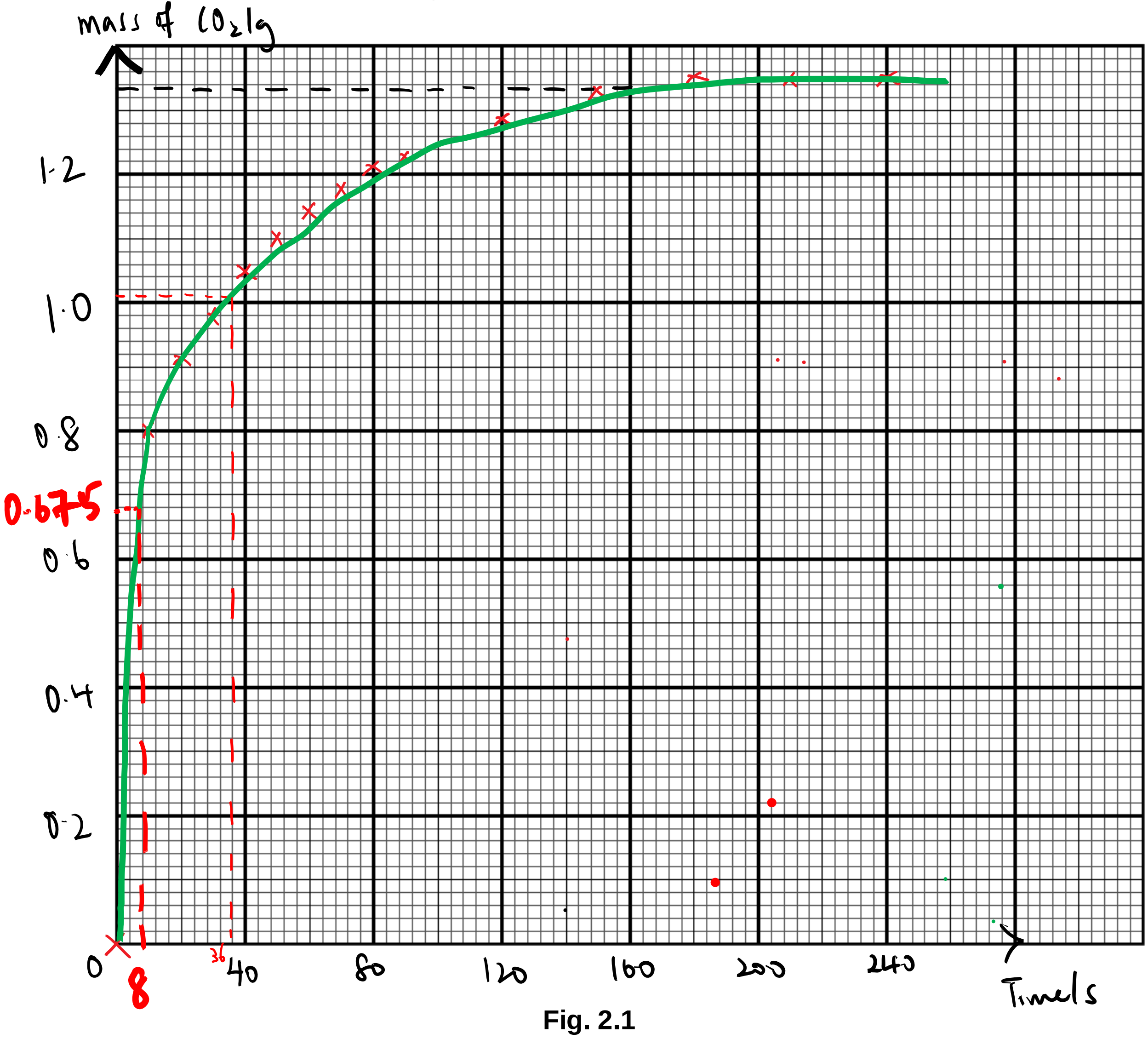


Fig. 2.1

[3]

(ii) By means of a suitable extrapolation drawn on your graph in **Fig. 2.1**, determine a value for the mass of CO_2(g) evolved when the reaction is complete.

mass of CO_2(g) evolved = 1.35 g [1]

(iii) The observed half-life ($t_{1/2}$) of a reaction would be constant if the reaction proceeds with an overall order of 1. The table below shows the percentage of reactants and products in the reaction vessel at different instances of time elapsed:

time elapsed	% of reactants	% of products
0	100	0
$t_{1/2}$ x 1	50	50
$t_{1/2}$ x 2	25	75
$t_{1/2}$ x 3	12.5	87.5
	⋮	
$t_{1/2}$ x ∞	0	100

Assume that the reaction proceeds with an overall order of 1.

Using your answer from **(a)(ii)**, calculate the theoretical total mass of $CO_2(g)$ evolved after the first half-life has elapsed, and then after the second half-life has elapsed.

Mass of CO_2 produced at 1st $t_{1/2}$ = ½ x 1.35 = 0.675 g

Mass of CO_2 produced at 2nd $t_{1/2}$ = ¾ x 1.35 = 1.01 g

total mass of $CO_2(g)$ evolved after first half-life = 0.675 g

total mass of $CO_2(g)$ evolved after second half-life = 1.01 g [1]

(iv) Hence, determine from your experiment whether the acid-carbonate reaction has a consistent half-life, and state if the reaction has an overall order of 1.

Show your working clearly on your graph in **Fig. 2.1** and in the space below.

1st $t_{1/2}$ = 8s

2nd $t_{1/2}$ = 36 – 8 = 28s

Since $t_{1/2}$ is not constant, the reaction does not have an overall order of 1.

[2]

(v) Rate = $k[K_2CO_3]^a[H^+]$, where *a* is an integer value of either 0, 1, or 2.

Identify a possible value of *a*.

a could be 1 or 2

[1]

(b) **Planning**

The 'initial rates method' can also be used to determine the orders of reaction. Unlike the 'continuous method', multiple reactions have to be carried out, each time varying the concentrations of certain solutions.

Although the initial rate of a single reaction can be determined from the gradient of the tangent to a graph plotted at $t = 0$ (such as in **Fig 2.1**), the process is tedious as the graphs for multiple experiments have to be plotted.

A simplified 'initial rates method' experiment would involve determining the time elapsed for a certain *condition* to be met, then simply taking the reciprocal of time elapsed as the initial rate. A common example of such an experiment is iodine-clock reaction, whereby the time taken for the colouration formed to obscure text is measured.

It is important to keep the measured durations of time elapsed for the reactions short (maximum 120s), or the reciprocal becomes a poor approximation of rate.

(i) Plan an experiment using the simplified "initial rates method" by carrying out multiple reactions to determine the order of reaction with respect to K_2CO_3, *a*, for the reaction between K_2CO_3 and HNO_3.

You may assume that you are provided with

- **FA 1**,
- the same apparatus used in **Experiment 2(a)**,
- 4.0 mol dm^{-3} of nitric acid, $HNO_3(aq)$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the quantities you would choose for the experiment and why,
- the procedure for the multiple reactions carried out,
- the measurements you would take,
- an outline of how you would use your results to determine the value of *a* non-graphically.

You may wish to consider the best mode of presentation for your answers.

Concentrations chosen depends on $[HNO_3]$ from previous part. Fix mass, **measure time taken to obtain fixed mass**. Pick a fixed mass of longest time allowed (120s) from graph in (a), then use higher concentrations (which will result in shorter times).

Run	Vol of HNO_3 / cm^3	Vol of FA 1 / cm^3	Vol of H_2O / cm^3	Total Vol / cm^3	Time / s	Rate / s^{-1}
1	20.0	20.0	60.0	100.0	120	
2	20.0	40.0	40.0	100.0		
3	20.0	60.0	20.0	100.0		

For a single run,

1. Measure out the volumes of FA 1, HNO_3 and H_2O as indicated in the tables above, using 25.0 / 50.0 cm^3 measuring cylinders.
2. Transfer HNO_3 and H_2O into a 250 cm^3 conical flask first, and place it on a weighing balance.

3. Record the initial mass, and take note of the final mass to stop the stopwatch.
4. Transfer FA 1 into the conical flask and start the stopwatch simultaneously.
5. Stop the stopwatch when 1.29 g of CO_2 is released and record the time elapsed.
6. Repeat steps 1-5 for the different runs.
7. Rate $\propto$ 1/t, thus calculate 1/t

If rate (or 1/t)

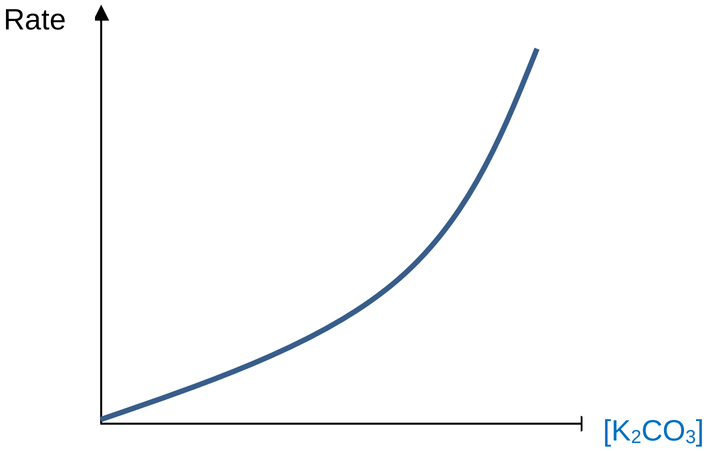
- remains the same from Run 1 to Run 2 to Run 3, reaction is 0th order wrt to K_2CO_3
- doubles from Run 1 to Run 2 to Run 3, reaction is 1st order wrt to K_2CO_3
- more than doubles from Run 1 to Run 2 to Run 3, reaction is 2nd order wrt to K_2CO_3

[6]

(ii) The orders of reaction can also be determined graphically.

Assuming that HNO_3 is in large excess, and *a* = 2, label the x-axis and sketch the expected rate-concentration graph that you would expect to obtain from **(b)(i)**.

Explain your answer briefly.



explanation ………………………………………………………………………………………..

…………………………………………………………………………………………………

………………………………………………………………………………………………... [2]

When HNO_3 is in large excess, order of reaction wrt to HNO_3 is 0.

∴ Rate = $k[K_2CO_3]^2$ and the graph has a " $y=mx^2$ " shape as rate ∝ [K_2CO_3].

[Total: 22]

3 Qualitative Analysis of an unknown salt mixture

FA 4 is a salt mixture comprising of an insoluble salt and a soluble salt. It contains **two cations** and **two anions**.

(a) Transfer 1 spatula of **FA 4** into a test tube and observe its appearance.

State, with explanation, a possible deduction that can be made about the identity of (at least) one of the ions present in **FA 4**.

It contains a transition metal since it is coloured. [1]

(b) 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.	To the test tube from **(a)**, add 2 cm depth of HNO_3, then dropwise until all the **FA 4** dissolves. The resulting solution will be known as '**FA 5 solution**'.	A green solution is formed. Gas produced forms a white ppt in $Ca(OH)_2$.
2.	Add about 1 cm depth of **FA 5 solution** to a fresh boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	Blue ppt forms, turns deep blue in excess NaOH(aq). Gas produced turns red litmus paper blue.
3.	Add about 1 cm depth of **FA 5 solution** into a test-tube. To this test-tube, add silver nitrate dropwise.	White ppt forms, soluble in excess NH_3(aq).

[4]

(c) Based on your observations, deduce the identities of the ions present in **FA 5**.

cation 1: Cu^{2+} cation 2: NH_4^+ anion 1: CO_3^{2-} anion 2: Cl^-

[2]

(d) Explain in detail, the observations in **(b)(2.)**.

Blue ppt of $Cu(OH)_2$ forms upon addition of NaOH. At the same time, NH_4^+ present in the solution reacts with NaOH to produce some NH_3, which is evolved when the solution is warmed and turns red litmus blue. ;

When more NaOH is added, sufficient NH_3 is produced to form the deep blue complex of $[Cu(H_2O)_2(NH_3)_4]^{2+}$. ; [2]

[Total: 9]

4 Planning

Consider the following organic compounds.

butanal   but-3-enol   1-hydroxypropan-2-one   propanone

Plan an investigation, using test-tube reactions, which would allow you to identify each of these four organic compounds.

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. [6]

Unknowns: butanal, but-3-enol, 1-hydroxypropan-2-one, propanone
Step 1: Place 1 cm^3 of each unknown into clean test tubes. To each test tube, add of 2 cm^3 of Tollen's reagent, then warm in a water bath for 5 min.
Observation: A silver mirror forms only for butanal. Butanal is identified.

Unknowns: but-3-enol, 1-hydroxypropan-2-one, propanone
Step 2: Place 1 cm^3 of each remaining unknown into clean test tubes. To each test tube, add 1-2 drops of acidified $KMnO_4$, then warm in a water bath for 5 min.
Observation: Purple $KMnO_4$ turns purple for only but-3-enol and 1-hydroxypropan-2-one. Effervescence of a gas that forms a white ppt in $Ca(OH)_2$ observed for only but-3-enol. But-3-enol is identified.

Unknowns: 1-hydroxypropan-2-one, propanone
Step 3: Place 1 cm^3 of each remaining unknown into clean test tubes. To each test tube, add 1-2 drops of acidified $K_2Cr_2O_7$, then warm in a water bath for 5 min.
Observation: Orange $K_2Cr_2O_7$ forms only for 1-hydroxypropan-2-one. 1-hydroxypropan-2-one is identified.

Unknowns: propanone
Step 4: Place 1 cm^3 of the remaining unknown into a clean test tube. To this test tube, add excess 2,4-dinitrophenylhyrazine, then warm in a water bath for 5 min.
Observation: An orange precipitate forms for propanone. Propanone is identified.

other possible solutions include:

Unknowns: 1-hydroxypropan-2-one, propanone
Step ??: Place 1 cm^3 of the remaining unknown into a clean test tube. To this test tube, add 1 spatula of Na(s), test gas evolved with lighted splint.
Observation: Effervescence observed for 1-hydroxypropan-2-one. Gas extinguishes lighted splint with a 'pop' sound. 1-hydroxypropan-2-one is identified.

[Total: 6]

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

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

Paper 1 Multiple Choice

23 September 2019

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, CT and NRIC / FIN on the Answer Sheet in the spaces provided.

There are **thirty** 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 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 **19** printed pages.

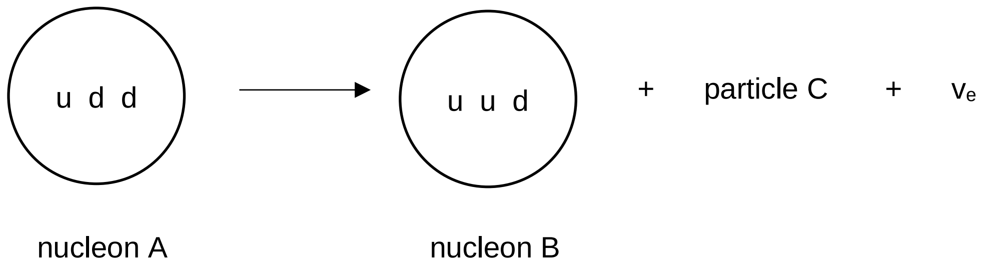
1 4th July 2012, the discovery of the Higgs boson validated the Standard Model of elementary particles, a widely accepted framework for understanding sub-atomic particles.

In the Standard Model, nucleons can be further divided into more basic particles, called quarks. Quarks occupy spaces and have charges; some positive, some negative.

The following table list the characteristics of some sub-atomic particles in the Standard Model.

Type of particle	Symbol	Size and polarity of electronic charge, *e*
Up quark	u	$+\frac{2}{3}$
Down quark	d	$-\frac{1}{3}$
electron	e	–1
neutrino	v_e	0

In a radioactive reaction, the following process occurs in the nucleus of an atom.



Which of the following statements are correct?

1 The charge of nucleon B is +1.

2 Particle C is deflected towards the positive plate in an electric field.

3 The process can be described by $^{22}\text{Ne} \rightarrow {}^{22}\text{Na}$.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

2 An oxygen candle is used to provide an emergency supply of oxygen in spacecraft. It contains sodium chlorate in a chemical mixture. When ignited, the mixture burns at 600 °C. At this temperature, thermal decomposition of the sodium chlorate occurs, releasing oxygen gas and forming sodium chloride as the only products.

When sodium chlorate decomposes, 0.150 moles of oxygen gas and 0.100 mole of sodium chloride are formed.

What is the oxidation state of chlorine in the chlorate?

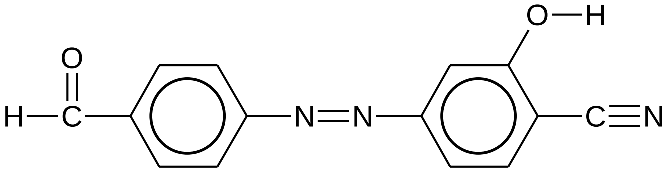
A +3 **B** +5 **C** +6 **D** +11

3 Cations with a high charge density can polarise adjacent anions. This results in ionic bonds with covalent character. However, if the oxidation state is high enough, a covalent bond will form instead.

Which of the following correctly lists the most ionic and the most covalent halide compounds?

	Most ionic	Most covalent
A	SnF_2	$PbCl_4$
B	PbF_2	$SnCl_4$
C	SnF_4	$PbCl_2$
D	PbF_4	$SnCl_2$

4 Compound Z has the following structure.



compound Z

Which bond angle is not present in a molecule of compound Z?

A 105° **B** 109° **C** 120° **D** 180°

5 *Use of the Data Booklet is relevant to this question.*

A mass of 0.253 g of a volatile liquid is injected into a gas syringe at 97 °C. The initial reading of the gas syringe, before the injection of the liquid, is 5 cm^3. The final reading, after complete vaporisation of the liquid, is 81 cm^3. The temperature was kept constant at 97 °C.

Atmospheric pressure is 1 atm.

What is the M_r of the volatile liquid?

A 26 **B** 89 **C** 95 **D** 101

6 *Use of the Data Booklet is relevant to this question.*

For the energy cycle given below, which enthalpy change is correctly stated?

$$\begin{tikzcd}
\mathrm{Ca(s)} \arrow[d, "\Delta H_2"'] & + & \mathrm{C(s)} \arrow[d, "\Delta H_3"'] & + & \frac{3}{2}\mathrm{O_2(g)} \arrow[d, "\Delta H_4"'] \arrow[rr, "\Delta H_1"] & & \mathrm{CaCO_3(aq)} \arrow[dd, "\Delta H_8"'] \\
\mathrm{Ca(g)} \arrow[d, "\Delta H_5"'] & + & \mathrm{C(g)} & + \arrow[d, "\Delta H_6"'] & \mathrm{3O(g)} & & \\
\mathrm{Ca^{2+}(g)} & + & & \mathrm{CO_3^{2-}(g)} \arrow[rrr, "\Delta H_7"] & & & \mathrm{CaCO_3(s)}
\end{tikzcd}$$

All values are given in kJ mol^{-1}.

1 $\Delta H_7 = \Delta H_8 - \Delta H_{hyd}(\mathrm{Ca^{2+}}) - \Delta H_{hyd}(\mathrm{CO_3^{2-}})$

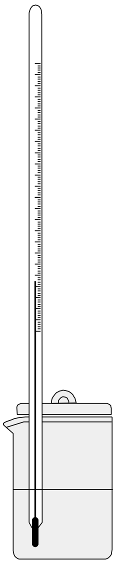
2 $\Delta H_5 = 1740$

3 $\Delta H_{atm}(\mathrm{Ca}) = \Delta H_1 + \Delta H_8 - (\Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7)$

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

7 The set-up shown is used to determine the enthalpy change of reaction for the neutralisation of oxalic acid, $H_2C_2O_4$, using a calibration method.

$$2NaOH(aq) + H_2C_2O_4(aq) \xrightarrow{\Delta H_{rxn}} Na_2C_2O_4(aq) + 2H_2O(l)$$



Experiment 1

- 50 cm^3 of 2.0 mol dm^{-3} NaOH(aq) was added to 50 cm^3 of 2.0 mol dm^{-3} HC*l*(aq).
- Temperature of solution rise by 10.0 °C.

Experiment 2

- 50 cm^3 of 2.0 mol dm^{-3} NaOH(aq) was added to 50 cm^3 of 2.0 mol dm^{-3} $H_2C_2O_4$(aq).
- Temperature of solution rise by 8.5 °C.

Using the results from experiments 1 and 2, and given standard enthalpy change of neutralisation is –57.4 kJ mol^{-1}, what is the correct magnitude for the experimental value of ΔH_{rxn} in kJ mol^{-1}?

A $\frac{57.4 \times 8.5 \times 2}{10}$ **B** $\frac{57.4 \times 8.5}{10 \times 2}$

C $\frac{57.4 \times 8.5}{10}$ **D** $\frac{57.4 \times 10 \times 2}{8.5}$

8 For which of the following processes is the sign of $\Delta G^\ominus$ and $\Delta S^\ominus$ different?

1 Addition of silicon chloride to water.

2 Bubbling chlorine gas into potassium iodide solution.

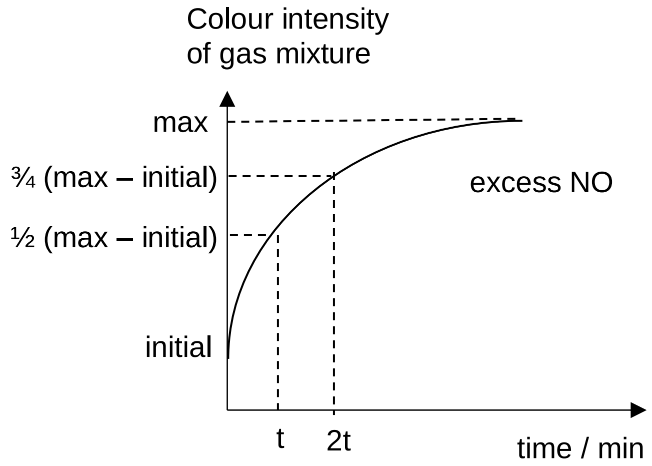
3 Thermal decomposition of magnesium carbonate.

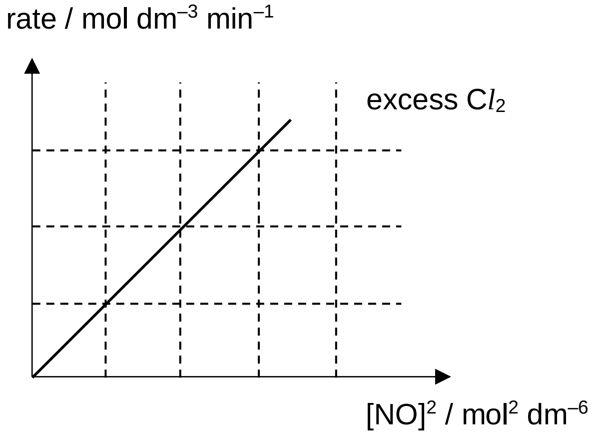
A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

9 Nitrosyl chloride, NOC*l*, is a yellow gas produced by the reaction of colourless nitrogen monoxide gas and chlorine gas.

$$2NO + Cl_2 \rightarrow 2NOCl$$

To investigate the kinetics of the production of nitrosyl chloride, experiments were carried out and the following graphs obtained.





Which of the following can be deduced from these results?

1 The reaction is first order with respect to Cl_2.

2 A possible mechanism for the reaction is:

$$NO + Cl_2 \longrightarrow NOCl_2$$

$$NOCl_2 + NO \longrightarrow 2NOCl$$

3 The rate constant has units of mol^2 dm^{-6} min^{-1}.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

10 The decomposition of hydrogen peroxide in aqueous solution is a first order process.

If 10 % of the hydrogen peroxide in a solution of concentration 0.10 mol dm^{-3} decomposes in 5 minutes at a certain temperature, what is the concentration, in mol dm^{-3}, of a 1.00 mol dm^{-3} hydrogen peroxide solution after 5 minutes at the same temperature?

A 0.10 **B** 0.50 **C** 0.80 **D** 0.90

11 The pH of human blood is constant at about 7.40.

Which ion present in the human body will remove contaminating $H^+(aq)$ ions from the blood to keep the pH constant?

A CO_3^{2-} **B** HCO_3^- **C** $H_2PO_4^-$ **D** PO_4^{3-}

12 Values of three solubility products are given.

$$K_{sp}\ (AgIO_3) = 3.2 \times 10^{-8}\ mol^2\ dm^{-6}$$

$$K_{sp}\ (Ag_2CrO_4) = 9.0 \times 10^{-12}\ mol^3\ dm^{-9}$$

$$K_{sp}\ (Ag_3AsO_4) = 1.0 \times 10^{-22}\ mol^4\ dm^{-12}$$

A conical flask contains 0.10 mol dm^{-3} potassium iodate(V), 0.10 mol dm^{-3} potassium chromate(VI) and 0.10 mol dm^{-3} potassium arsenate(V), all in solution together.

Drops of aqueous silver nitrate were added incrementally until the first precipitate appears.

What is the concentration of silver ions, in mol dm^{-3}, present?

A 9.5×10^{-6}

B 3.2×10^{-7}

C 1.0×10^{-7}

D 3.3×10^{-8}

13 *Use of the Data Booklet is relevant to this question*.

Free energy change of a reduction half-equation is related to the standard electrode potential by the equation.

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

The free energy, $-\Delta G^{\ominus}/F$, for the reduction of uranium species are given in the table.

half-equation	$-\Delta G^{\ominus}/F$ (V)
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	+0.16
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.27
$U^{4+} + e^- \rightleftharpoons U^{3+}$	−0.52
$U^{3+} + 3e^- \rightleftharpoons U$	−4.98

Units of $-\Delta G^{\ominus}/F$ are in voltage, V.

Excess magnesium powder was added to 1.0 mol dm^{-3} solution of UO_2^+ at 25 °C. What is the stable species of uranium formed?

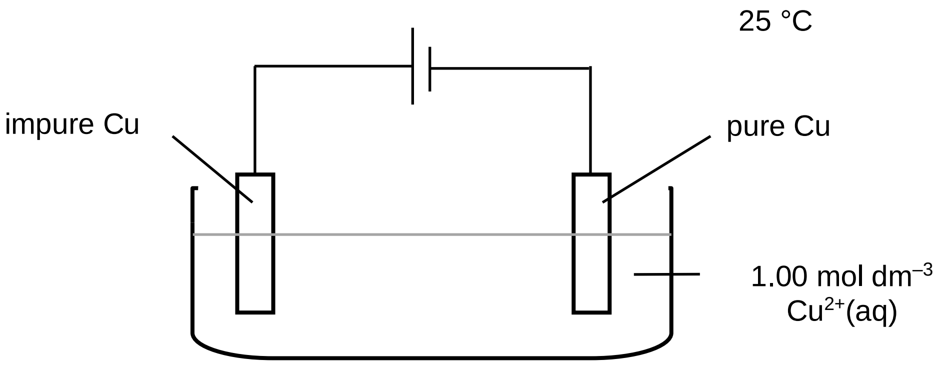
A U

B U^{3+}

C U^{4+}

D UO_2^{2+}

14 An electrolytic cell is set up for the purification of a mass of impure copper as shown.



The sample of impure Cu is known to contain nickel and silver as minor impurities.

Which of the following factor, when used in a larger quantity, results in more pure copper deposit on the cathode?

A concentration of Cu^{2+} electrolyte

B current

C mass of impure Cu

D surface area of pure Cu

15 In addition to the Group 2 elements, several elements behave similarly in forming only cations with +2 charge.

On losing two electrons, which of the following element acts as the strongest reducing agent?

A Cd **B** Ni **C** Sr **D** Zn

16 Transition metal ions can react in a number of different ways. Listed are three different reactions of transition metal ions with relevant observations.

Which observation is due to ligand exchange only?

1 When a yellow solution of ammonium vanadate(V) is added to zinc powder, the solution changes colour eventually to violet as vanadium(II) ions are made.

2 When a purple solution of chromium(III) sulfate is warmed, a green solution containing $[Cr(H_2O)_5SO_4]^+$ is made.

3 When a pink solution of cobalt(II) ions is added to tartrate ions, $^-OOCCH_2(OH)CH_2(OH)COO^-$, followed by hydrogen peroxide solution, a green solution of $[Co(OOCCH_2(OH)CH_2(OH)COO)_3]^{3-}$ is made which eventually returns to a pink solution again.

A 1, 2 and 3 **B** 1 and 3 only **C** 2 and 3 only **D** 2 only

17 An aqueous solution containing both potassium chloride and potassium iodide is treated with an excess of aqueous silver nitrate. The precipitate formed is filtered off and washed with distilled water. The precipitate is then shaken with aqueous ammonia and filtered off again.

Which ion is present in the final filtrate?

A chloride

B iodide

C potassium

D silver

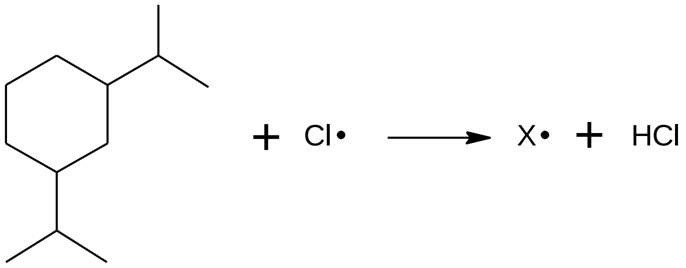
18 An organic molecule has

- the composition, by mass, C, 40%; H, 6.7%; O, 53.3%,
- the ability to rotate plane polarised light,
- no cyclic structure.

What is the smallest number of carbon atoms this molecule can have?

A 1 **B** 2 **C** 3 **D** 4

19 When heated with chlorine, the hydrocarbon 1,3-diisopropylcyclohexane undergoes free radical substitution. In a propagation step, the free radical X• is formed by the loss of one hydrogen atom.



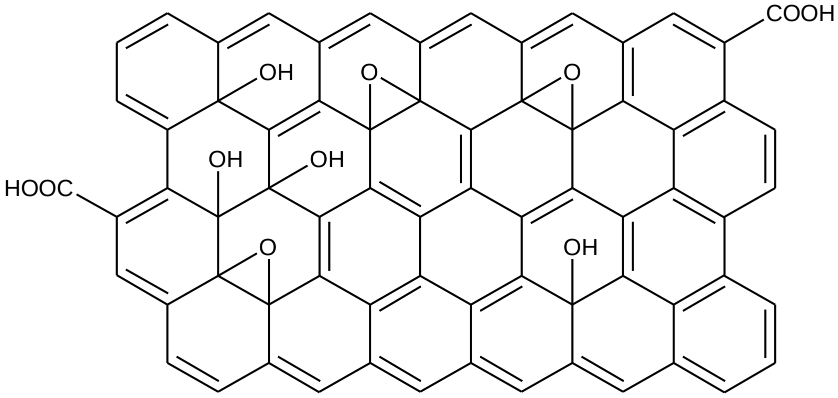
1,3-diisopropylcyclohexane

How many different forms of X• are theoretically possible?

A 6 **B** 7 **C** 8 **D** 9

20 A. Geim and K. Novoselov shared the 2010 Nobel prize for the discovery and characterisation of graphene, which is a single layer of graphite. A graphene sheet is 100 times stronger than steel, and conducts heat and electricity efficiently.

More recently, oxygen atoms have been added to graphene in order to modify its physical properties. A graphene sheet is normally non-polar and impermeable to all gases and liquids. A graphene oxide layer, however, will allow water molecules to pass through.



example of a graphene oxide layer

Which of the following statement is incorrect?

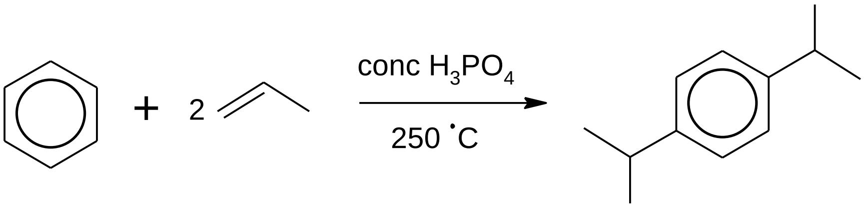
A A graphene sheet is insoluble in water.

B A graphene sheet is very strong as overlapping p-orbitals on the carbon atoms strengthens the C–C bonds.

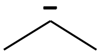
C All carbon atoms in a graphene oxide layer are on the same plane.

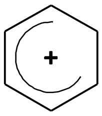
D There are σ bonds formed by $2sp^2$–$2sp^3$ overlap in a graphene oxide layer.

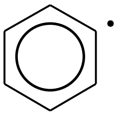
21 The following industrial reaction involves benzene and propene.

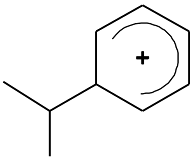


Which of the following intermediate is likely formed in this reaction.

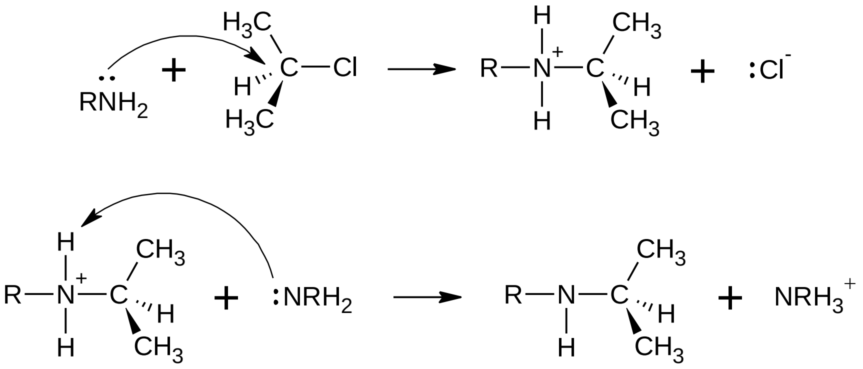
A 

B 

C 

D 

22 Amines can react in various ways in organic reactions: as nucleophiles, Brønsted bases and oxidising and reducing agent.



In the reaction mechanism shown, what are the ways in which amines react as?

1 Nucleophile

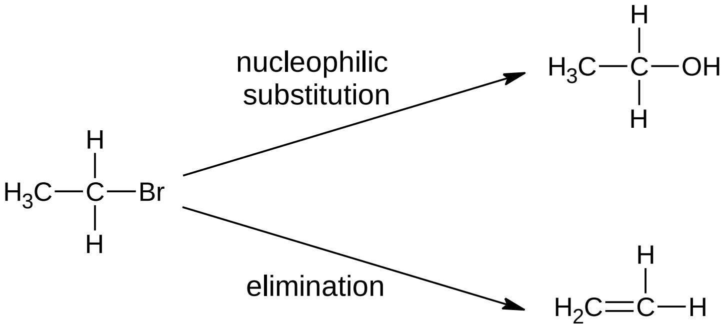
2 Brønsted base

3 Oxidising agent

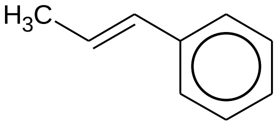
A	1, 2 and 3	**B**	1 and 2 only	**C**	2 and 3 only	**D**	1 only

23 A halogenoalkane can react with hydroxide ions, OH^-, in two ways,

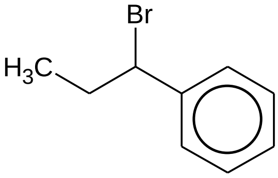
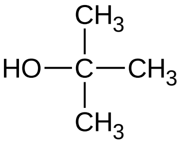
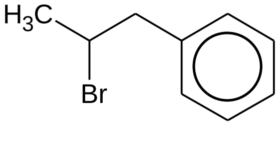
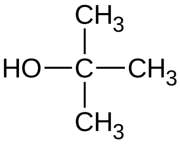
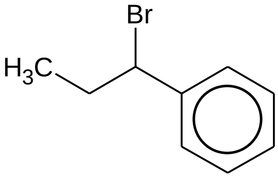
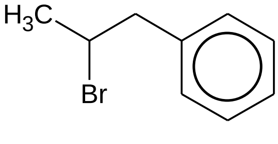
- to form an alcohol in a nucleophilic substitution reaction, or
- to form an alkene in an elimination reaction.



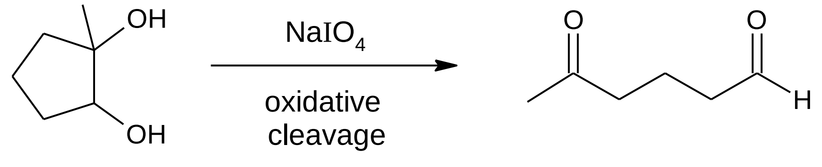
Compound H has the structure shown.



Which of the following halogenoalkane and solvent pair, when reacted with OH^-, will give the best yield for compound H?

	halogenoalkane	solvent
A		
B		
C		H_2O
D		H_2O

24 Vicinal diols are organic compounds where there are two –OH groups on adjacent carbons. On treatment with sodium periodate, $NaIO_4$, the carbon-carbon bond between the two diols is cleaved to form aldehydes or ketones.



vicinal diol

A vicinal diol, D, which contains six carbon atoms, reacts with $NaIO_4$ to form compounds E and F.

Compound E gives a yellow precipitate with alkaline aqueous iodine.

Compound F gives a red-brown precipitate with alkaline Cu^{2+} solution.

What is the organic product formed when D is warmed with acidified $K_2Cr_2O_7$?

A $HOOCCH_2CH_2CH_2COCH_3$

B $CH_3CH(OH)COCH_2CH_2CH_3$

C $(CH_3)_2C(OH)COCH_2CH_3$

D $HOOCCOC(CH_3)_3$

25 Which liquid is the best conductor of electricity?

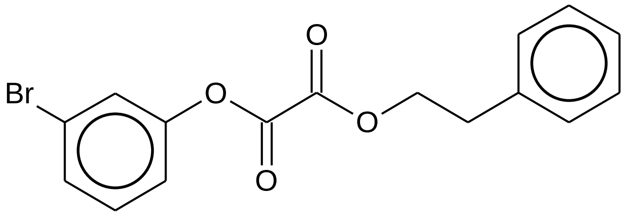
A aqueous pyruvic acid, CH_3COCO_2H with a concentration of 1 mol dm^{-3}

B aqueous propanoic acid, $CH_3CH_2CO_2H$ with a concentration of 1 mol dm^{-3}

C aqueous ethanoic acid, CH_3CO_2H with a concentration of 1 mol dm^{-3}

D pure ethanoic acid

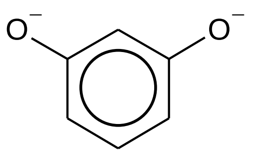
26 Compound K reacts with hot alkaline aqueous manganate(VII).



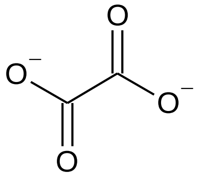
compound K

Which of the following compound is formed?

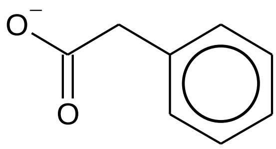
A



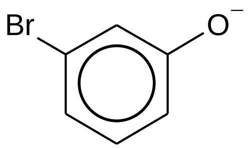
B



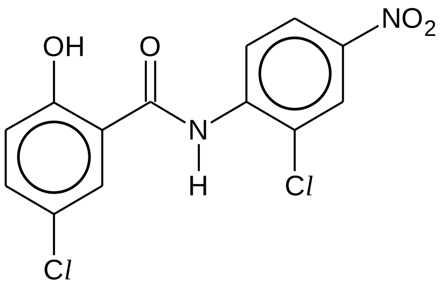
C



D



27 Niclosamide is an essential medicine used in the treatment of tapeworm infestations.



niclosamide

Which of the following reducing agent does not react with niclosamide?

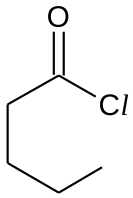
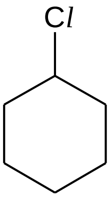
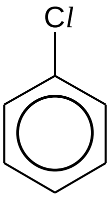
A H_2 with Ni metal

B LiA*l*H_4 in dry ether

C NaBH_4 in ethanol

D Sn in concentrated HC*l*

28 One mole of each of the following compounds was boiled with NaOH (aq) for two minutes, and then dilute HNO_3 (aq) and $AgNO_3$ (aq) were added. The appearance of the precipitate was recorded.

P	Q	R
		
Thick fluffy mass of white precipitate formed.	Some white precipitate formed.	No precipitate observed.

Which of the following statements explain the observations?

1 Lone pairs of electrons of C*l* in P overlap with π-electrons of the C=O group, electrons delocalised with C=O group disperse the partial positive charge.

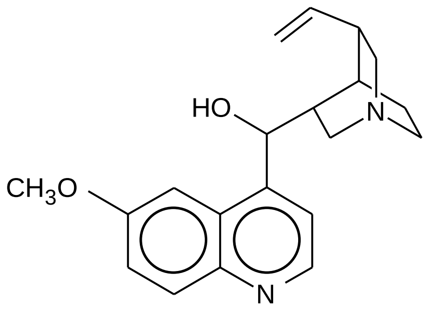
2 C*l* atom causes the C–C*l* bond to have a partial positive charge on the carbon atom.

3 The π-electron cloud in the aromatic ring of R repels OH^- nucleophiles.

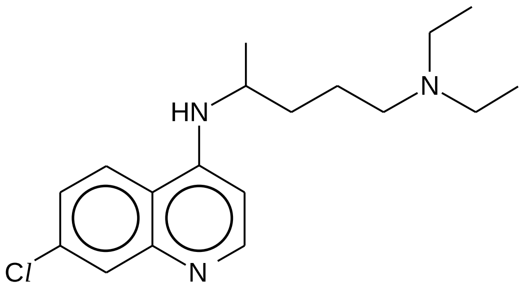
A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

29 *Jesuit's bark* was brought to Europe from South America by missionaries and proved useful in the treatment of malaria. Quinine, the active compound, is found in the bark of the cinchona tree and used originally by natives of Peru and Bolivia to treat shivering in cold weather.

Nowadays, a similar alkaloid, chloroquine is commonly used for the treatment of malaria.



quinine



chloroquine

Which reagents react with both quinine and chloroquine?

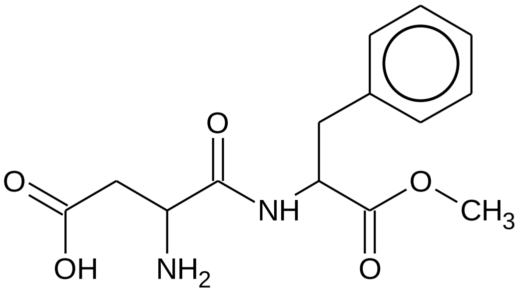
1 aluminium oxide

2 aqueous bromine

3 ethanoyl chloride

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

30 Coca-Cola® No Sugar is a sugar and calorie free drink developed to taste like Coca-Cola classic. It uses the artificial sweetener aspartame.

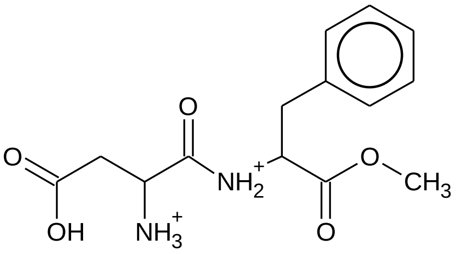


aspartame

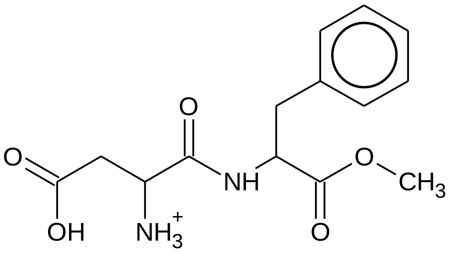
Aspartame has pK_a values of 3.2 and 7.9.

Given that Coca-Cola® No Sugar has a pH of 2.5, what is the structure of the major species of aspartame present?

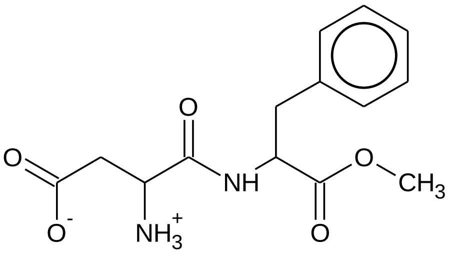
A



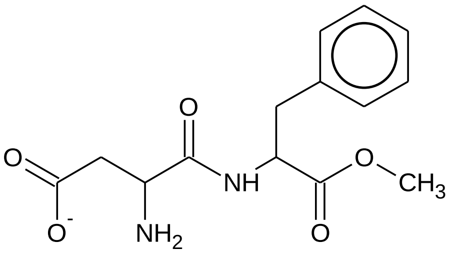
B



C



D



NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY **9729/02**

Paper 2 Structured Questions **17 September 2019**

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, 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	**/18**
2	**/13**
3	**/14**
4	**/15**
5	**/15**
Total	**/75**

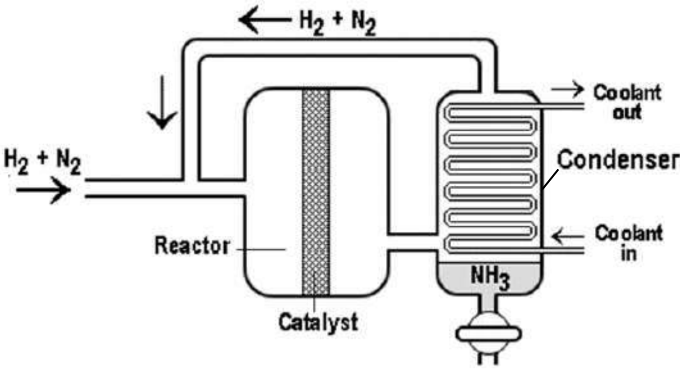
This document consists of **20** printed pages.

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

1 **(a)** Ammonia is one of the world's most produced inorganic chemical due to its many uses. The current method of producing ammonia is the Haber-Bosch process.

This involves reacting nitrogen and hydrogen in a recycled process as shown. Nitrogen and hydrogen are pumped into the reactor where reaction to form ammonia takes place. The output from the reactor then goes into a condenser.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H < 0$$



(i) An optimal temperature of 500 °C is used inside the reactor. Explain why this temperature is used.

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.... [2]

(ii) Finely divided iron is used as catalyst inside the reactor. Outline the mode of action of the iron catalyst in this reaction.

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.... [2]

(iii) Using a Boltzmann diagram, explain why rate increases in the presence of catalyst.

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.... [3]

(iv) The condenser helps to cool the gases and in doing so, maximises the yield of ammonia. Explain in terms of structure and bonding how this is achieved.

....

....

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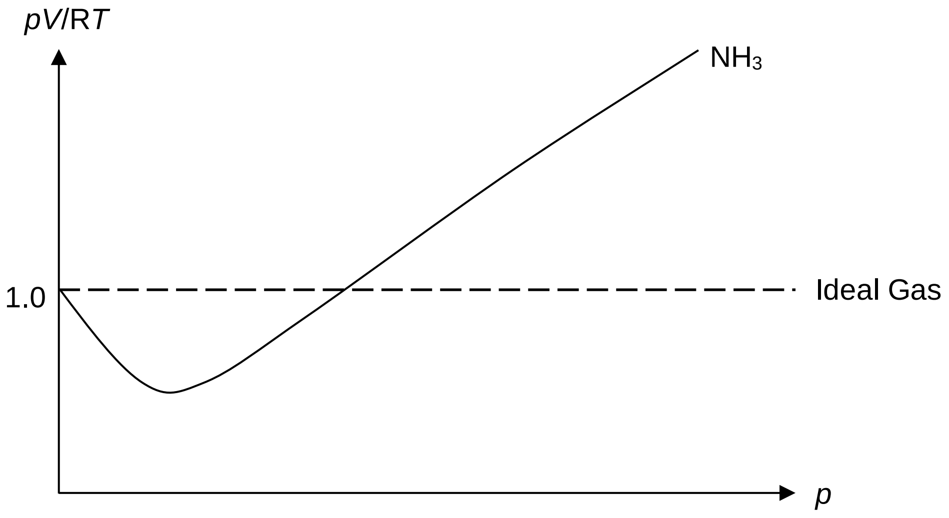
....

....

.... [2]

(v) Hydrazoic acid, HN_3, is a compound of nitrogen and hydrogen like ammonia.

The plots of pV/RT against p for one mole of an ideal gas and one mole of ammonia are given below.



On axes above, sketch a graph to illustrate the behaviour of one mole of hydrazoic acid. Explain your answer.

....

....

....

.... [2]

(b) Globally, approximately 88 % of ammonia is used as fertilisers. Research is actively carried out to seek new uses for ammonia in other areas.

For example, when NH_3(aq) is added to a solution of Zn^{2+}(aq), a solution of $[Zn(NH_3)_4]^{2+}$(aq) can be formed. It is then possible to design an electrochemical cell based on the following half equations.

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76V$$

$$[Zn(NH_3)_4]^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) + 4NH_3(aq) \qquad E^\ominus = -1.04V$$

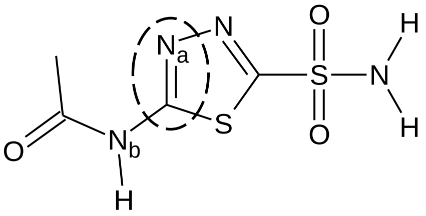
(i) Draw a fully labelled diagram of the electrochemical cell that could be set up, showing the polarity of the electrodes during discharge.

[2]

(ii) Write a balanced equation for the overall reaction that occurs during the discharging process. Hence calculate $\Delta G^\ominus$ of the electrochemical cell.

[2]

(c) Ammonia is used in the pharmaceutical industry for synthesising of drugs. An example is acetazolamide, a drug used for treating heart failure.



acetazolamide

(i) The molecule of acetazolamide contains both σ (sigma) and π (pi) bonds.

With respect to the C=N_a bond circled, draw a labelled diagram to show how orbitals overlap to form σ (sigma) and π (pi) bonds.

[1]

(ii) Suggest how the basicity of N_a might compare to that of N_b. Explain your answer with reference to your answer in (c)(i).

....

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....

....

.... [2]

[Total:18]

2 Copper has a wide range of common uses, such as electrical wiring and water piping because it is relatively inexpensive and has a high resistance to corrosion.

Copper is also an unreactive metal which does not react directly with dilute acids. Therefore, the enthalpy change of reaction, ΔH_r, for the following reaction, cannot be determined directly.

$$Cu(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2(g) \quad \Delta H_r$$

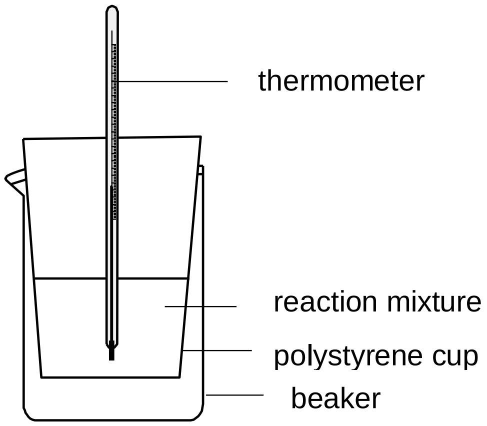
In order to determine a value for ΔH_r, you will therefore need to find the enthalpy change of reaction for two reactions that do occur. One of these reactions involve adding a reactive metal M to dilute sulfuric acid.

$$nM(s) + H_2SO_4(aq) \longrightarrow M_nSO_4(aq) + H_2(g) \quad \Delta H_1$$

The other reaction is a displacement of copper from aqueous copper(II) sulfate using metal M.

$$nM(s) + CuSO_4(aq) \longrightarrow M_nSO_4(aq) + Cu(s) \quad \Delta H_2$$

The value for the enthalpy change of the displacement reaction ΔH_2 can be determined using a graphical method by finding the maximum temperature change ΔT_{max}. The following experiment is carried out and the metal M used in this experiment can be assumed to be in excess.



Determination of ΔT_{max}

1 Weigh accurately the mass of the metal powder M.

2 Measure 50 cm^3 of 0.3 mol dm^{-3} $CuSO_4(aq)$ and pour it into the polystyrene cup.

3 Measure the temperature of $CuSO_4(aq)$ every half minute.

4 At the 3rd minute, pour the metal powder M into the polystyrene cup.

5 Record the temperature of the solution at the 4th minute and thereafter at every half minute until the 10th minute.

However, the polystyrene cup used in the experiment can also absorb heat, so a separate experiment is performed to find the heat capacity of the polystyrene cup. This process is known as the calibration of the calorimeter.

One way to do this is to use a common metal of known specific heat capacity. A piece of nickel bar can be heated to around 100 °C and then dropped into the polystyrene cup containing water. The heat capacity of the polystyrene cup can then be calculated from the known specific heat capacity of nickel.

(a) Suggest, with the aid of a labelled diagram, why copper is suitable to be used in electrical wiring.

....

.... [2]

(b) **(i)** The $E^\ominus$ values of some redox reactions are shown below.

reaction	$E^\ominus$ / V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	+0.00
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38

By considering the $E^\ominus$ values given, suggest the most suitable metal from the following list to be used as metal M in both reactions. Give reasons for your choice.

barium calcium magnesium silver

....

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.... [2]

(ii) Using the metal you have chosen in (b)(i), construct an energy cycle to show how ΔH_r can be calculated from ΔH_1 and ΔH_2.

[1]

(iii) Outline how you would determine the heat capacity of the polystyrene cup, using a nickel bar of approximately 50 g.

You should include brief details of the apparatus you would use, the procedure you would follow, and the measurements you would make.

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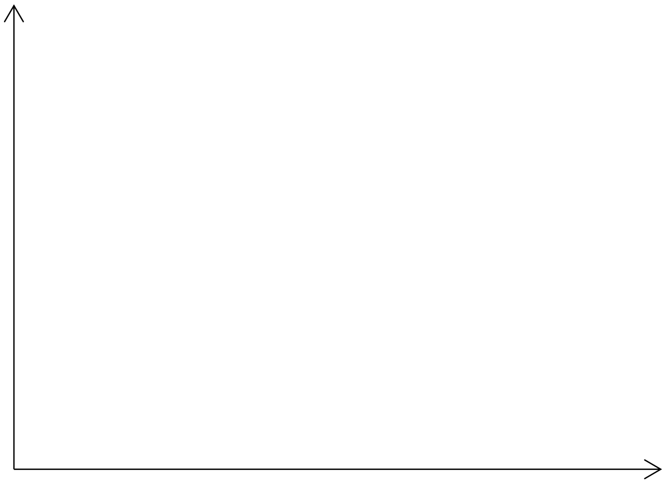
.... [3]

(iv) Sketch, with clearly labelled axes, the graph that you would expect to obtain in the experiment described on page 7 and show how the value of ΔT_{max} can be obtained.



[1]

(v) The heat capacity of the polystyrene cup was found to be 9.7 J K^{-1} in (b)(iii) and the value of ΔT_{max} was found to be 34.8 °C in (b)(iv).

Calculate the value of ΔH_2.

[2]

(c) Calcium is found in the same Period as copper in the Periodic Table. However, Ca has a significantly larger atomic radius than Cu.

Explain why Cu has a smaller atomic radius.

....

....

....

.... [2]

[Total:13]

3 The numerical value of the solubility products of some iron containing salts at 298 K are given below.

salt	value of solubility product
iron(II) hydroxide, $Fe(OH)_2$	8.0×10^{-16}
iron(II) disulfide, FeS_2	1.3×10^{-27}
iron(III) hydroxide, $Fe(OH)_3$	4.0×10^{-38}

In this question, give each of your numerical answers to one decimal place.

(a) **(i)** Write an expression for the solubility product of iron(III) hydroxide, stating its units.

.... [1]

(ii) From the data above, calculate a value for the solubility of iron(III) hydroxide.

[1]

(iii) Solid $Fe(NO_3)_2$ was added to a solution containing 0.25 mol dm^{-3} of sodium disulfide and 0.40 mol dm^{-3} of sodium hydroxide at 298 K.

Calculate the concentration of disulfide ions remaining in the solution when the first trace of iron(II) hydroxide appears.

[2]

When a precipitate is formed, $\Delta G^{\ominus}_{\text{ppt}}$ is given by the following expression.

$$\Delta G^{\ominus}_{\text{ppt}} = 2.303\ \text{RT}\log K_{\text{sp}}$$

(b) **(i)** Use the data above to calculate $\Delta G^{\ominus}_{\text{ppt}}$, in kJ mol^{-1}, for FeS_2.

[1]

(ii) The standard enthalpy change of formation of the precipitate FeS_2 is –178.0 kJ mol^{-1}. Use your answer in (b)(i) to calculate $\Delta S^{\ominus}_{\text{ppt}}$.

[2]

(iii) Explain the significance of the sign of your answer in (b)(ii).

....

....

.... [1]

(c) When $FeCl_3$ is mixed with CaC_2O_4 in NH_4Cl(aq), a yellow salt, X, is formed as one of the products. X has the following composition by mass

C, 19.3 %; Fe, 14.9 %; H, 3.2 %; N, 11.2 %; O, 51.4 %

X is ionic with a formula mass of 373.8. One formula unit of X contains one type of anion and one type of cation in the ratio of 1:3.

(i) Calculate the empirical formula of X.

[1]

(ii) Suggest the formulae of each of the ions present in X.

Cation: .... Anion: ....

[2]

(iii) Suggest the coordination number of the iron-containing ion and hence state its shape.

Coordination number: ……………… Shape: ....

[1]

(iv) Explain why the salt is yellow in colour.

....

....

....

.... [2]

[Total: 14]

4 **(a)** The Contact Process produces sulfuric acid in high concentrations needed for industrial processes. V_2O_5 is the catalyst used in this process.

SO_2 is first produced by heating sulfur in oxygen. It is then oxidised to SO_3 by air.

The oxidation of SO_2 to SO_3 is reversible and exothermic.

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$

(i) SO_2 and O_2 were mixed in a 2:1 mole ratio. Given that the partial pressure of SO_2 in the equilibrium mixture was 24 kPa and the total pressure of the flask was 104 kPa, determine the equilibrium partial pressures of O_2 and SO_3. Hence, calculate K_p, giving the units.

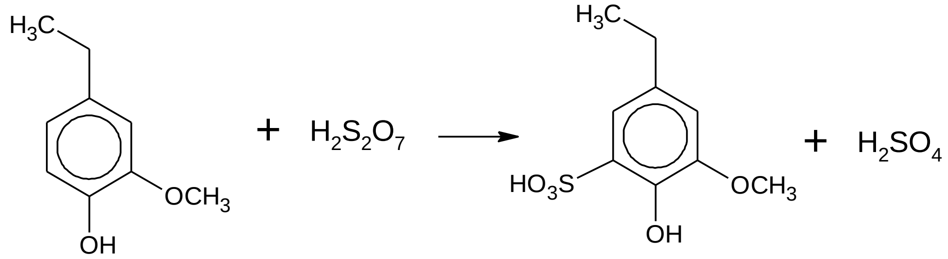
[2]

In the next step of the Contact Process, oleum and sulfuric acid are produced according to the equations below.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7\ \text{(oleum)}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The oleum produced can react with 4-ethylguaiacol, a key flavour component that gives robusta coffee beans the spicy and earthy notes.



4-ethylguaiacol

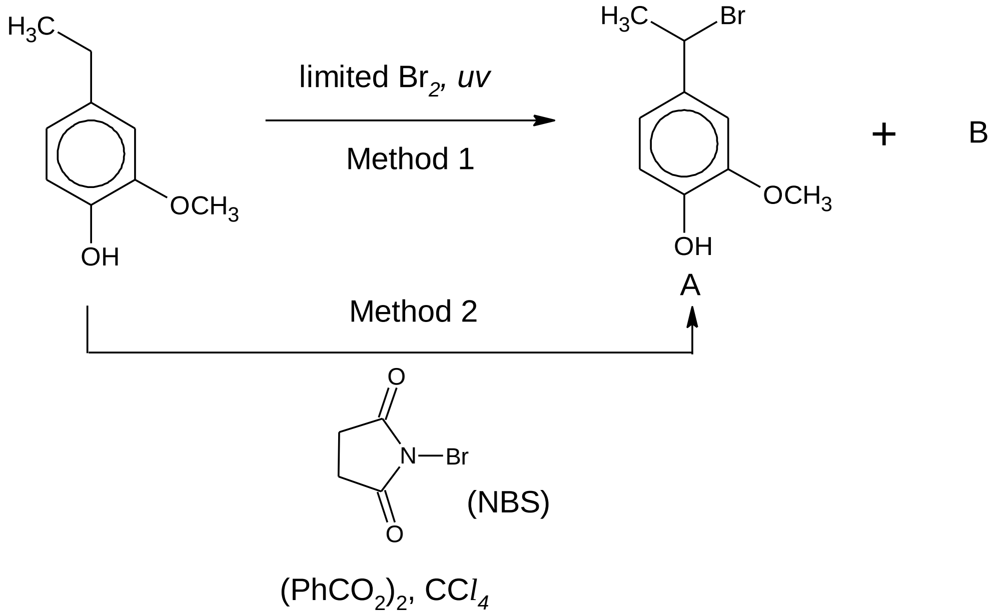
Assume that oleum ionises as shown.

$$H_2S_2O_7 \rightleftharpoons HSO_4^{-} + SO_3H^{+}$$

(ii) Propose a mechanism for this reaction of 4-ethylguaiacol, showing the structure of the intermediate, lone electron pairs, and movement of electrons pairs by using curly arrows.

[3]

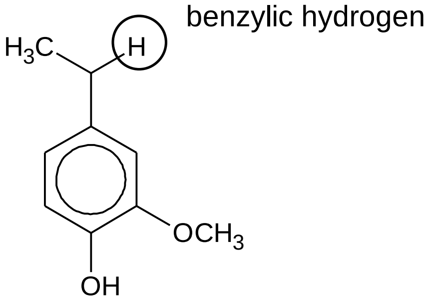
(b) 4-ethylguaiacol can undergo bromination using the following methods.



(i) Give the structure of monobrominated product B and the ratio of A to B formed in method 1, assuming that –OCH_3 is inert.

[2]

(ii) In method 2, the presence of n-bromosuccinimide (NBS) results in side-chain bromination occuring exclusively at the benzylic position, the yield of A is 97 % in this reaction.



The NBS bromination occurs by a radical chain pathway.

- The first step involves a bromine radical abstracting a benzylic hydrogen atom, forming a benzylic radical and HBr.
- This is followed by the benzylic radical reacting with a bromine molecule to yield the product and bromine radical.

Suggest the two-step mechanism, using curly arrows to show the movement of electrons.

[2]

(iii) The bromine molecule that reacts with the benzylic radical in the second step of the mechanism in (b)(ii) is produced by a concurrent reaction of HBr with NBS.

The reaction involves homolytic bond fissions in the molecules.

Using the reaction of HBr with NBS, explain the term, *homolytic fission* and provide a balanced equation for this reaction.

....

.... [2]

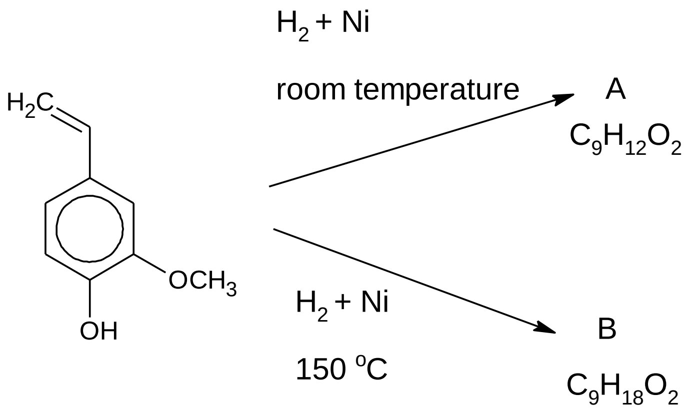
(iv) Method 2 forms A as the only monobrominated product with 97 % yield where bromination occurs exclusively at the benzylic position. Explain why other products do not form in method 2.

....

.... [1]

(c) Organic reductions commonly use nickel catalyst but not all possible functional groups can be reduced. Heating increases the catalytic ability of nickel.

The following reactions illustrate reductions using different conditions.



(i) Suggest the identities of A and B.

A	B

[2]

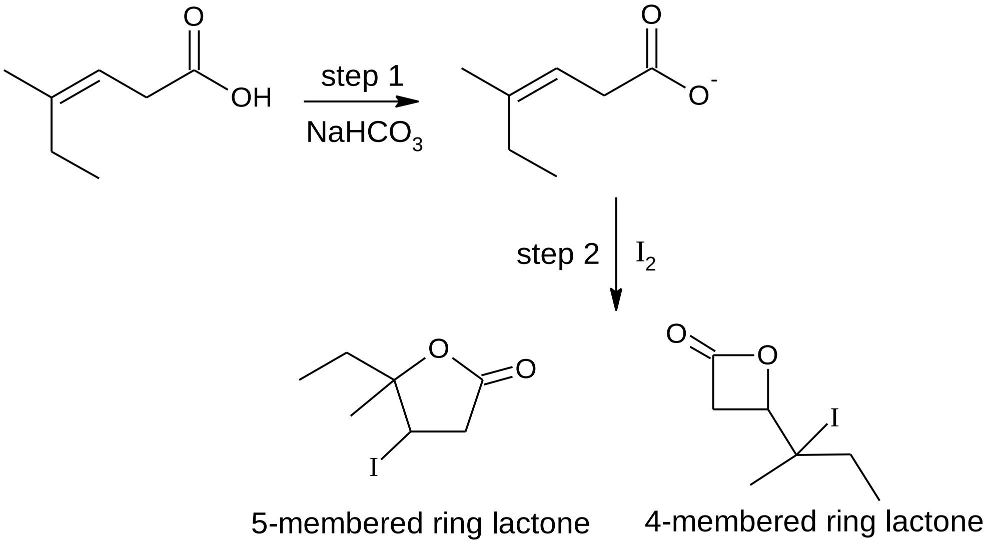
(ii) Explain why B only forms at very high temperature.

....

.... [1]

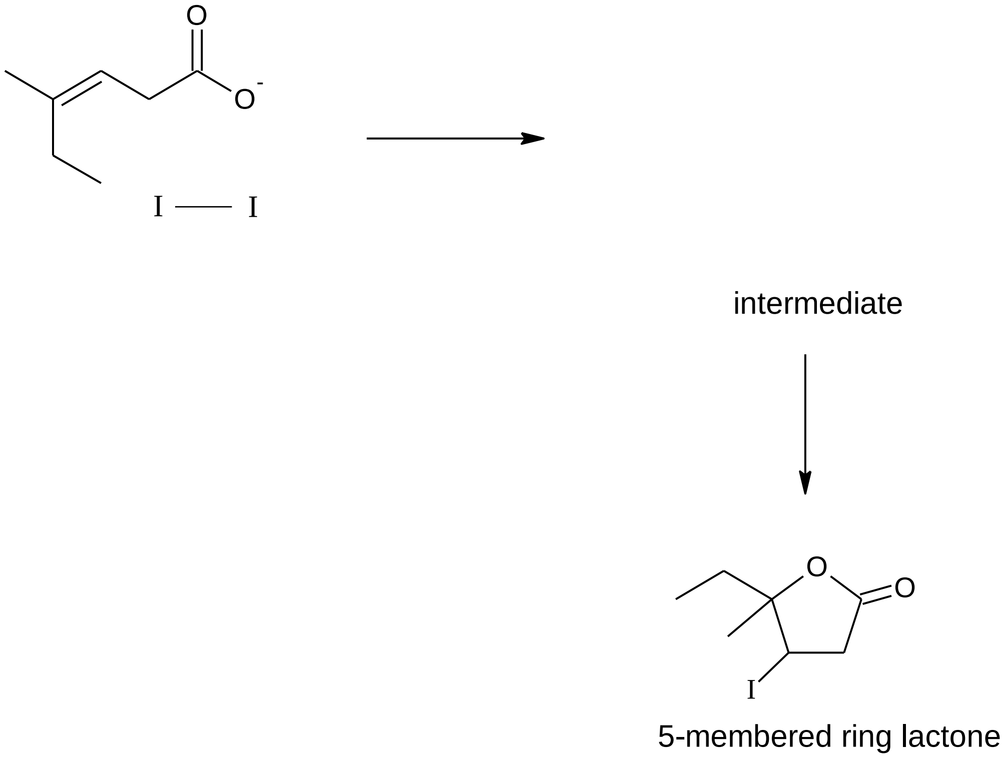
[Total: 15]

5 Lactones contain the ester functional group and are often used as flavours or fragrances. They could be synthesised using the reaction scheme given below.



(a) **(i)** The reaction between the carboxylate ion and iodine in step 2 is an electrophilic addition.

Complete the diagram to suggest a mechanism to show how a 5-membered ring lactone is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. Indicate the slow step of the mechanism.



[2]

(ii) Explain why $NaHCO_3$ is added in step 1.

....

.... [1]

(iii) Suggest two reasons for the preferential production of the 5-membered ring lactone instead of the 4-membered ring lactone.

....

....

....

.... [2]

(iv) Outline a simple chemical test that could be carried out to see if any 4-membered ring lactone is produced in the reaction mixture in step 2.

....

....

....

.... [2]

(v) With reference to the *Data Booklet*, explain why the product will be more stable when Cl_2 is used in step 2.

....

....

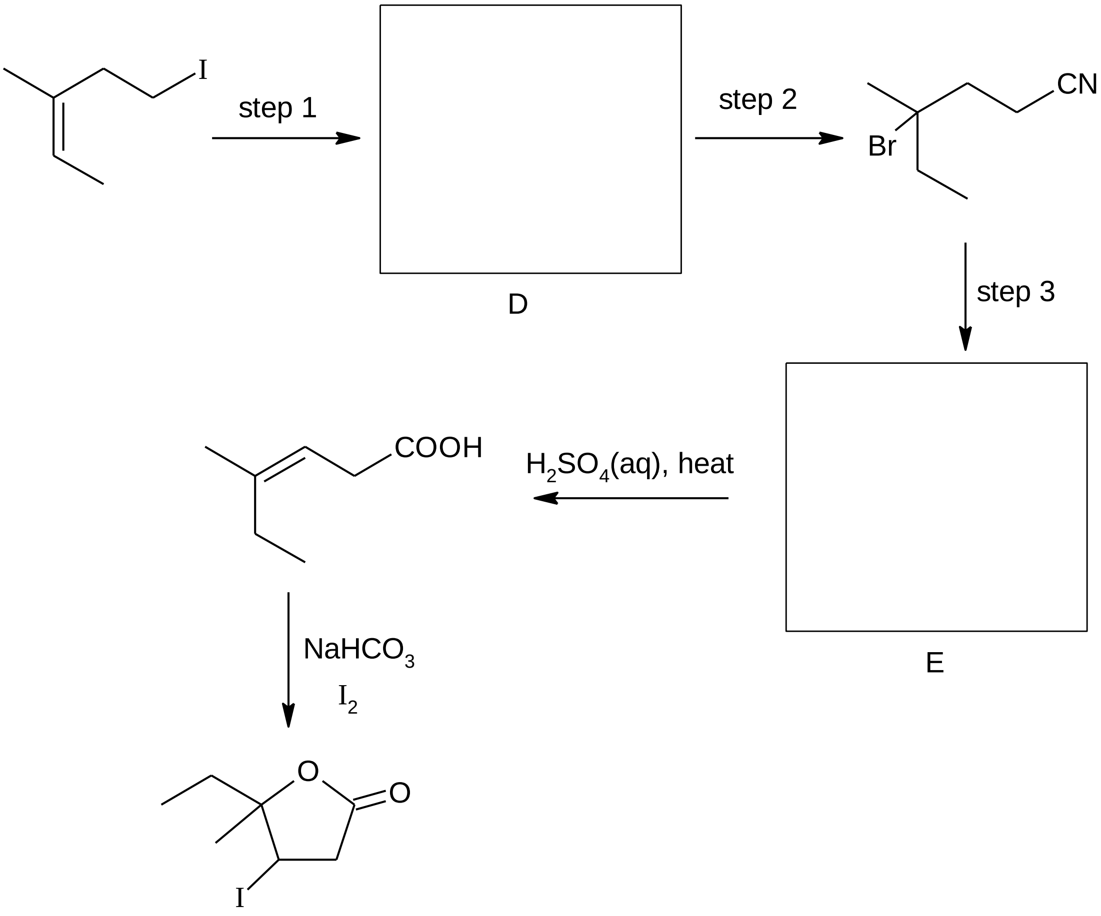
....

.... [1]

(b) The 5-membered ring lactone formed in step 2, exists as a mixture of stereoisomers. Draw the structures of each stereoisomer of the 5-membered ring lactone.

[2]

(c) The reaction scheme below shows how the 5-membered ring lactone could be synthesised. Suggest the reagents and conditions needed for step 1, 2 and 3. Draw the structures of D and E in the boxes.



5-membered ring lactone

step 1 ....

step 2 ....

step 3 ....

[5]

[Total: 15]

H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/03**

Paper 3 Free Response **19 September 2019**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Booklet
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.

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 from this section.

1 **(a)** When ethanoic acid reacts with ethanol to form ethyl ethanoate and water, the following equilibrium is established.

$$CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l) \qquad \Delta H = -3.8 \text{ kJ mol}^{-1}$$

A student mixed 1.48 g of ethanoic acid in a conical flask with 0.92 g of ethanol and 1.80 g of water. He then carefully added 0.98 g of concentrated sulfuric acid to catalyse the reaction. The flask was sealed and placed in a thermostatic water bath set at 25 °C for 5 days.

After 5 days, the student added phenolphthalein indicator to the flask and titrated the entire contents of the conical flask with 0.800 mol dm^{-3} $Ba(OH)_2$. The indicator turned pink when 23.30 cm^3 of $Ba(OH)_2$ had been added.

(i) Calculate the amount of $Ba(OH)_2$ that has reacted with H_2SO_4. [1]

(ii) Write a balanced equation for the reaction of ethanoic acid with $Ba(OH)_2$. Using your answer in (a)(i), calculate the amount of ethanoic acid present at equilibrium. [2]

(iii) Write an expression for the equilibrium constant, K_c, for this reaction and calculate the value of K_c, stating its units. [3]

(iv) Suggest and explain what would happen to the position of this equilibrium and the value of K_c if the temperature is decreased. [2]

(b) **(i)** The addition of an acid to water generates heat and this process is termed as dilution. The dilution of ethanoic acid can be represented with the equation below.

$$CH_3COOH(l) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Calculate the enthalpy change of dilution of ethanoic acid given the following:

	ΔH_f^θ / kJ mol^{-1}
$CH_3COO^-(aq)$	–486
$H^+(aq)$	0
$CH_3COOH(l)$	–485

[1]

(ii) In the presence of heat, ethyl ethanoate, $CH_3CO_2CH_2CH_3$ is able to react with $Ba(OH)_2$ as seen in the equation below:

$$2CH_3CO_2CH_2CH_3(l) + Ba(OH)_2(aq) \rightarrow (CH_3CO_2^-)_2Ba^{2+}(aq) + 2C_2H_5OH(l)$$

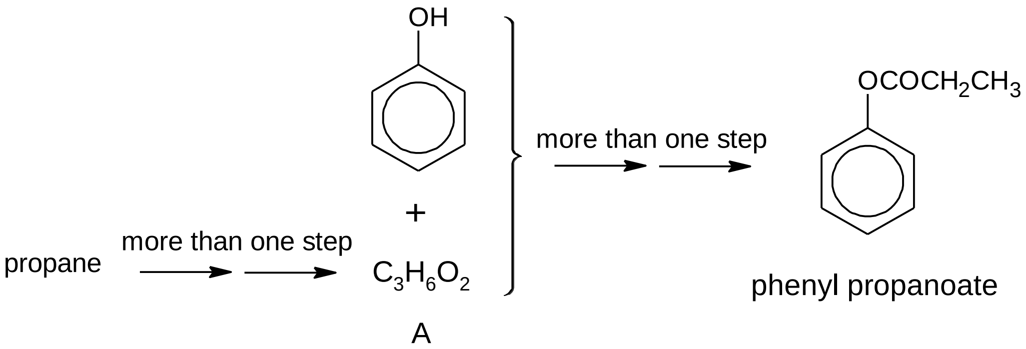
State the type of reaction occurring. [1]

(iii) Construct a fully labelled energy level diagram to calculate the enthalpy change of the reaction in (b)(ii).

Your diagram should include the data given in (a), (b)(i) and the following data.

Standard enthalpy change of neutralisation of $CH_3COOH(aq)$ and $Ba(OH)_2$
= –55 kJ mol^{-1} [3]

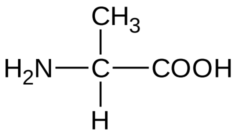
(c) Suggest a synthesis of phenyl propanoate starting from propane according to the scheme below. State the structure of compound A. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.



[5]

[Total: 18]

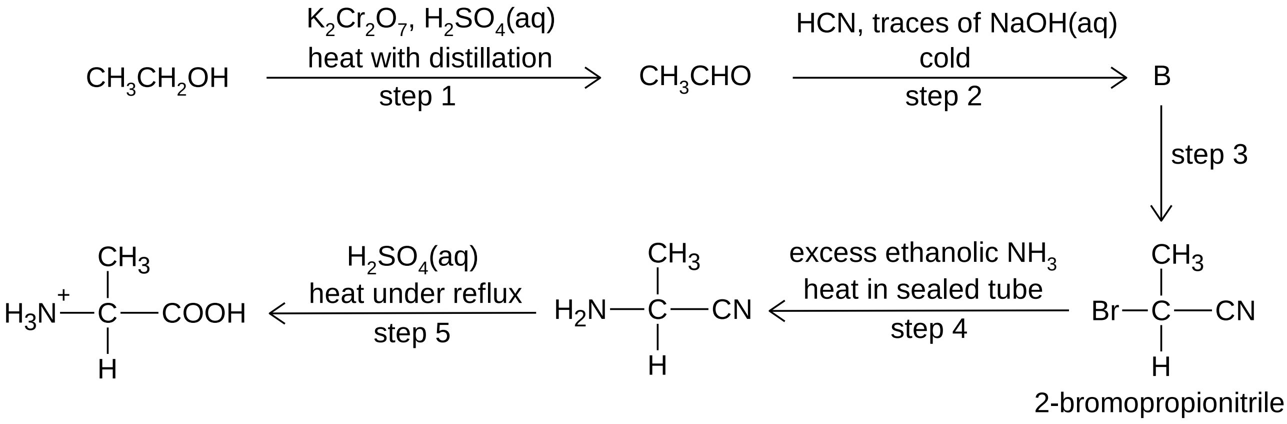
2 Alanine is a non-essential α-amino acid in humans and widely used for biosynthesis of proteins.



$$H_2N-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-COOH$$

alanine

Protonated alanine can be synthesised in the laboratory from ethanol.

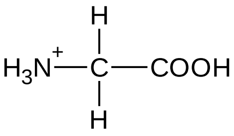


(a) **(i)** Heating with distillation in step 1 is required for the synthesis of aldehyde to prevent the aldehyde from further oxidising to carboxylic acid. Explain why heating with distillation is suitable in isolating the aldehyde. [1]

(ii) Draw the displayed formula of compound B. [2]

(iii) Describe the mechanism in step 2. [3]

(iv) Protonated glycine can also be synthesised from methanol, CH_3OH, using the reaction scheme shown above.



$$H_3\overset{+}{N}-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-COOH$$

protonated glycine

Suggest why the relative rate of step 2 will be higher in the synthesis of protonated glycine. [2]

(v) Suggest the reagent and condition for step 3. [1]

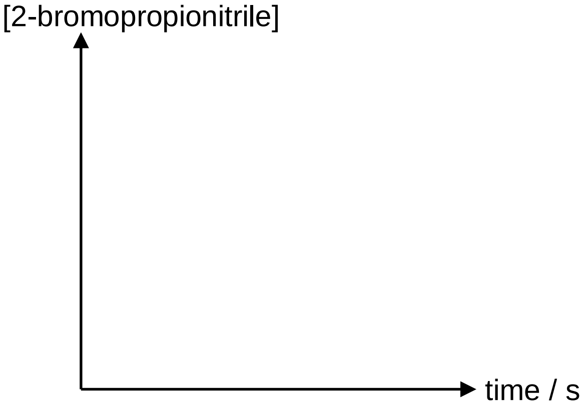
(b) To prove that the mechanism in step 4 is S_N2, two separate experiments were performed and the rate equation was found to be

$$\text{rate} = k[NH_3][\text{2-bromopropionitrile}]$$

- In experiment 1, the rate of reaction was monitored with increasing concentration of NH_3.
- In experiment 2, concentration of 0.1 mol dm^{-3} of 2-bromopropionitrile was monitored over time.

(i) Copy the two graph axes below onto your answer booklet. Draw the graph for each experiment and explain the shape of your graphs.

Experiment 1



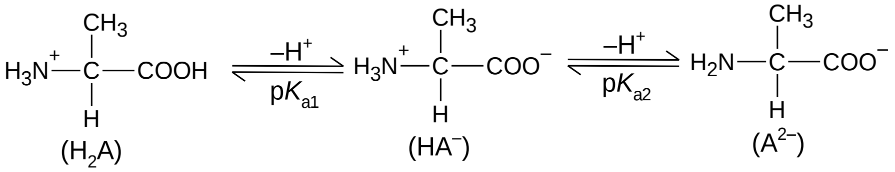
Experiment 2

[2]

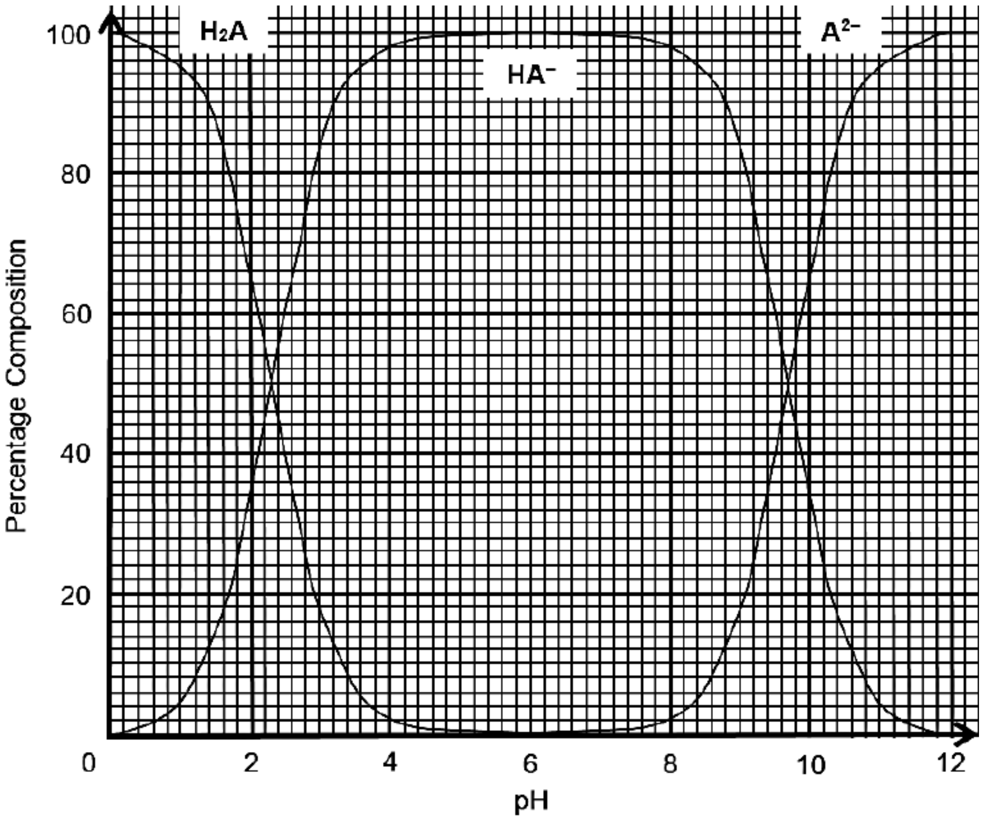
(ii) Suggest a suitable concentration of NH_3 in experiment 2. Explain your answer. [1]

(iii) Suggest why the mechanism in step 4 is unlikely to be S_N1. [1]

(c) Protonated alanine (H_2A) dissociates in two stages as shown below.



The graph below shows how the percentage composition of H_2A, HA^- and A^{2-} change with pH.



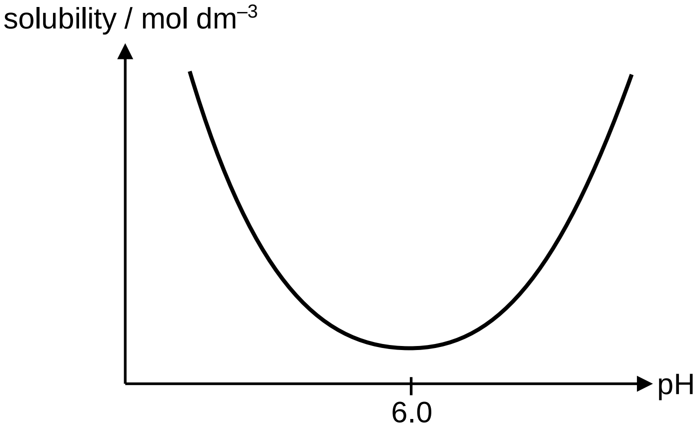
(i) State the values of pK_{a1} and pK_{a2} of alanine. [1]

(ii) A buffer of pH 10.3 is prepared by adding 0.100 mol of protonated alanine (H_2A) in 1 dm^3 of water and solid NaOH was subsequently added.

Using the graph above, determine the amount of HA^- and A^{2-} present in the buffer and hence, calculate the mass of solid NaOH added. [2]

(iii) Assuming 1 dm^3 of water is added to the buffer prepared in (c)(ii), explain qualitatively if the new buffer will result in a greater or smaller change in pH compared to the original buffer, when same amount of HC*l*(aq) is added. [2]

(iv) The solubility of alanine under different pH was investigated. The graph below shows the results of solubility against pH.



Isoelectric point is the pH at which the amino acid has a net zero charge.

With reference to the structures of H_2A, HA^- and A^{2-}, explain

- the low solubility of alanine at its isoelectric point of 6.0.
- the high solubility of alanine at low and high pH. [4]

[Total: 22]

3 This question looks at the chemistry of some compounds formed by transition metal ions and halides.

(a) When aqueous potassium iodide is mixed with aqueous copper(II) sulfate, a yellow brown precipitate is formed and the solution loses its blue colour. When the resulting mixture is shaken with hexane, a purple layer is formed which floats on top of the mixture. A white solid, D, remains which has a mass composition made up of one-third copper and two-third iodine.

(i) Deduce the empirical formula of white solid D. [1]

(ii) Write the electronic configuration of copper in white solid D. [1]

(iii) The filled orbitals of copper in white solid D have different shapes. Draw the shape of the orbital present in the largest quantity. [1]

(iv) Write an ionic equation, with state symbols, for the reaction of copper(II) sulfate with potassium iodide. Identify clearly the species responsible for the different colours observed during the reaction. [2]

(v) Standard redox potentials may be used to predict the feasibility of a reaction. Use E^θ values from the *Data Booklet* to show that the reaction between aqueous copper(II) sulfate and potassium iodide is unlikely to occur. [1]

(vi) By using your answer to (a)(iv), explain clearly in terms of changes in E^θ values, why this reaction does, in fact, occur. [1]

(b) When 1.00 g of a red solid, G, with formula K_xNiF_6, was reacted with water, 48 cm^3 of oxygen (measured at 293 K and 1 atm) was evolved and a green acidic solution, H, was formed. H consists of KF, NiF_2 and HF.

Solution H was divided into 2 equal portions.

Titration of one portion with 0.20 mol dm^{-3} NaOH required 19.90 cm^3 for neutralisation.

The other portion was electrolysed using a current of 0.40 A and it took 16 minutes to completely deposit the nickel metal at the cathode.

(i) Using the formula of the complex ion present in red solid G, explain what is meant by the term complex ion. You may assume the oxidation state of the metal in the complex ion is +n. [1]

(ii) Suggest a reason why the metal is able to form a complex ion identified in (b)(i). [1]

(iii) Calculate the amount of oxygen evolved. [1]

(iv) Calculate the amount of hydrogen ions and nickel ions in solution H. [2]

(v) Using your answers to (b)(iii) and (b)(iv), deduce the value of *x* with the aid of an equation. [2]

(vi) Write an equation to suggest the product formed at the other electrode during electrolysis of solution H. Use E^θ values from the *Data Booklet* to explain why it is formed.

[2]

(c) A spectrochemical series is a list of ligands based on the strength of their interaction with metal ions. It was first proposed in 1938 based on the results of absorption spectra of cobalt complexes. The ligands are ranked based on the energy gap, ΔE, formed between the split d-orbitals when the ligand is bonded to the cobalt metal centre. A partial spectrochemical series listing of ligands is given below.

$$\text{small } \Delta E \xrightarrow{\hspace{8cm}} \text{large } \Delta E$$

$$I^- < Br^- < Cl^- < F^- < NCS^- \text{ (N–bonded)*} < CH_3CN < NH_3 < H_2NCH_2CH_2NH_2$$

**N-bonded means the ligand binds to the metal centre at the nitrogen atom*

Ligands on the left of this series are generally regarded as weaker ligands. On the other hand, ligands on the right are stronger ligands.

Propose suitable explanations for the following trends observed in the spectrochemical series.

(i) Halide ligands decrease in strength down the Group. [1]

(ii) CH_3CN is a stronger ligand than NCS^- (N-bonded). [1]

(iii) $H_2NCH_2CH_2NH_2$, a bidentate ligand, is a stronger ligand than NH_3, a monodentate ligand. Consider the standard Gibbs free energy change for the following ligand exchange reaction in your answer.

$$[Co(NH_3)_6]^{3+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Co(H_2NCH_2CH_2NH_2)_3]^{3+}(aq) + 6NH_3(aq)$$

[2]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Samples of anhydrous magnesium ethanoate, $Mg(CH_3COO)_2$ and barium ethanoate, $Ba(CH_3COO)_2$, were heated to a temperature of 600 ^oC causing them to decompose.

White residues were formed in both cases and a common gaseous product, X, with molecular formula of C_3H_6O was also given off. X gives a yellow precipitate upon warming with alkaline aqueous iodine. In addition, the decomposition of magnesium ethanoate also produced a second gaseous product, which forms a white precipitate with calcium hydroxide solution.

(i) Identify the gaseous product, X. [1]

(ii) Write a balanced equation with state symbols for each decomposition reaction. [2]

(iii) Account for the difference in the decomposition products. [2]

(b) During an earthquake, the heat generated by the friction of the fault in the Earth's crust may be large enough to decompose the mineral rocks present in the fault, releasing chemicals like sulfur dioxide, SO_2, and aluminium oxide, Al_2O_3.

One method for the removal of sulfur dioxide is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Based on your knowledge of chemical periodicity, suggest whether Al_2O_3 can also be used to remove SO_2. [1]

(ii) State and explain the pH of the solutions formed when MgO, Al_2O_3 and SO_3 are separately added to water. [3]

(c) Phenol, phenylmethanol and benzoic acid are three compounds containing benzene rings. None of these compounds is particularly soluble in water. Both phenol and benzoic acid dissolve in NaOH(aq), but only benzoic acid dissolves in Na_2CO_3(aq).

State what these observations indicate about the relative acidities of the three compounds, and explain this trend in acidity. [3]

(d) Compound P, $C_6H_{11}O_2Cl$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate and decolourises hot, acidified potassium manganate(VII). When compound P is heated with excess aqueous sodium hydroxide, compound Q, $C_6H_{12}O_3$, is formed. Aqueous iodine is subsequently added to the hot mixture of this reaction and compound R, $C_4H_4O_5Na_2$, is formed. P reacts with excess concentrated sulfuric acid at 170 °C to give three possible isomeric products S, T and U.

S, but not T and U, reacts with excess ammonia to form an amine.

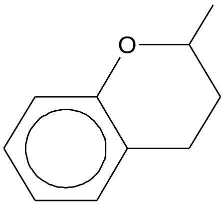
(i) Suggest the structures of P, Q and R, explaining your reasoning. [6]

(ii) Describe and explain how the ease of hydrolysis of S differs from that of T and U. [2]

[Total: 20]

5 **(a)** A is an aromatic compound. It undergoes various reactions as stated below:

- 1 mol of A, $C_{10}H_{13}OCl$, reacts with 2 mol of aqueous Br_2 to give P.
- 3 mol of A reacts with 1 mol of methylamine to give R.
  R reacts immediately with cold silver nitrate to give a white precipitate.
- 1 mol of A reacts with 1 mol of sodium hydroxide at room temperature to form a homogeneous solution.
- 1 mol of A reacts with 1 mol of sodium and gives the following compound,



Suggest structures for A and P. Explain all the reactions, taking into account the molar ratios of the reactants when applicable. [7]

(b) B, a constitutional isomer of A, is also an aromatic compound and reacts very differently with the above mentioned reagents.

- B does not react with aqueous Br_2, methylamine or sodium hydroxide.
- B does not react with hot acidified potassium dichromate(VI) but with hot acidified potassium manganate(VII), B gives $C_8H_5O_4Cl$.
- B does not react with alkaline aqueous iodine.
- 1 mol of B reacts with 1 mol of sodium.
- B does not exhibit enantiomerism.

(i) Based on the above information, state all the possible functional groups in B. [1]

(ii) Hence suggest a structure of B, giving the skeletal formula for the structure. [2]

(c) Anhydrous aluminium chloride, $AlCl_3$ is a powerful Lewis acid, and is used as a catalyst in Friedel-Crafts alkylation of aromatic compounds.

Anhydrous $AlCl_3$ adopts three different structures, depending on the temperature and the state (solid, liquid, gas). Solid $AlCl_3$ exists as cubic close packed layers. In the liquid state, aluminium trichloride exists as the dimer Al_2Cl_6. Al_2Cl_6 dimers are also found in the vapour phase.

(i) Draw a dot-and-cross diagram for the dimer of aluminium chloride, and state the bond angle about the A*l* atom. [2]

(ii) A 0.52 g sample contains a mixture of $AlCl_3$ and its dimer. It takes up a volume of 70 cm^3 at a temperature of 150 ^{O}C and a pressure of 1 atm.
By determining the average M_r of the mixture, deduce the percentage composition of the aluminium chloride dimer under these conditions. [3]

(iii) How would you predict the average M_r of the mixture to change as the temperature is increased? Explain your answer. [1]

(iv) With the aid of an equation, explain why the hydrated form of aluminium chloride cannot act as a Lewis acid. [2]

(d) Beryllium dichloride has properties similar to those of aluminium chloride.

Beryllium dichloride and ammonia reacts in the molar ratio 1:2. By considering the number of bonding and non-bonding electron pairs, explain the molar ratio and draw a diagram to show the bonding in the product. [2]

[Total: 20]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

CLASS		TUTOR'S NAME	

CHEMISTRY **9729/04**

Paper 4 Practical **19 August 2019**

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 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, 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	**/ 28**
2	**/ 11**
3	**/ 16**
Total	**/ 55**

This document consists of **19** printed pages.

1 Determination of the percentage by mass of ethanedioic acid

FA 1 is a solution made by dissolving an unknown mass of a mixture of ethanedioic acid, $H_2C_2O_4$, and sodium ethanedioate, $Na_2C_2O_4$.

In aqueous solution, both ethanedioic acid and sodium ethanedioate release all their ethanedioate ions, $C_2O_4^{2-}$. These ions react with manganate(VII) ions as shown.

$$2MnO_4^{-}(aq) + 16H^{+}(aq) + 5C_2O_4^{2-}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

You will carry out titrations to find the percentage by mass of ethanedioic acid in the mixture.

FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4.

(a) (i) Titration of FA 1 against FA 2

1. Fill a burette with **FA 2**.
2. Pipette 25.0 cm^3 of **FA 1** into a conical flask.
3. Use the measuring cylinder to add 30.0 cm^3 of **FA 3** to the same conical flask.
4. Place the conical flask on the tripod and gauze and heat until the temperature of the solution is approximately 70 °C.
5. **Carefully** remove the flask from the tripod.
   Add a few drops of **FA 2** from the burette and swirl the mixture until it turns colourless.

Note: If the reaction mixture does not decolourise or turns brown, reheat it to about 70 °C. Swirl the mixture till it decolourises.
If the brown colour remains, discard the contents of the flask and begin a new titration.

6. Continue the titration until a permanent pale pink is obtained.
7. Record your titration results, to an appropriate level of precision, in the space provided on page **3**.
8. Repeat points 2 to 7 until consistent results are obtained.

Titration results

[2]

(ii) From your titration results, obtain a suitable volume of **FA 2**, $V_{\textbf{FA 2}}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{\textbf{FA 2}}$ = ... cm^3
[3]

(iii) Calculate the total number of moles of ethanedioate ions present in 25.0 cm^3 of **FA 1**.

moles of ethandioate ions present = ...
[1]

(b) **Titration of FA 1 against FA 4**

A separate experiment was carried out by titrating **FA 1** against **FA 4** containing 0.0400 mol dm^{-3} sodium hydroxide from a burette.
It was found that 25.0 cm^3 of **FA 1** required **26.75 cm^3** of **FA 4** for complete reaction.

Calculate the number of moles of ethanedioic acid present in 25.0 cm^3 of **FA 1**.

moles of ethandioic acid present = ...
Need a home tutor? Visit smiletutor.sg [1]

(c) **(i)** Calculate the mass of sodium ethanedioate, $Na_2C_2O_4$, present in 25.0 cm^3 of **FA 1**.
[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of sodium ethanedioate present = ...
[1]

(ii) Calculate the mass of ethanedioic acid, $H_2C_2O_4$, present in 25.0 cm^3 of **FA 1**. Hence calculate the percentage by mass of ethanedioic acid in the solid mixture used to prepare **FA 1**.
[A_r: C, 12.0; O, 16.0; H, 1.0]

percentage by mass of $H_2C_2O_4$ = ...
[2]

(d) Explain why the solution in the conical flask was heated to approximatly 70 °C before titration.

....

....[1]

(e) Student **B** suggested improving the accuracy of the titration results by decreasing the concentration of **FA 2** to 0.0150 mol dm^{-3}.

State and explain if the student's suggestion would make the titration results more accurate.

....

....[1]

(f) The **FA 2** that was initially added into the conical flask took some time to decolourise. As the titration continued, the rate of decolourisation changed due to the products formed.

To investigate the kinetics of the reaction in part **(a)**, a separate experiment was carried out to observe the rate of carbon dioxide produced over a period of time.

30.0 cm^3 of **FA 2** was added from a measuring cylinder to a conical flask containing 20.0 cm^3 of **FA 1** and 50.0 cm^3 of **FA 3** and the stop watch was started. The volume of carbon dioxide was collected by downward displacement of water using a measuring cylinder and the volume of gas was recorded at 30 s intervals.

(i) Sketch the graph, in **Fig 1.1**, you would expect to obtain for this experiment and use it to explain why **FA 2** decolourises at different rates throughout the titration.

Fig 1.1

....

....

....

....

....

....[3]

(ii) A similar experiment described in **(f)(i)** was carried out using 20.0 cm^3 of **FA 1** with 30.0 cm^3 of another oxidising agent, aqueous potassium persulfate, $K_2S_2O_8$, in the presence of Fe^{3+}(aq) catalyst. The volume of carbon dioxide produced was similarly recorded at 30 s intervals. Sketch in **Fig 1.2,** a graph you would expect for this new experiment

Fig 1.2

[1]

(g) Planning

The kinetics of a chemical reaction can be studied by using the initial rates method. In this method, we note the time taken for a reaction to reach an identification point early in the reaction.

Reaction between iodide ions, I^-, and persulfate ions, $S_2O_8^{2-}$ is an example where its initial rate can be determined.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

If a small and same amount of aqueous sodium thiosulfate is added to every reaction mixture together with starch before the start of the reaction, the iodine produced during the reaction will react immediately with the thiosulfate ions present.

When the small amount of thiosulfate ions have reacted with the iodine produced, a blue-black iodine-starch complex will appear, indicating the experiment has reached the identification point.

By keeping the amount of thiosulfate ions small, the time taken for the reaction to reach the identification point is therefore used to determine the initial rate of that reaction.
The same procedure is repeated with different volumes of reactants and deionised water while keeping the total volume of the reaction mixture constant.

In this question, you are to investigate how the rate of reaction between potassium persulfate and potassium iodide depends on the concentration of potassium persulfate.

(i) You are to plan a series of experiments to determine the time taken for the reaction between potassium persulfate and potassium iodide to reach a same identification point for all the experiments and show how changing the concentration of potassium persulfate will affect the rate of reaction.

You may assume you are provided with:

- 0.60 mol dm^{-3} aqueous potassium iodide, KI,
- 0.20 mol dm^{-3} aqueous potassium persulfate, $K_2S_2O_8$,
- 0.020 ml dm^{-3} aqueous sodium thiosulfate, $Na_2S_2O_3$,
- starch indicator,
- equipment normally found in a school or college laboratory.

A first experiment is carried out using the following quantities
(precision is according to the apparatus used):

25 cm^3 potassium iodide,
40 cm^3 potassium persulfate,
10 cm^3 sodium thiosulfate,
0 cm^3 deionised water,
5 cm^3 starch indicator.

In your plan you should include brief details of:

- the apparatus that you would use,
- the procedure that you would follow,
- how you would ensure your results obtained are reliable,
- a table showing all volumes and precision of each solution you would use and the measurements that you would take.

Table

....

....

....

....

....

....

....

....

....

....

....

....

....

....[8]

(ii) Write an ionic equation, including state symbols, for the reaction between the iodine produced and the thiosulfate ions, $S_2O_3^{2-}$, present in the reaction mixture.

....[1]

(iii) Hence calculate the rate of producing iodine if the time taken for experiment 1 was 134 seconds.

[2]

(iv) A preliminary experiment carried out by another student, using approximate volumes of solution, showed that the time taken for an experiment to reach identification point doubled when the potassium persulfate was diluted with an equal volume of water.

Sketch with clearly labelled axes, on **Fig 1.3**, an appropriate graph to represent the results of the student's preliminary experiment.

Fig 1.3

[1]

[Total: 28]

2 Determination of the concentration of sodium hydroxide

When hydrochloric acid is mixed with aqueous sodium hydroxide, the neutralisation reaction releases heat causing a rise in the temperature of the solution.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

In this experiment you will mix different volumes of hydrochloric acid and sodium hydroxide but the total volume will be kept constant. For each mixture you will record the temperature rise.

Since the total volume remains the same, the temperature rise is a direct measure of the heat given out by the reaction. The maximum heat given out occurs when all the acid present is exactly neutralised by all the alkali present. By determining the volumes when this occurs, you can determine the concentration of the sodium hydroxide.

FA 5 is 2.00 mol dm^{-3} aqueous hydrochloric acid, HC*l*.
FA 6 is aqueous sodium hydroxide, NaOH.

(a) Prepare a table in the space provided on page **12** in which to record, to an appropriate level of precision:

- the volume of **FA 5**, $V_{FA 5}$,
- the volume of **FA 6**, $V_{FA 6}$,
- the initial temperature of **FA 5**, T_i,
- the maximum temperature of the solution, T_{max},
- the temperature rise, ΔT, where $\Delta T = T_{max} - T_i$.

Experiment 1

1. Using a measuring cylinder, transfer 40.0 cm^3 of **FA 5** into a polystyrene cup placed in a 250 cm^3 beaker.
2. Record the initial temperature of **FA 5**, T_i, in the space below.
3. Using another measuring cylinder, transfer 10.0 cm^3 of **FA 6** into the same cup.
4. Stir the mixture thoroughly and record in your table the maximum temperature, T_{max} of the solution.
5. Empty the polystyrene cup, rinse thoroughly with water and shake dry.

Experiments 2 to 6

Repeat experiment 1 five times, using 34.0, 28.0, 22.0, 16.0, 10.0 cm^3 respectively, of **FA 5**, at point 1.

In each case, you will need to add sufficient **FA 6** to make sure that the total volume is 50.0 cm^3.

Record all required volumes, temperature taken and calculated values in your table.

Results

[3]

(b) **(i)** Plot a graph of temperature rise, ΔT, on the y-axis against the volume of **FA 5** on the x-axis on page **13**. Draw two best-fit lines taking into account all of your plotted points.

(ii) From your graph, determine the volume of **FA 5** required to exactly react with **FA 6**.

volume of **FA 5** = ...

[4]

(c) **(i)** Calculate the number of moles of hydrochloric acid present in the volume of **FA 5** in **(b)(ii)**.

moles of hydrochloric acid in **FA 5** = ...

[1]

(ii) Calculate the concentration of **FA 6**.

concentration of **FA 6** = ...

[1]

(d) A student decided to modify the original experiment. The total volume of the solution was increased to 70 cm^3 and temperature rises were recorded for 15, 20, 25, 30, 40, 45, 50, 55, 60 and 65 cm^3 of **FA 6**.

Discuss how these two changes would affect the accuracy with which the concentration of **FA 6** could be determined.

....

....

....

....

....

....[2]

[Total: 11]

3 Investigation of some organic and inorganic reactions

Carry out the following tests. Carefully record your observations in Tables **3.1** and **3.2**

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured. Test and identify any gases evolved. If there is no observable change, write **no observable change**.

FA 7, **FA 8** and **FA 9** are all solutions of carbohydrates.

- Sugars and starch are carbohydrates.
- Some sugars contain an aldehyde group and hence act as reducing agents.
- Other sugars do not contain an aldehyde group.

Sandell's solution reacts in a similar way to Fehling's reagent.

You will need to heat Sandell's solution in a hot water bath when using it in tests.

Table 3.1

		test	observations		
			FA 7	**FA 8**	**FA 9**
(a)	**(i)**	Add 2 or 3 drops of aqueous iodine.			
	(ii)	Add 2 or 3 drops of acidified potassium manganate(VII) and **allow to stand for two minutes.**			
	(iii)	Add 3 cm depth of Sandell's solution and place the tube in the hot water bath for two minutes.			

[3]

(iv) Identify the following and explain your reasoning:

the carbohydrate that could be starch: ....

explanation :..

....

the carbohydrate that contains an aldehyde group: ....

explanation: ....

....

[2]

(v) Describe a different test, other than using Sandell's solution and Fehling's reagent, that could be carried out to identify the presence of an aldehyde group. Describe how the test would be carried out and the expected observation if the result is positive.

Do not carry out your test.

test: ....

....

observation: ....

....

[1]

FA 10 and **FA 11** are two of the components of Sandell's solution. Each contains one cation and one anion. Carry out the following tests and record all your observations in the table.

Table 3.2

		test	observations	
			FA 10	**FA 11**
(b)	**(i)**	Add a few drops of aqueous silver nitrate.		
	(ii)	Add a few drops of aqueous barium nitrate or aqueous barium chloride, then		
		add dilute nitric acid.		
	(iii)	Add a few drops of aqueous iodine.		
	(iv)	Add a 1 cm depth of aqueous iron(II) sulfate.		
	(v)	Add a 1 cm depth of **FA 11**.		☒

[6]

(vi) Identify the ions in **FA 10** and **FA 11**.

FA 10 cation: .... anion: ....

FA 11 anion: ....

[2]

(vii) Write an ionic equation, including state symbols, for the reactions of **FA 10** in **(b)(iii)** and **(b)(v)**.

equation for **(b)(iii)**: ....

equation for **(b)(v)**: ....

[2]

[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)

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

H2 Chemistry Prelim Exam Answers

Paper 1 Answer Key

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

Paper 1 Worked Solutions

1 **(A)**

Charge of nucleon A = $(+\frac{2}{3}) + 2(-\frac{1}{3}) = 0$

Charge of nucleon B = $2(+\frac{2}{3}) + (-\frac{1}{3}) = +1$

Hence, A is a neutron, B is a proton. Statement 1 is correct.

Statement 2: A neutrino does not have a charge.

Hence the charge of C must be -1. C will be attracted to the positive plate.

Statement 2 is correct.

Statement 3: $^{22}_{10}\text{Ne} \rightarrow {}^{22}_{11}\text{Na}$ is correct.

When a neutron breaks up into a proton, mass number remains constant; proton number increase by 1.

2 **(B)**

The ratio of O_2: Cl^- is 3:2. In chlorates (or any oxoanions), O exist as oxides with OS -2. Hence each O is oxidised from -2 in chlorates to 0 in oxygen gas.

Total number of electrons lost by three O_2 molecules = 3 x 2 x 2 = 12
Total number of electrons gained by two Cl^- = 12
Number of electrons gained by each Cl^- = 6

Change in OS of Cl = -6
Final OS – Initial OS = -6
Initial OS = -1 – (-6) = +5

3 **(B)**

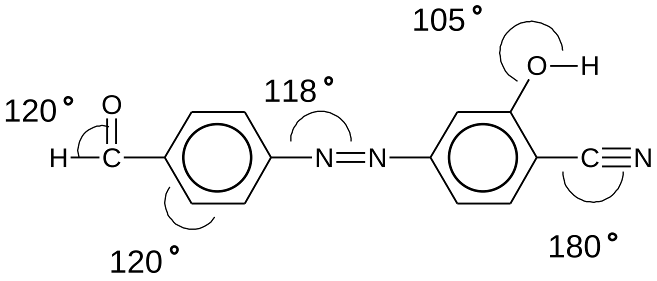
Cations with higher charge and smaller ionic radius have higher charge density, will polarise anion electron cloud more to form a more covalent bond.

For ionic compounds of Group 14 halides, we look for cation with smaller 2+ charge and larger ionic radius (further down the group), hence Pb^{2+} ($\therefore PbF_2$).

For covalent compounds, we look for cation with larger 4+ charge and smaller ionic radius (up the group), hence Sn^{4+} ($\therefore SnCl_4$).

(Note: Although not tested here, students should know that anions with larger electron cloud, are more easily polarised, form more covalent bonds. Hence chlorides form more covalent bonds than fluorides.)

4 **(B)**



There are no sp^3 hybridised carbon atom with 4 bond pairs and 0 lone pairs to give a 109° bond angle.

5 **(D)**

At constant temperature and pressure, $V \propto n$.

The initial 5 cm^3 is due to air particles. The final reading of 81 cm^3 includes the volume due to the air particles. After subtracting off 5 cm^3, the volume due to the volatile liquid only is 76 cm^3.

$$M_r = \frac{mRT}{pV}$$

$$M_r = \frac{0.253 \times 8.31 \times (273+97)}{101\ 325 \times 76 \times 10^{-6}}$$

$$M_r = 101.0$$

6 **(C)**

This question test how well students know the definitions of the different enthalpy changes.

Statement 1:
$\Delta H_7 \equiv LE(CaCO_3)$ and $\Delta H_8 \equiv -\Delta H_{sol}(CaCO_3)$
From $\Delta H_{sol} = \sum\Delta H_{hyd} - LE$,
$LE = \sum\Delta H_{hyd} - \Delta Hsol$
$= \Delta H_{hyd}(Ca^{2+}) + \Delta H_{hyd}(CO_3^{2-}) - (-\Delta H_8)$
Hence statement 1 is wrong.

Statement 2:
$\Delta H_7 \equiv$ 1st + 2nd IE of Ca = 590 + 1150 = 1740
Hence statement 2 is correct.

Statement 3:
$\Delta H_2 \equiv \Delta H_{atm}(Ca)$
From Hess's law,
$\Delta H_1 = \Delta H_2 + (\Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7) - \Delta H_8$
rearrange, $\Delta H_2 = \Delta H_1 + \Delta H_8 - (\Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7)$
Hence statement 3 is correct.

7 **(A)**

Calibration methods account for heat loss by assuming a constant heat capacity C of the set-up.

In experiment 1, reaction is a neutralisation reaction.
Total amount of heat evolved depends on amount of water formed. n(water) = 2.0 x 50/1000

Using heat evolved = heat absorbed and letting C be heat capacity in kJ K^{-1}.
2.0 x 50/1000 x 57.4 = C x 10.0 -Eqn ①

For experiment 2, we calculate the enthalpy change of neutralisation for one mole of the weak acid $H_2C_2O_4$. $n(H_2C_2O_4)$ reacted = 2.0 x 50/1000 x ½ (as NaOH is limiting)

Using heat evolved = heat absorbed
2.0 x 50/1000 x ½ x $|\Delta H_{rxn}|$ = C x 8.5 -Eqn ②

Taking Eqn②/Eqn①, $\frac{2.0 \times 50/1000 \times \frac{1}{2} \times |\Delta H_{rxn}|}{2.0 \times 50/1000 \times 57.4} = \frac{C \times 8.5}{C \times 10.0}$

Hence $|\Delta H_{rxn}| = \frac{57.4 \times 8.5 \times 2}{10}$

8 **(D)**

Statement	Equation	$\Delta G^\ominus$	$\Delta S^\ominus$
1	$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$	–	+
2	$Cl_2(g) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$	–	–
3	$MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	+	+

Statement 1 only is correct.

9 **(B)**

Graph of colour intensity against time shows 1st order characteristics with constant half-lives. Since NO was used in excess, the variable is $[Cl_2]$. As reaction proceeds, rate decreases proportionally (flatter gradient) with decreasing $[Cl_2]$. Reaction is 1st order wrt Cl_2.

Graph of rate against $[NO]^2$ shows a straight line with constant positive gradient passing through origin, rate is directly proportional to $[NO]^2$. Hence 2nd order wrt to NO.

Statement 1 is correct.

Statement 2 test whether students can draw the link between orders of reaction and stoichiometric coefficient in the mechanism. 1st order wrt to Cl_2 and 2nd order wrt NO tells us one molecule of Cl_2 and two molecule of NO takes part in the reaction up to and including the slow step of the reaction.
Hence, for the given mechanism, when the slow step is the second step, the mechanism will be consistent with the rate equation.

Statement 3 is wrong.
For an overall 3rd order reaction, units of k = $\dfrac{\text{mol dm}^{-3}\text{ min}^{-1}}{\left[\text{mol dm}^{-3}\right]\left[\text{mol dm}^{-3}\right]^2}$ = $\text{mol}^{-2}\text{ dm}^6\text{ min}^{-1}$.

10 **(D)**

At constant temperature, decomposition of hydrogen peroxide is a first order reaction, hence rate is directly proportional to $[H_2O_2]$. The time taken to use up 10% of initial amount remains constant. After 5 minutes, 90% of initial $[H_2O_2]$ will remain.

Prove:
rate = $k[H_2O_2]$
When $[H_2O_2]$=0.10 mol dm^{-3}, rate = 0.1k. 10% of 0.10 mol dm^{-3} is 0.01 mol dm^{-3}. At a rate of 0.1k, it takes 5 mins to use up 0.01 mol dm^{-3} of H_2O_2.
When $[H_2O_2]$=1.00 mol dm^{-3}, rate = k. 10% of 1.00 mol dm^{-3} is 0.10 mol dm^{-3}. When the amount to be used up increase by 10x and the rate also increase by 10x, the increases cancel out and the time taken will remain constant at 5 mins.

11 **(B)**

Human blood is buffered by the H_2CO_3, HCO_3^- system.

The weak base will react with and remove small amounts of $H^+(aq)$ in the blood to maintain a relatively constant pH of 7.4.

$HCO_3^- + H^+ \rightarrow H_2CO_3$

12 **(C)**

For precipitation, ionic product ≥ Ksp. Substitute $[IO_3^-] = 0.10$ mol dm^{-3}, $[CrO_4^{2-}] = 0.10$ mol dm^{-3}, $[AsO_4^{3-}] = 0.10$ mol dm^{-3} into the corresponding ionic products.

$AgIO_3$: $[Ag^+][IO_3^-] \geq 3.2 \times 10^{-8}$ mol^2 dm^{-6}
$[Ag^+] \geq 3.2 \times 10^{-7}$ mol dm^{-3}

Ag_2CrO_4: $[Ag^+]^2 [CrO_4^{2-}] \geq 9.0 \times 10^{-12}$ mol^3 dm^{-9}
$[Ag^+] \geq 9.5 \times 10^{-6}$ mol dm^{-3}

Ag_3AsO_4: $[Ag^+]^3 [AsO_4^{3-}] \geq 1.0 \times 10^{-22}$ mol^4 dm^{-12}
$[Ag^+] \geq 1.0 \times 10^{-7}$ mol dm^{-3}

The first precipitate is Ag_3AsO_4 and it appears at the smallest $[Ag^+]$ of 1.0×10^{-7} mol dm^{-3}.

13 **(A)**

Rearranging $\Delta G^\ominus = -nFE^\ominus$, $-\Delta G^\ominus/F = nE^\ominus$

A quick calculation of $E^\ominus$ will give the more standard reduction potential values.

half-equation	$-\Delta G^\ominus/F$ (V)	$E^\ominus$ / V
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	+0.16	+0.16
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.27	+0.27
$U^{4+} + e^- \rightleftharpoons U^{3+}$	−0.52	−0.52
$U^{3+} + 3e^- \rightleftharpoons U$	−4.98	−1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$		−2.38

Mg metal is a reducing agent that will reduce UO_2^+ and itself oxidised to Mg^{2+}.

Using $E_{cell}^\ominus = E_{red}^\ominus - E_{oxd}^\ominus$, we can see $E_{cell}^\ominus > 0$ (and reaction will be spontaneous) when $E_{red}^\ominus > E_{Mg2+/Mg}^\ominus$.

Since $E_{UO2+/U4+}^\ominus > E_{U4+/U3+}^\ominus > E_{U3+/U}^\ominus > E_{Mg2+/Mg}^\ominus$, UO_2^+ will be reduced by Mg metal all the way to U.

14 **(B)**

Using the equations Q=It and Q=nzF,
where n = amount of Cu deposited, z = 2 for $Cu^{2+} + 2e \rightarrow Cu$

$$n = \frac{It}{zF}$$

The amount of charge supplied will affect the amount of Cu deposited. The amount of charge, Q, is affected by current used and the length of time for which the current is run.

15 **(C)**

The strongest reducing agent has the lowest 1st + 2nd ionisation energies.

IEs decrease down the group and increase across the period. Sr is in group 2, to the left of Cd, both in Period 4. Hence Sr should have lower 1st + 2nd IEs than Cd.

A glance at the data booklet should tell you that the first two IEs of Sr is lower than for both Ni and Zn.

16 **(D)**

Statement 1:
$2VO_3^{-} + 3Zn \rightarrow 2V^{2+} + 3Zn^{2+}$. Vanadium is reduced from +5 OS in VO_3^{-} to +2 in V^{2+}.

Statement 2:
$Cr(H_2O)_6^{3+} + SO_4^{2-} \rightarrow Cr(H_2O)_5(SO_4)^{+} + H_2O$. Chromium undergoes ligand exchange reaction where a water ligand is replaced with a sulfate(VI) ligand. Cr remains +3 cation.

Statement 3:
Tartrate anion $^{-}OOCCH_2(OH)CH_2(OH)COO^{-}$ has a charge of -2.
In $[Co(tartrate)_3]^{3-}$, the oxidation state of Co is +3. Hence Co has been oxidised by hydrogen peroxide from Co(II) to Co(III). Once $[Co(tartrate)_3]^{3-}$ is formed, it will be reduced back to Co(II) by hydrogen peroxide. $[Co(II)(tartrate)_3]^{4-}$ is acting as a homogeneous catalyst for the disproportionation of hydrogen peroxide.

17 **(A)**

Steps	$\mathrm{C}l^-$	I^-
add $AgNO_3$(aq)	AgCl ppt	AgI ppt
Filter + wash with H_2O	Residue	Residue
add NH_3(aq)	soluble to form $\mathrm{C}l^-$ and $Ag(NH_3)_2^+$ complex	insoluble AgI ppt
Filter	$\mathrm{C}l^-$ and $Ag(NH_3)_2^+$ in filtrate	AgI ppt in residue
Note: All the K^+ ions should have been washed off in the first filtration		

18 **(C)**

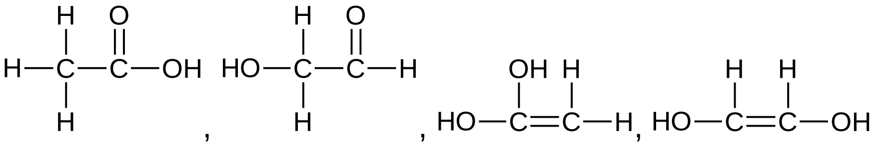
Element	C	H	O
% mass	40	6.7	53.3
Amt	3.33	6.7	3.33
Ratio	1	2	1

Empirical Formula is CH_2O.

Consider Molecular Formula (MF) in increasing number of carbon atoms.

MF is CH_2O:
The C atom is unsaturated, no chiral carbon possible.

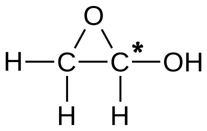
MF is $C_2H_4O_2$:



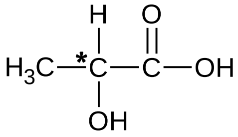
$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$, $\mathrm{HO{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H}$, $\mathrm{HO{-}\overset{OH}{C}{=}\overset{H}{C}{-}H}$, $\mathrm{HO{-}\overset{H}{C}{=}\overset{H}{C}{-}OH}$

All straight chain structures are not chiral.

Only a cyclic structure can give a chiral carbon.

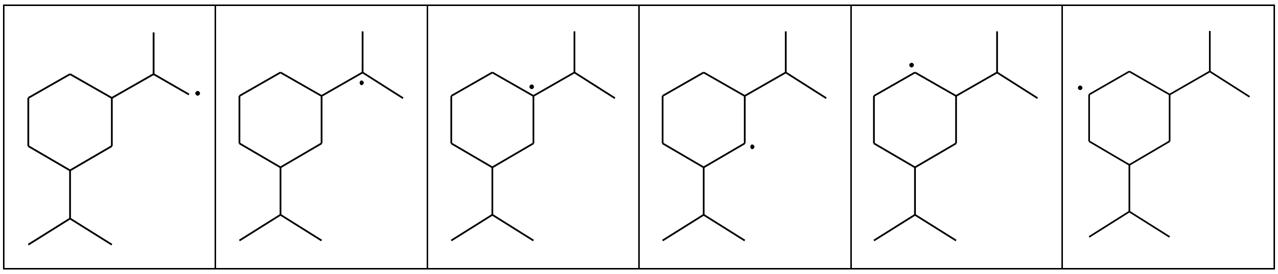


Hence, the smallest number of C atoms must be 3, MF is $C_3H_6O_3$:



$\mathrm{H_3C{-}\overset{H}{\underset{OH}{C^*}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$

19 **(A)**



20 **(C)**

A: Correct. Graphene sheet is one layer of carbon atoms in graphite structure. It is non-polar with delocalised π electrons above and below the plane of carbon atoms that repel water. Hence a graphene sheet is insoluble in water.

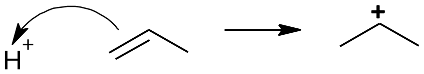
B: Correct. Each C atom of a graphene sheet (graphite layer) is sp^2 hybridised with p-orbitals that overlap with p-orbitals of adjacent carbon atoms. The partial double bond formed strengthens the C-C bond.

C: Incorrect. There are sp^3 hybridised carbon atoms in the graphene oxide layer which have tetrahedral shape. This caused the carbon layer to become "puckered", with some carbon atoms above and below the plane.

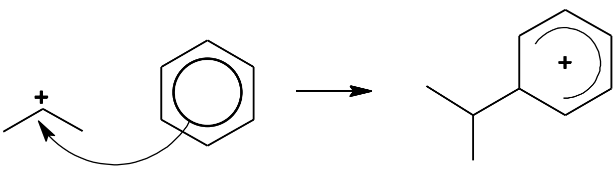
D: Correct. There are σ bonds between sp^3 hybridised carbon and/or oxygen atoms.

21 **(D)**

H_3PO_4 is used as a strong acid catalyst in the EA of H_2O to propene.

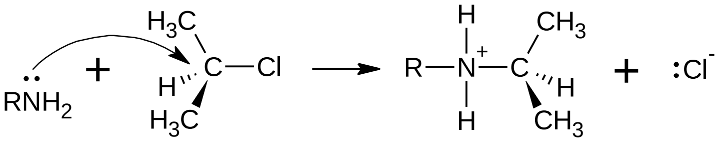


Once the strong electrophile (a carbocation) is formed, it will undergo ES with the benzene.



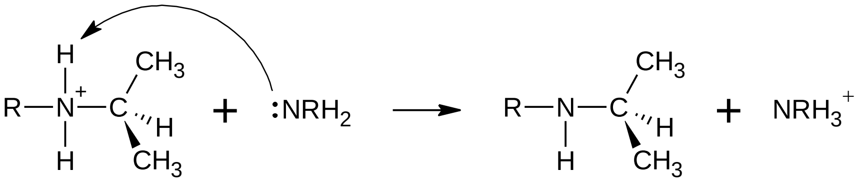
22 **(B)**

Step 1:



RNH_2 is acting as a nucleophile to attack the electron deficient carbon of the C-Cl bond.

Step 2:

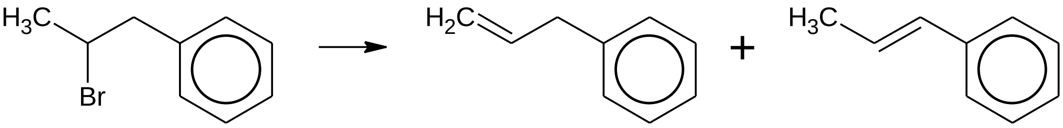


RNH_2 is acting as a Bronsted base. RNH_2 accepts a H^+ from the intermediate to form its conjugate acid RNH_3^+.

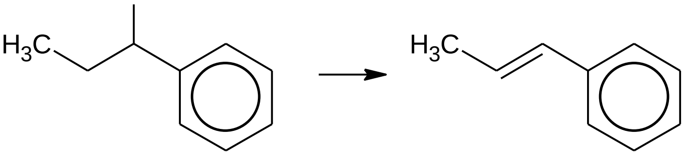
There are no changes in oxidation states for any element in these reactions.

23 **(A)**

In alcohol solvent, the OH^- negative charge is not well dispersed, hence OH^- acts as a base to remove a H^+ from the bromoalkane, Br^- will leave at the same time. Net result is elimination of HBr to form alkene using NaOH in alcohol.

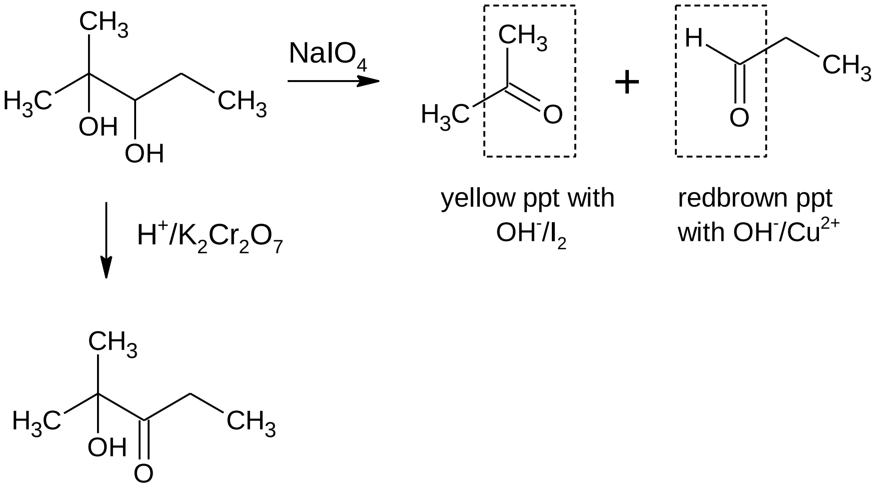


(2-bromopropyl)benzene can form two structurally different alkenes upon elimination of HBr.



(1-bromopropyl)benzene can only form one alkene structure.

24 **(C)**



yellow ppt with OH^-/I_2

redbrown ppt with OH^-/Cu^{2+}

25 **(A)**

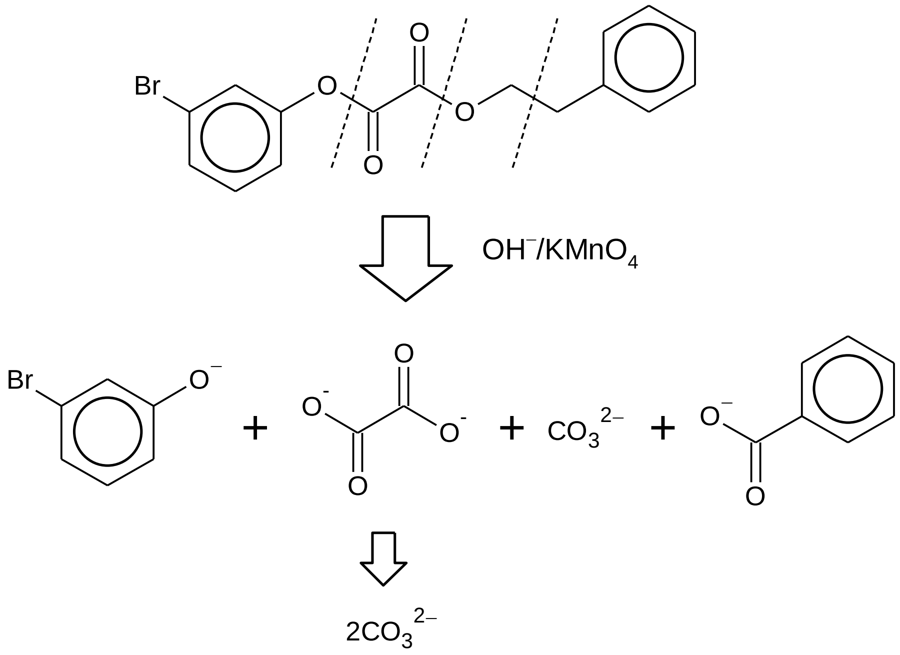
The best electrical conductor has the highest ionic concentration, which depends on extent of dissociation of weak acid, in turn due to strength of acid.

Pyruvic acid, with an electron-withdrawing CH_3CO– acyl group that disperse the negative charge on –COO^- of conjugate base, is the strongest weak acid.

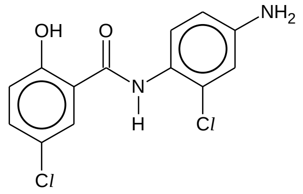
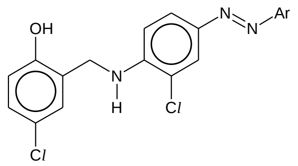
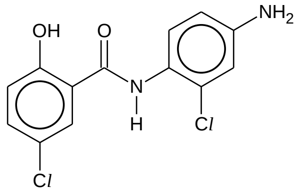
CH_3– and CH_3CH_2– groups of ethanoic acid and propanoic acid respectively are electron-donating groups that intensify the negative charge on –COO^- of conjugate base, are weaker acids.

Pure ethanoic acid, like all simple covalent liquids, only undergo auto-ionisation, producing minuscule amounts of ions.

26 **(D)**



27 **(C)**

H$_2$ with Ni metal	LiA*l*H$_4$ in dry ether	NaBH$_4$ in ethanol	Sn in concentrated HC*l*
		no reduction	

28 **(C)**

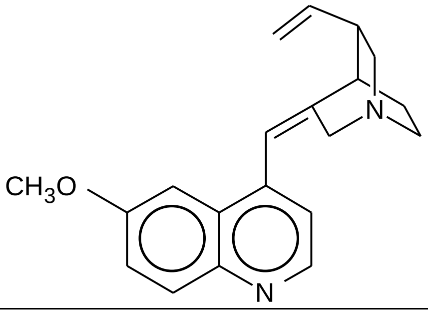
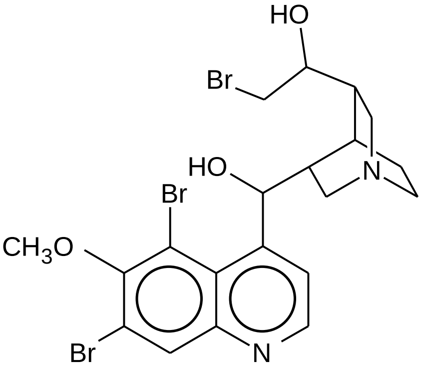
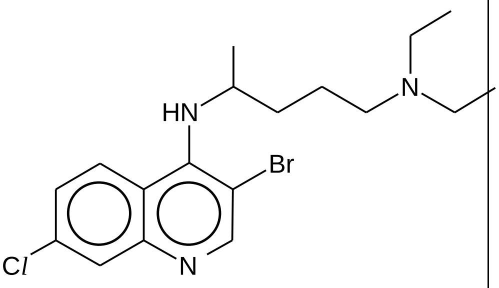
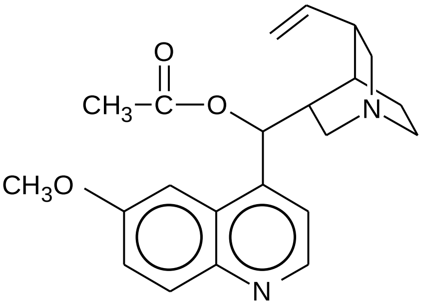
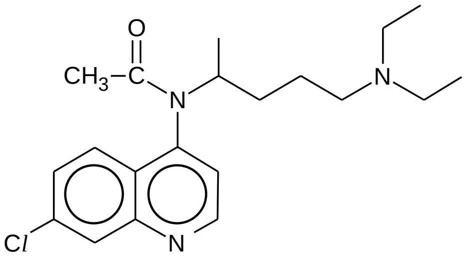
Ease of hydrolysis: P > Q > R

Statement 1 is only partially correct, more importantly, it cannot explain why acyl chlorides are hydrolysed so readily. C*l* is a net electron-withdrawing group as electron-withdrawing electronic effect of electronegative C*l* is stronger than the electron-donating resonance effect due to weak 3p–2p overlap.

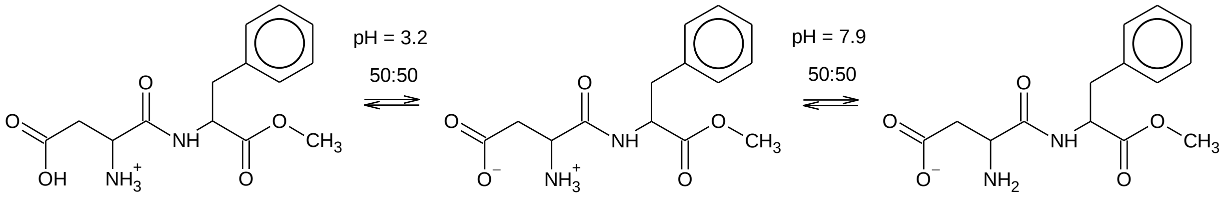
Statement 2 is correct. C*l* is an electronegative atom, causes a partial positive charge on the carbon of the C-C*l* bond.

Statement 3 is correct. One of 3 reasons why nucleophilic substitutions of chlorobenzene do not occur. The other two being stronger partial double bond and C-C*l* in chlorobenzene does not have a partial positive charge due to π electrons.

29 **(C)**

	quinine	chloroquine
aluminium oxide		no elimination reaction
aqueous bromine		
ethanoyl chloride		

30 **(B)**

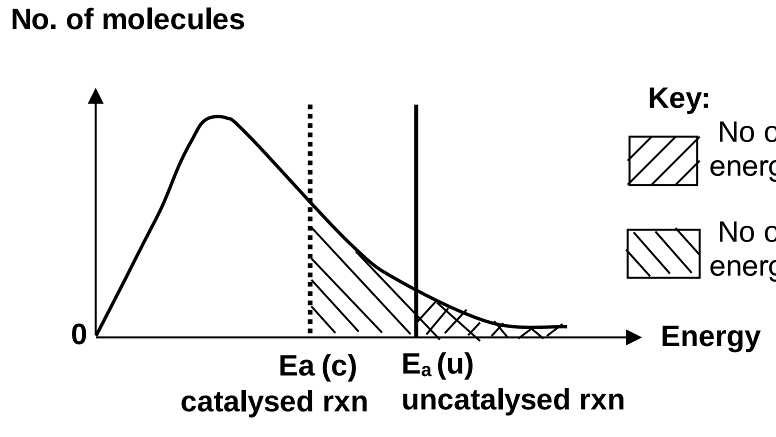


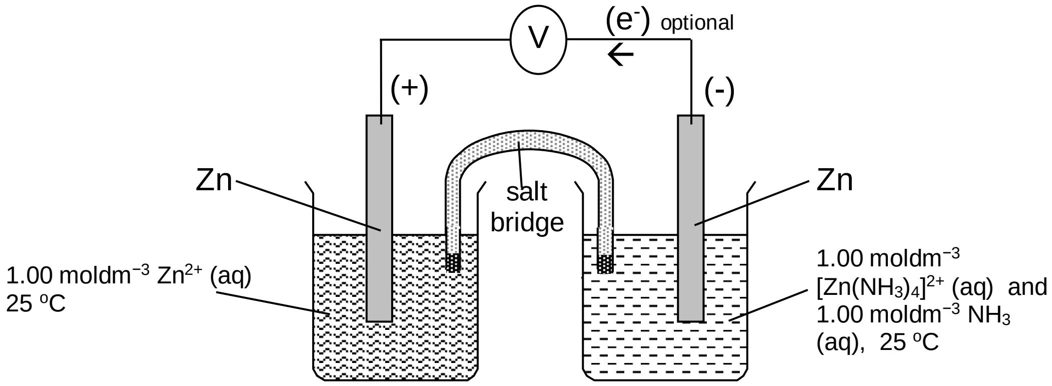
most dominant species below pH 3.2

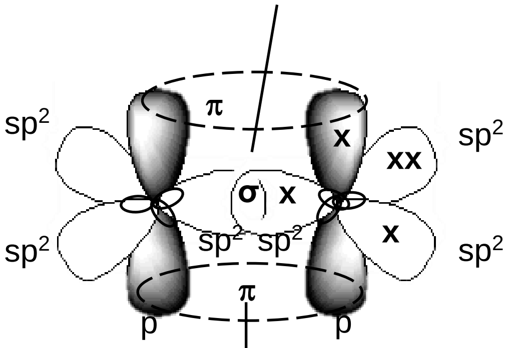
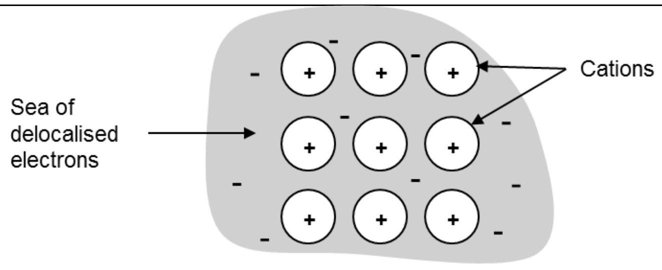
most dominant species between pH 3.2 and pH 7.9

most dominant species above pH 7.9

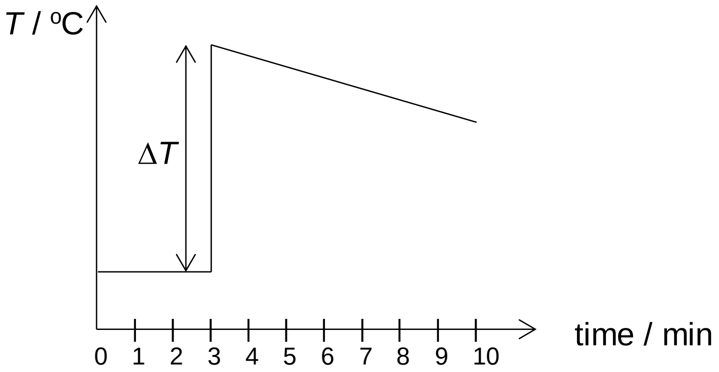
Paper 2 Answers

1	**(a)**	**(i)**	At a low temperature, by Le Chatelier's Principle, the forward exothermic reaction is favoured to produce more heat. Hence the position of equilibrium will shift to the right to increase yield of ammonia. [1] However the system will take a long time to reach equilibrium. Hence an optimal temperature of 500 ^{o}C is used to ensure rate of reaction is not too slow and makes the production process become uneconomical. [1]
		(ii)	The iron catalyst is in solid state while nitrogen and hydrogen are in gaseous state. It functions as a heterogeneous catalyst as it is in a different phase as compared to nitrogen and hydrogen. [1] Nitrogen and hydrogen (reactants) will be adsorbed to the surface of the catalyst. Bonds in the reactant molecules are weakened which lowers the activation energy. New bonds are then formed between adjacent reactant molecules to form the menthol. The product formed will be desorbed from the surface of the catalyst. [1]
		(iii)	• The catalyst provides an alternative reaction pathway with a lower activation energy, E_a (c) compared to the uncatalysed reaction, E_a. • More molecules will possess energy greater than this lowered activation energy. • The frequency of effective collisions increases. Hence, according to the Collision Theory, the rate of reaction increases. 3 pts: [2], 2 pts: [1]  [1] Diagram

		(iv)	Ammonia has a simple molecular structure with hydrogen bonding between molecules. Nitrogen and hydrogen have simple molecular structure with instantaneous dipole-induced dipole interactions between molecules. [1] Ammonia has a higher boiling point than nitrogen and hydrogen due to the stronger hydrogen bonds between molecules. The condenser helps to lower temperature so that ammonia is condensed into liquid while nitrogen and hydrogen remains as gases and is recycled back into the reactor. [1]
		(v)	Sketch of HN_3 shows more deviation from ideal gas than ammonia. [1] Both hydrazoic acid and ammonia have simple molecular structure. Hydrazoic acid has a large electron cloud which is more polarisable, resulting in stronger instantaneous dipole-induced dipole interaction between its molecules than the hydrogen bonds between ammonia molecules. The stronger id-id interactions causes hydrazoic acid to deviate more from ideal gas behavior. [1]
	(b)	**(i)**	 • label the electrode and ions in each half cell with concentration and temperature • salt bridge, voltmeter and label the polarity of the electrodes correctly [2]

		(ii)	[R]: $Zn^{2+} + 2e^{-} \rightarrow Zn$ [O]: $Zn + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2e^{-}$ Overall: $Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$ [1] $\Delta G^{\ominus} = -nFE^{\ominus} = -2 \times 96500 \times 0.28 = -54040\ J\,mol^{-1} = -54.0\ kJ\,mol^{-1}$ [1] Or $\Delta G^{\ominus} = -nFE^{\ominus} = -2 \times 96500 \times 0.28 / 1000 = -54.04\ kJ\,mol^{-1} = -54.0\ kJ\,mol^{-1}$
	(c)	**(i)**	$\underline{sp^2\ orbital}$ of N and C $\underline{head\text{-}on}$ overlap to form σ bond  **x** : valence electrons of N. For reference in cii. $\underline{p\ orbital}$ of N and C $\underline{side\text{-}way}$ overlap to form π bond [1]
		(ii)	N_a is more basic than N_b. In N_a, lone pair of electrons are present in the sp^2 orbital that is pointing away from/perpendicular to the delocalised π electron cloud formed with neighboring carbon atom, hence it does not overlap with the delocalised π electron cloud and the lone pair are not delocalised, making the lone pair of electrons available for dative bonding with H^+. [1] N_b is part of amide. Lone pair of electron in N_b is present in the unhybridised p orbital of N, which overlaps with π electron cloud of C=O (and delocalised π electron cloud containing $C=N_a$), resulting in lone pair of electrons on N delocalising into the π electron cloud of C=O (and delocalised π electron cloud containing $C=N_a$) and are unavailable for forming a dative bond with H^+. Amides are hence considered to be neutral. [1]
2	**(a)**		 [1] Copper has a giant metallic lattice structure of Cu^{2+} cations surrounded by a sea of delocalised valence electrons, which can act as mobile charge carriers to conduct electricity. [1]

	(b)	**(i)**	Magnesium. • Mg, Ca and Ba can undergo both reactions but Ag cannot. The $E^{\ominus}$ values for Mg, Ca and Ba are more negative than $E^{\ominus}(H^+/H_2)$ and $E^{\ominus}(Cu^{2+}/Cu)$, hence they can be oxidised in both reactions 1 and 2. Ag cannot be oxidised by Cu^{2+} and H^+ since $E^{\ominus}(Ag^+/Ag)$ is more positive. [1] (Accept $E^{\ominus}_{cell}$ calculation to prove that reactions are feasible / not feasible.) • Ca and Ba are too reactive and will react violently with acid since reducing power increases down the group. The $E^{\ominus}(M^{2+}/M)$ values get more negative down the group, implying oxidation of metal becomes more favourable, and the reducing strength of metal increases and the reactivity of group 2 metals with acid increases down the group. Ca and Ba reacts vigorously, but reaction of Mg with cold water is very slow. [1]
		(ii)	$\begin{tikzcd} Cu(s) + H_2SO_4(aq) + Mg(s) \arrow[rr, "\Delta H_r"] \arrow[dr, "\Delta H_1"'] & & CuSO_4(aq) + H_2(g) + Mg(s) \arrow[dl, "\Delta H_2"] \\ & MgSO_4(aq) + H_2(g) + Cu(s) & \end{tikzcd}$ [1] energy cycle
		(iii)	1. Using the electronic balance, measure accurately the mass of the Ni bar. 2. Heat a water bath in a beaker on a hot plate until the water is boiling. 3. Tie the Ni bar using a string and lower it into the boiling water bath for 10 min (or any length of time sufficient for the temperature to equilibrate). 4. Measure the temperature of the water bath using a 1°C thermometer. (accept 0.2 °C division thermometer) 5. Measure 100 cm^3 of water using a 100 cm^3 measuring cylinder and pour it into a polystyrene cup. 6. Measure the initial temperature of the water using a 1°C thermometer. (accept 0.2 °C division thermometer) 7. Remove the Ni bar from the boiling water bath and place it in the polystyrene cup. 8. Measure the highest temperature reached. Marking points: • Measure mass of Ni bar, • and volume of water using measuring cylinder. • Use thermometer to measure initial temperature of water bath, • and the highest temperature reached. • Use of boiling water bath to heat Ni bar • and allow time for Ni bar to be heated fully (mention heating for 10 min/time for temperature of Ni bar and water bath to equilibrate) 6 points. [1] for 1-2 point [2] 3-5 points [3] all 6 points

		(iv)	 [1] Label axes with correct units, correct shape of graph and labelling of ΔT
		(v)	Heat evolved = mcΔT + CΔT = (50 x 4.18 x 34.8) + (9.7 x 34.8) = 7610 J [1] n($CuSO_4$) = 50/1000 x 0.3 = 0.015 mol ΔH_2 = –7610 / 0.015 x 10^{-3} = –507 kJ mol^{-1} [1]
	(c)		Cu has more protons, hence it has a higher nuclear charge. However, the additional electrons are added to the penultimate 3d orbitals. The d subshell shield less efficiently than s and p subshells. [1] Hence, Cu has a larger effective nuclear charge. The valence shell of Cu are more strongly attracted to the nucleus and hence Cu has a smaller atomic radius. [1]

3	**(a)**	**(i)**	$K_{sp} = [Fe^{3+}]\,[OH^-]^3$ units: $mol^4\ dm^{-12}$ [1]
		(ii)	$K_{sp} = 4.0 \times 10^{-38}$ $27x^4 = 4.0 \times 10^{-38}$ Solubility = 2.0×10^{-10} mol dm^{-3} [1]
		(iii)	$FeS_2(s) \rightleftharpoons Fe^{2+}(aq) + S_2^{2-}(aq)$ $K_{sp} = [Fe^{2+}]\,[S_2^{2-}]$ $1.3 \times 10^{-27} = [Fe^{2+}]_{min}(0.25)$ $[Fe^{2+}]_{min} = 5.2 \times 10^{-27}$ mol dm^{-3} $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Fe^{2+}]\,[OH^-]^2$ $8.0 \times 10^{-16} = [Fe^{2+}]_{min}(0.40)^2$ $[Fe^{2+}]_{min} = 5.0 \times 10^{-15}$ mol dm^{-3} [1] for 2nd calculation – 1st working to prove that FeS_2 is a less soluble salt. When the first trace of $Fe(OH)_2$ appears, $[Fe^{2+}] = 5.0 \times 10^{-15}$ mol dm^{-3} To calculate the $[S_2^{2-}]$ present: $K_{sp} = [Fe^{2+}]\,[S_2^{2-}]$ $5.0 \times 10^{-15}\,[S_2^{2-}] = 1.3 \times 10^{-27}$ $[S_2^{2-}] = 2.6 \times 10^{-13}$ mol dm^{-3} [1] for final answer
	(b)	**(i)**	$\Delta G^{\theta}_{ppt} = 2.303RT \log K_{sp}$ $= 2.303\,(8.31)(298)\log\,(1.3 \times 10^{-27})$ = – 153 333 J mol^{-1} = – 153.3 kJ mol^{-1} [1] for value & correct dp (minus 1 overall if answers in (i) & (ii) are not 1 dp)
		(ii)	$\Delta G^{\theta}_{ppt} = \Delta H^{\theta}_{ppt} - T\Delta S^{\theta}_{ppt}$ $-153.3 = (-178.0) - 298\,\Delta S^{\theta}_{ppt}$ ΔS^{θ}_{ppt} = – 0.08277 kJ mol^{-1} K^{-1} (or 8.28×10^{-2} kJ mol^{-1} K^{-1}) ΔS^{θ}_{ppt} = – 82.8 J mol^{-1} K^{-1} [1] for value & sign [1] for correct units

(iii) $\Delta S^{\theta}_{\text{ppt}}$ is negative which suggests that there is a decrease in entropy due to the formation of an ordered lattice as the solid precipitate forms (or there are less aqueous particles). There are less ways to arrange the particles. [1]

(c) **(i)**

Element	C	Fe	H	N	O
% composition by mass	19.3	14.9	3.2	11.2	51.4
A_r	12.0	55.8	1.0	14.0	16.0
Amount/mol	1.608	0.2670	3.21	0.800	3.213
Mole ratio	6	1	12	3	12

Empirical formula of Y: $C_6FeH_{12}N_3O_{12}$ [1]

(ii) Anion: $[Fe(C_2O_4)_3]^{3-}$ [1] Cation: NH_4^+ [1]

(iii) Coordination number: 6 Shape: octahedral [1]

(iv) In the presence of $C_2O_4^{2-}$ ligands, the partially filled 3d orbitals split into two energy levels, with an energy gap, ΔE.

The d electrons in the lower energy level absorbed energy in the visible spectrum corresponding to energy gap and become excited to a vacant d orbital at the higher energy level (d-d transition).

The complementary colour of violet corresponding to unabsorbed wavelengths of yellow is transmitted.

All 3 points – [2] 2 Points – [1]

4 (a) (i)

	$2SO_2$ +	O_2	$\rightleftharpoons$	$2SO_3$
Initial p/atm	2x	x		0
Change in p/atm	-2y	-y		+2y
Eqm p/atm	2x-2y	x-y		2y

(to show ratio of SO_2 and O_2 is 2:1. Table not required)

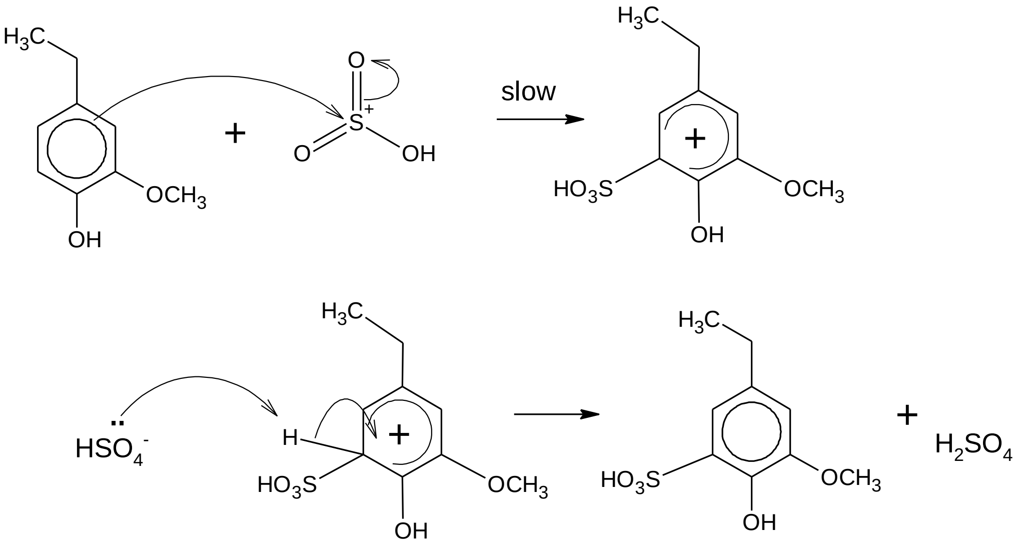
At eqm, P_{SO2} is twice of P_{O2}
P_{O2} = 12 kPa

P_{SO3} 104 – 24 – 12 = 68 kPa

[1]

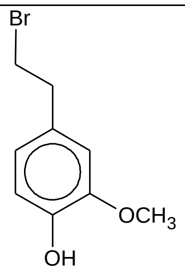
$K_p = 68^2 / [(24)^2(12)] = 0.669\ kPa^{-1}$ answer and units: [1]

(ii) Electrophilic substitution [1]



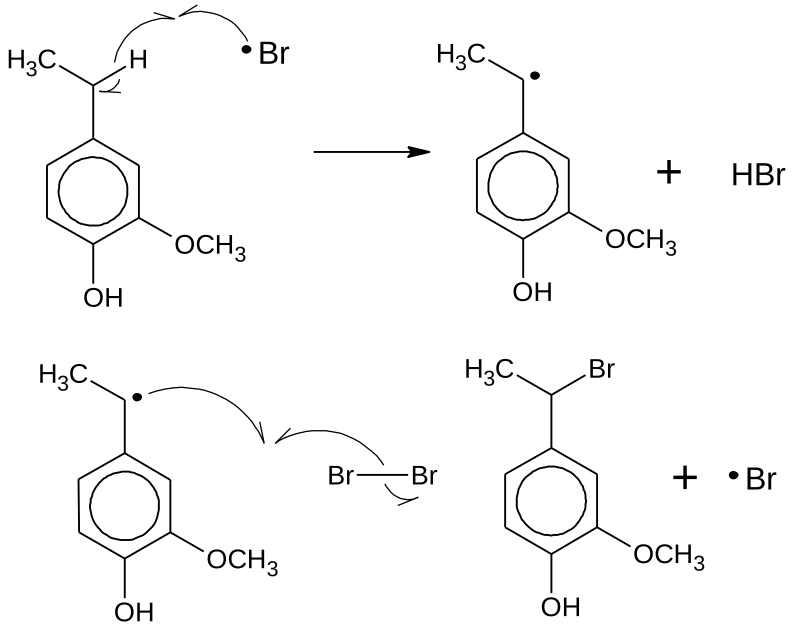
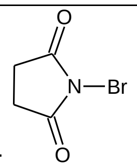
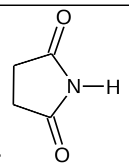
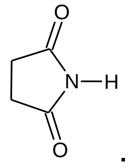
[2]

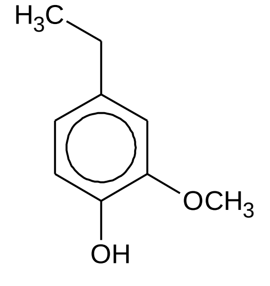
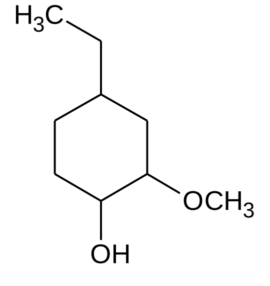
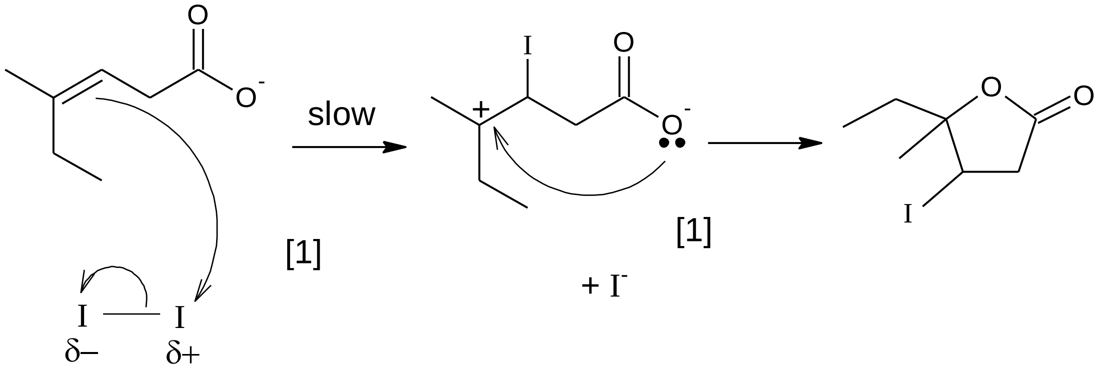
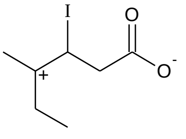
(b) (i)

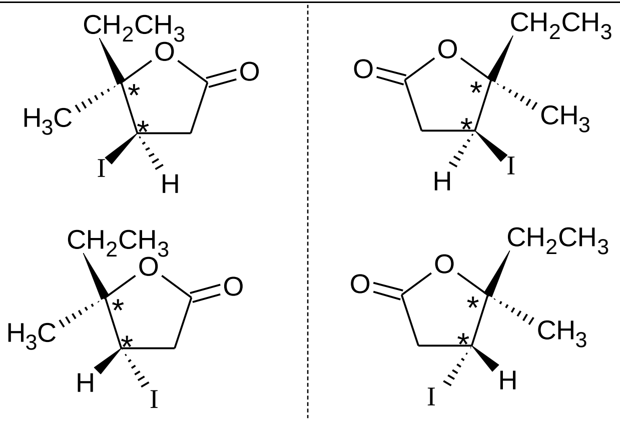
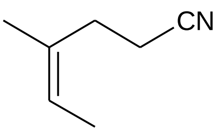
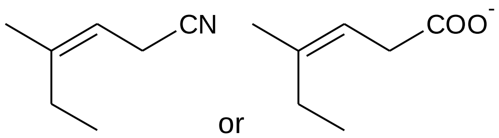


B: A:B = 2:3

[1] structure
[1] ratio

		(ii)	 Equations: [1] each
		(iii)	HBr +  → Br_2 +  [1] Homolytic fission involves <u>breaking</u> covalent bond with <u>each bonded atom taking an electron</u> to form a radical. [1] H-Br and N-Br break homolytically before forming Br_2 and  . (Alternatively, show arrows)
		(iv)	The benzylic radical is <u>very stable</u>. The p orbital of radical C overlaps with the pi electron cloud system of the benzene ring. The <u>lone electron is delocalised into the benzene ring</u>. [1]

	(c)	**(i)**	 **A**  **B** [1] each
		(ii)	The benzene is very stable due to the delocalised pi electron cloud. [1]
5	**(a)**	**(i)**	
		(ii)	$NaHCO_3$ reacts with the carboxylic acid to generate carboxylate ion which is a stronger nucleophile. [1]
		(iii)	4-membered ring lactone experience more significant ring strain, hence it is less stable. [1] There are more electron donating alkyl groups on the intermediate formed for 5-membered ring lactone,  that will disperse the positive charge on the carbon atom. The intermediate is more stable. [1]

		(iv)	Add $K_2Cr_2O_7$, H_2SO_4(aq), heat. [1] If orange $K_2Cr_2O_7$ turns green, 4-membered ring lactone is produced in step 2. If orange $K_2Cr_2O_7$ remains, 4-membered ring lactone is not produced in step 2. [1] $KMnO_4$ is not accepted. Alkene in the carboxylate ion (reactant) could be oxidised by $KMnO_4$.
		(v)	Bonds formed: BE (C-Cl) = 340 kJ mol^{-1} > BE(C-I) = 240 kJ mol^{-1} Bonds broken: BE (Cl-Cl) = 244 kJ mol^{-1} > BE(I-I) = 151 kJ mol^{-1} The enthalpy change of reaction will be more exothermic. The product will be of a lower energy level, hence it is more stable. [1]
	(b)		 mirror plane [2]
	(c)		step 1: ethanolic KCN, heat under reflux [1] step 2: HBr(g), room temperature [1] step 3: ethanolic NaOH, heat under reflux [1]  [1] D  [1] E

Paper 3 Answers

<table>
<tr><td>1</td><td>(a)</td><td>(i)</td><td>Amount of $Ba(OH)_2$ = amount of H_2SO_4 = 0.98 / 98.1 = 0.00999 mol [1]</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>$2CH_3CO_2H + Ba(OH)_2 \rightarrow (CH_3CO_2)_2Ba + 2H_2O$ [1]

Amount of $Ba(OH)_2$ that reacts with ethanoic acid
= 23.30 / 1000 × 0.800 – 0.09989 = 0.00865 mol
Amount of ethanoic acid = 2 × n($Ba(OH)_2$)
= 2 × 0.00865 = 0.0173 mol [1] allow ecf if equation is not balanced</td></tr>
<tr><td></td><td></td><td>(iii)</td><td>$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$ [1]

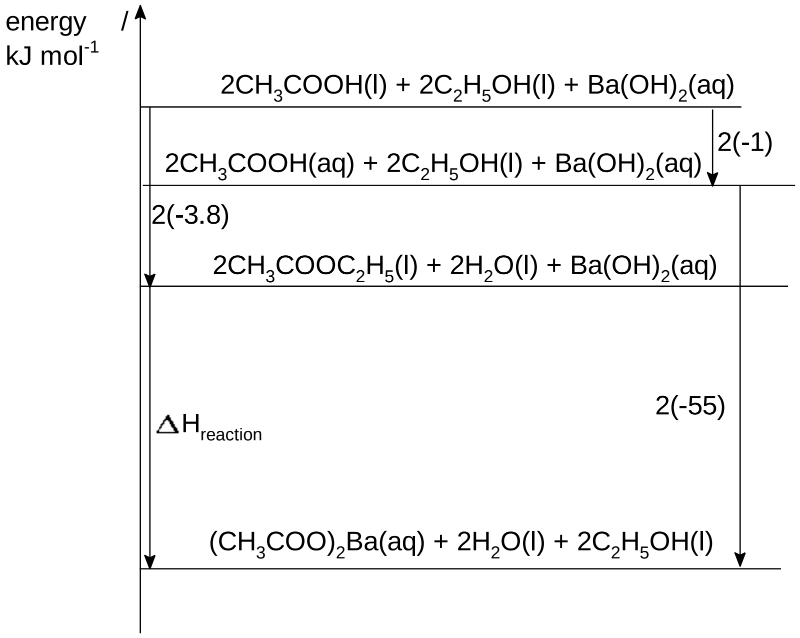
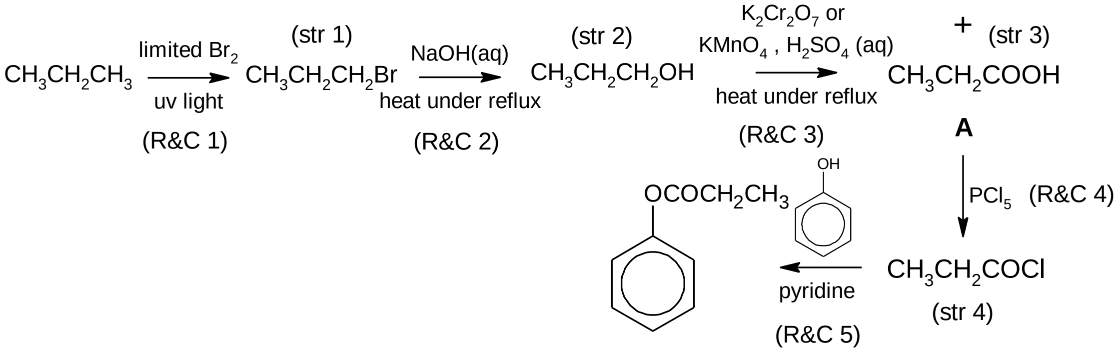
<table>
<tr><th></th><th>CH_3CO_2H</th><th>C_2H_5OH</th><th>$\rightleftharpoons$</th><th>$CH_3CO_2CH_2CH_3$</th><th>H_2O</th></tr>
<tr><td>Initial / mol</td><td>1.48 / 60.0 = 0.02466</td><td>0.92 / 46.0 = 0.02</td><td></td><td>0</td><td>1.8 / 18.0 = 0.10</td></tr>
<tr><td>Change / mol</td><td>-0.007366</td><td>-0.007366</td><td></td><td>+0.007366</td><td>+0.007366</td></tr>
<tr><td>Eqm / mol</td><td>0.0173 Allow ecf from (ii)</td><td>0.01263</td><td></td><td>0.007366</td><td>0.1073</td></tr>
</table>

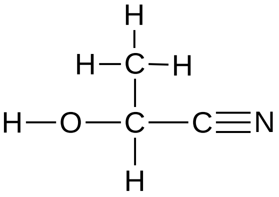
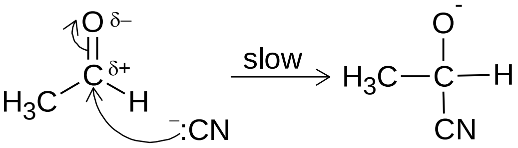
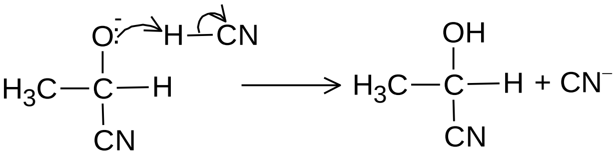
[1] for working out the equilibrium amount of C_2H_5OH, $CH_3CO_2C_2H_5$ and H_2O

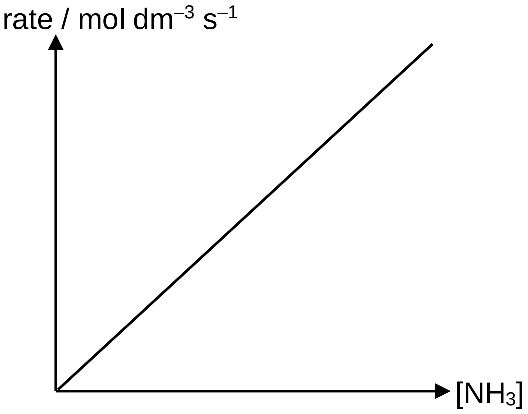
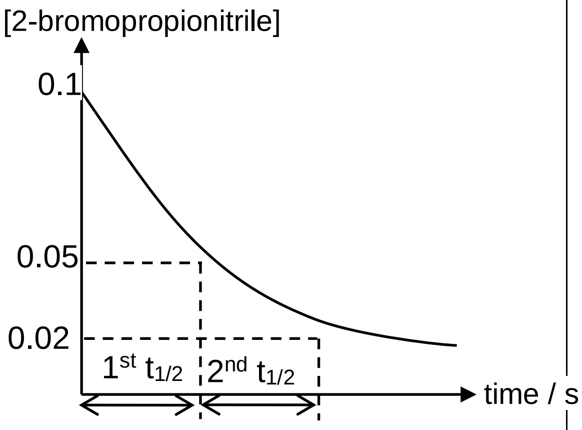
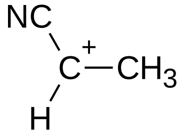
Let V be the volume.

$K_c = \frac{[\frac{0.007366}{V}]\,[\frac{0.1073}{V}]}{[\frac{0.0173}{V}]\,[\frac{0.01263}{V}]} = 3.62$, no units [1]</td></tr>
<tr><td></td><td></td><td>(iv)</td><td>By Le Chatelier’s Principle, as temperature is decreased, the forward exothermic reaction will be favoured to compensate for the heat lost, hence position of equilibrium shifts to the right. [1]

As forward reaction is favoured, more products are produced, hence value of K_c increases. [1]</td></tr>
</table>

	(b)	**(i)**	$\Delta H = \Delta H_f\ (CH_3COO^-) + \Delta H_f\ (H^+) - \Delta H_f\ (CH_3COOH)$ $= -486 + 0 - (-485) = -1$ kJ mol^{-1} [1]
		(ii)	Alkaline hydrolysis (nucleophilic acyl substitution) [1]
		(iii)	 By Hess' Law, $\Delta H(\text{reaction}) + 2(-3.8) = 2(-1) + 2(-55)$ $\Delta H(\text{reaction}) = -104.4$ kJ mol^{-1} [1] [2] correct energy level diagram Deduct marks for incomplete cycle, state symbols, missing species in the non-balanced equations.
	(c)	 Each step (R&C and intermediate) is awarded 1 mark.	

2	**(a)**	**(i)**	Aldehyde is unable to form intermolecular hydrogen bonding between molecules and has a low boiling point compared to an alcohol. Thus, the aldehyde will vaporise quickly (or extracted) once it is formed which subsequently condense and collect in the distillate. [1]
		(ii)	 Compound B [1] for correct structure and [1] for displayed formula
		(iii)	Nucleophilic Addition $NaOH + HCN \rightarrow NaCN + H_2O$ [1] for equation and name of mechansim  [1] for correct curly arrow, δ charges, lone pair and negative charge on CN^- and labelling slow step  [1] for correct curly arrow, lone pair and negative charge on intermediate and balanced equation
		(iv)	At step 1, methanol and ethanol are oxidised to methanal and ethanal respectively. There are zero and one electron-donating groups bonded to the C=O group of methanal and ethanal respectively. The carbonyl carbon of methanal is more electron-deficient than that of ethanal. [1] Therefore, the carbonyl carbon of methanal has a larger partial positive charge compared to that of ethanal, making it more susceptible towards nucleophilic attack. [1] or Methanal has two hydrogen atoms bonded to the C=O group compared to one sterically bulky methyl group in ethanal. Hence, CN^- nucleophile would face more steric hindrance when approaching the carbonyl carbon of the ethanal as compared to methanal. [1]

			Therefore, attacking nucleophiles are able to approach carbonyl carbon of methanal more readily than ethanal. [1]
		(v)	PBr_3, room temperature [1]
	(b)	**(i)**	 Experiment 1  Experiment 2 From experiment 1, the graph of rate against [ethanolic NH_3] is a straight line, with a positive gradient, passing through the origin (or rate is directly proportional to [ethanolic NH_3]). Hence, order of reaction with respect to ethanolic NH_3 is 1st order. [1] for experiment 1 graph and explanation From experiment 2, 1st $t_{1/2}$ = 2nd $t_{1/2}$, order of reaction with respect to 2-bromopropionitrile is 1st order. [1] for experiment 2 graph and showing 1st $t_{1/2}$ = 2nd $t_{1/2}$ on graph to prove 1st order
		(ii)	1 mol dm^{-3} (must be at least 10 times greater than 0.1 mol dm^{-3}). This is ensure that [ethanolic NH_3] is in large excess compared to [2-bromopropionitrile]. Thus the reaction is overall first order reaction (or pseudo first order reaction). [1]
		(iii)	 The carbocation formed from 2-bromopropionitrile is unstable as there is an electron withdrawing nitrile group that intensifies the positive charge. [1]

	(c)	**(i)**	At 1st maximum buffering capacity (percentage composition of $H_2A = HA^- = 50\%$), pH = pK_{a1} At 2nd maximum buffering capacity (percentage composition of $HA^- = A^{2-} = 50\%$), pH = pK_{a2} $pK_{a1} = 2.30$ $pK_{a2} = 9.70$ [1] for both values
		(ii)	At pH 10.3, the mixture contain 20% HA^- and 80% A^{2-}. Amount of HA^- = 0.100 × 20% = 0.0200 mol Amount of A^{2-} = 0.100 × 80% = 0.0800 mol [1] for both values $H_2A + OH^- \rightarrow HA^- + H_2O$ … eqn 1 $HA^- + OH^- \rightarrow A^{2-} + H_2O$ … eqn 2 Amount of NaOH required for eqn 1 = 0.1000 mol Amount of NaOH required for eqn 2 = 0.08000 mol Total amount of NaOH required = 0.1800 mol Mass of NaOH required = 0.1800 × 40.0 = 7.20 g [1]
		(iii)	The change in ratio of $\frac{[HA^-]}{[A^{2-}]}$ is larger when 1 cm^3 HC*l*(aq) is added. [1] Thus, the new buffer will result in a larger change in pH. [1] or Addition of small amount/volume of acid will have a larger change in concentration of acid and salt. [1] Hence, pH change is larger. [1]
		(iv)	At isoelectric point, alanine exist as a zwitterion (HA^-). There will be strong ionic bonding formed between the zwitterions. [1] The amount of energy released when ion-dipole interaction formed between zwitterion and water molecules, may not be sufficient to overcome all the ionic bonding between zwitterions and hydrogen bonding between water molecules. [1] At low and high pH, alanine exist as cation and anion respectively. At low pH, the cations repel each other and at high pH, the anions repel each other. [1] The ions form ion-dipole interaction with the surrounding water molecules and dissolve. The amount of energy released when ion-dipole interaction formed between ions and water molecules, is sufficient to overcome all the ionic bonding between alanine salt and hydrogen bonding between water molecules. [1]

3 (a) (i)

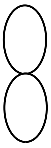
	Cu	**I**
mass ratio	1	2
amt / mol	0.01574	0.01576
Simplest ratio	1	1

Hence, the empirical formula of D is CuI.

[1] Table not required. Working can be shown as calculation.

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]

(iii) There are 3 s orbitals, 6 p orbitals and 5 d orbitals.
p orbital is dumb-bell shaped.



[1] only diagram required

(iv) $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$ [1]

blue — white solid D — yellow/brown solution which dissolves in hexane to form purple layer.

Forms a yellow brown precipitate when mixed.

[1] for all colours

(v) $E_{cell} = E_R - E_O$
$= E(Cu^{2+}/Cu^+) - E(I_2/I^-)$
$= +0.15 - (+0.54)$
$= -0.39$ V <0 hence not feasible. [1]

(vi) As Cu^+ is precipitated by iodide, $[Cu^+(aq)]$ decreases, position of equilibrium of $Cu^{2+} + e^- \rightleftharpoons Cu^+$ shifts to the right and $E(Cu^{2+}/Cu^+)$ becomes more positive, making reduction more feasible/E_{cell} positive hence reaction is more feasible. [1]

	(b)	**(i)**	The complex ion $[NiF_6]^{x-}$ is a species that contains a central metal ion Ni^{n+} surrounded by F^- anions / ligands which forms coordinate bonds to the metal centre. [1]
		(ii)	Ni^{n+} is able to form a stable complex ion because it has energetically accessible vacant d-orbitals to accommodate the lone pairs of electrons donated by the ligands to form the dative bonds [1]
		(iii)	$n(O_2) = 48 / 24000 = 2.00 \times 10^{-3}$ mol [1]
		(iv)	Note: Solution H was divided into 2 equal portions for analysis. $n(H^+ \text{ in H}) = 2 \times n(OH^- \text{ required}) = 2 \times \frac{19.90}{1000} \times 0.20 = 7.96 \times 10^{-3}$ mol [1] $Q = I \times t = 0.40 \times 16 \times 60 = 384$ C $Q = nzF \Rightarrow n(Ni^{2+}) = (384 / (96500 \times 2)) \times 2 = 3.98 \times 10^{-3}$ mol [1]
		(v)	$n_{O_2} : n_{H^+} : n_{Ni^{2+}} = 2.00 : 7.96 : 3.98 = 1 : 4 : 2$ [1] $2K_xNiF_6 + 2H_2O \rightarrow 2xKF + 2NiF_2 + O_2 + 4HF$ Considering the number of F, $12 = 2x + 4 + 4 \Rightarrow x = \frac{12-8}{2} = 2$ [1] Hence, compound E is K_2NiF_6.
		(vi)	$2 H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$ [1] Oxygen gas is produced at the anode. H_2O and F^- are attracted to the anode. As the $E^\theta(O_2/H_2O) = +1.23$ is less positive than $E^\theta(F_2/F^-) = +2.87$, H_2O is preferentially oxidised to form O_2 at the anode. [1]

	(c)	**(i)**	Down the group, the halide ion increases in size hence the bond length of X →Co/M increases. This give rise to less effective orbital overlap and strength of dative bond formed with the metal ion decreases. [1] to adjust points required according to range of students answers
		(ii)	(A ligand is a species/molecule or anion with at least one lone pair of electrons that it can use to form a dative bond to the transition metal atom/ion.) CH_3CN contains an electron-donating alkyl group which makes the lone pair on N more available than that in NCS- to be used to form a dative bond to the transition metal centre, hence it is a stronger ligand. [1]
		(iii)	• ΔH for the reaction is approximately zero as the same (N→Co) bonds are broken and formed. • ΔS is positive as the number of particles increase, resulting in more ways to arrange the particles hence greater disorder. • Since $\Delta G = \Delta H - T\Delta S$ and $- T\Delta S$ is negative, ΔG is negative and hence ligand exchange of NH_3 with $H_2NCH_2CH_2NH_2$ is very feasible. 3 points [2]. 2 points [1]
4	**(a)**	**(i)**	Propanone, CH_3COCH_3 [1]
		(ii)	$Mg(CH_3COO)_2 (s) \rightarrow MgO(s) + CO_2(g) + CH_3COCH_3(g)$ [1] $Ba(CH_3COO)_2 (s) \rightarrow BaCO_3(s) + CH_3COCH_3(g)$ [1]
		(iii)	The Mg^{2+} ion is smaller than Ba^{2+} ion, hence its higher charge density [1] enables it to polarise the electron cloud of CH_3COO^- ion and distort the C-O bond to a greater extent resulting in complete decomposition. [1]
	(b)	**(i)**	Yes, since Al_2O_3 is an amphoteric oxide, it can react with an acidic oxide such as SO_2 to remove it. [1]
		(ii)	MgO in water: pH 8 – 9 Weakly alkaline solution formed as $Mg(OH)_2$ is only slightly soluble in water [1] (due to strong ionic bonds between Mg^{2+} and OH^- ions). Al_2O_3 in water: pH 7 Solution is neutral as Al_2O_3 is insoluble in water [1] (due to strong ionic bonds between Al^{3+} and O^{2-} ions). SO_3 in water: pH 1 - 2 Solution is acidic due to the formation of strong acid $H_2SO_4(aq)$. [1] $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$
	(c)		The relative acidities of the compounds are in the order: $C_6H_5CH_2OH < C_6H_5OH < C_6H_5CO_2H$

The acidity of a compound depends on the relative stability of its conjugate base. The more stable the conjugate base, the more acidic the compound will be.

The $C_6H_5CO_2^-$ is the most stable as the p orbital of the oxygen atom overlaps with the electron cloud of the –C=O bond and the lone pair of electrons on the oxygen atom delocalise into the –C=O. The negative charge is dispersed over the carbon atom and the two electronegative oxygen atoms, stabilising the $C_6H_5CO_2^-$ ion. [1]

In $C_6H_5O^-$, the p orbital of the oxygen atom overlaps with the electron cloud of the benzene ring and the lone pair of electrons on oxygen atom delocalise into the benzene ring. This causes the dispersion of the negative charge into the benzene ring, stabilising the phenoxide ion.

However the charge dispersion in phenoxide ion is less effective than the dispersion in benzoate ion because the 2 electronegative oxygen atoms in benzoic acids can better accommodate the negative charge. [1]

$C_6H_5CH_2O^-$ is destabilised as the electron-donating alkyl group intensifies the negative charge on oxygen. [1]

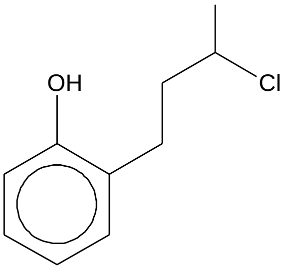
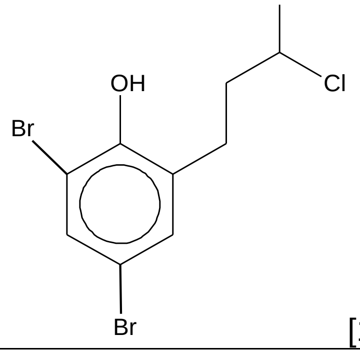
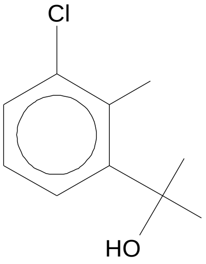
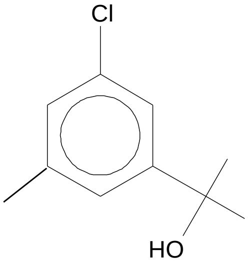
(d) **(i)**

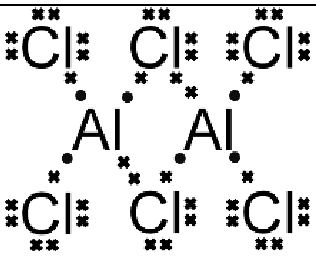
Chemistry	Deduction
P reacts with 2,4-DNPH to form an orange ppt.	P contains either an aldehyde or a ketone functional group and undergoes condensation reaction.
P decolourises hot, acidified $KMnO_4$.	P may contain primary/secondary alcohol functional group or aldehyde functional group and undergoes oxidation reaction.
P is heated with excess NaOH(aq) to form Q. This involves the loss of a C*l* atom.	P contains an alky chloride and undergoes nucleophilic substitution to form an alcohol Q.
I_2(aq) is subsequently added to the hot mixture to form R.	Q contains both $–COCH_3$ and $–CH(OH)CH_3$ groups and gives a positive iodoform test. Note: The loss of 2 C atoms denotes the formation of 2 CHI_3 molecules per molecule of P.
P reacts with excess conc H_2SO_4 at 170 °C.	The alcohol group in P undergoes elimination to form alkenes.
P reacts with excess conc H_2SO_4 at 170 °C to give three possible isomeric products.	P contains a secondary alcohol functional group. OR The alcohol group in P is not a primary alcohol.

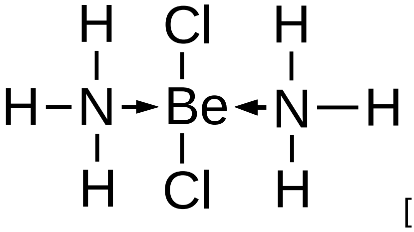
<table>
<tr><td></td><td></td><td></td><td><table><tr><td></td><td>OR
The structure of P is not $CH_3CH(Cl)CH(OH)CH_2COCH_3$. This structure of P will give 4 possible isomeric products.</td></tr></table>[1] for each correct deduction. Maximum [3].

P: $CH_3CH(OH)CH(Cl)CH_2COCH_3$ [1]
Q: $CH_3CH(OH)CH(OH)CH_2COCH_3$ [1]
R: $NaOCOCH(OH)CH_2COO^-Na^+$ [1]</td></tr>
<tr><td></td><td></td><td>**(ii)**</td><td>T and U are cis-trans isomers with a Cl atom directly attached to the double bond, hence they are less susceptible to hydrolysis. [1]

This is because the p orbital of the Cl atom overlaps with the π electron cloud of the C=C bond, resulting in a lone pair of electrons in the p orbital delocalising into the C=C bond. This gives rise to partial double bond character in the C–Cl bond, hence the bond is strengthened. [1]</td></tr>
</table>

5	**(a)**		A  [1] P  [1] • (Comparing the molecular formula of A and S, there is a loss of HCl when S is formed.) Hence A has 1 phenol group that undergoes reduction with 1 mol of Na to form a phenoxide ion • which then undergoes (intramolecular) nucleophilic substitution with the alkyl halide group to form S. • A has a 1 phenol group that undergoes electrophilic substitution with only 2 mol of aq Br_2, as position 2 is already occupied by a side chain. • A has a 1 phenol group that undergoes neutralisation with 1 mol of NaOH, to form a phenoxide ion which is soluble in water as it can form ion-dipole interactions. • Methylamine (a nucleophile) undergoes nucleophilic substitution with the alkyl halide group in A. • 3 mol of A is reacted as the subsequent products also undergo nucleophilic substitution with A, and forms R, a quaternary ammonium salt. • R has a free Cl ion which reacts immediately with $AgNO_3$ to form AgCl, a white precipitate. [1] for each bullet [can award max of 5mks]
	(b)	**(i)**	Aryl halide, tertiary alcohol [1]
		(ii)	 or  etc [1] for correct structure [1] for correct skeletal formula

			(accept any of the positional isomers) • B does not react with aqueous Br_2, methylamine or sodium hydroxide. $\Rightarrow$ phenol, alkene, halogenoalkane, carboxylic acid absent. To account for the Cl atom in the molecular formula, an aryl halide must to be present. • B does not react with hot acidified potassium dichromate(VI) but with hot acidified potassium manganate(VII), B gives $C_8H_5O_4Cl$. $\Rightarrow$ 1^{O} and 2^{O} alcohols absent. 2 carbon containing side chains present • B does not react with alkaline aqueous iodine. $\Rightarrow$ methyl alcohol and ketone absent • 1 mol of B reacts with 1 mol of sodium. $\Rightarrow$ based on this point and above info, one 3^{O} alcohol present • B does not exhibit enantiomerism. B should not have any chiral carbon present
	(c)	**(i)**	 Bond angle about Al: 109^{O} [1] [1] for diagram: • each atom has 8 electrons around it • distinguish between the electrons of Cl and Al • show dative bonds
		(ii)	$pV = nRT = \frac{m}{M}RT$ average M $= \frac{mRT}{pV} = \frac{0.52 \times 8.31 \times (150+273)}{101325 \times 70 \times 10^{-6}}$ [1] correct conversion of units $= 257.7$ g mol^{-1} [1] correct numerical answer Assume that sample contain x mole fraction of Al_2Cl_6 and $(1 – x)$ of $AlCl_3$ $(1-x)(133.5) + (x)(267) = 257.7$ $133.5 + 267x - 133.5x = 257.7$ $x = 0.930$ Hence the percentage composition of the dimer is <u>93.0 %</u> [1]
		(iii)	As T increases, Al_2Cl_6 dimers will dissociate to form $AlCl_3$ molecules. Hence average M_r will decrease [1] OR As T increase, solid $AlCl_3$ forms liquid Al_2Cl_6. Hence average M_r will increase. [1]

		(iv)	(A Lewis acid is an electron pair acceptor.) $AlCl_3$ (s) + $6H_2O$ (l) → $[Al(H_2O)_6]^{3}$Ä (aq) + $3Cl^{-}$ (aq) [1] The hydrated form of aluminium chloride exists $[Al(H_2O)_6]^{3}$Ä and Cl^{-} ions. In $[Al(H_2O)_6]^{3}$Ä, Al is surrounded by six water ligand/molecules and does not have empty orbitals to accept electron pairs and act as a Lewis acid. [1]
	(d)		In $BeCl_2$, Be has only 2 bonding electron pairs around it and can accept 4 more electrons to achieve an octet. NH_3 has a lone pair of electrons. [1] for stating the no of electrons pairs for Be and N Hence $BeCl_2$ can form 2 dative bonds with NH_3, accepting 2 lone pairs of electrons from 2 mol of NH_3.  [1] accept dot & cross diagram too

Paper 4 Answers

1 (a) (i)

	1	2	
Final burette reading / cm^3	25.35	25.45	
Initial burette reading / cm^3	0.00	0.00	
Volume of **FA 2** used / cm^3	25.35	25.45	

Correct headers and units for table [1]

Record volume and burette readings to 2 d.p. [1]

(ii)

$$\text{Ave } V_{\mathbf{FA\,2}} \text{ used} = \frac{25.35 + 25.45}{2} = 25.40 \text{ cm}^3$$

Consistent readings used, correct calculation, 2 d.p.[1]

titre value – reference value (δ) ≤ 0.20 Accuracy [1]

titre value – reference value (δ) ≤ 0.40 Accuracy [1]

(iii)

$$n_{MnO_4^-} \text{ reacted} = \frac{0.0200 \times 25.40}{1000} = 5.08 \times 10^{-4} \text{ mol}$$

$$n_{C_2O_4^{2-}} \text{ present in 25.0 cm}^3 = \frac{5}{2} \times 5.08 \times 10^{-4} = 1.27 \times 10^{-3} \text{ mol}$$

(b)

$$n_{NaOH} \text{ reacted} = \frac{0.0400 \times 26.75}{1000} \text{ mol}$$

$$n_{H_2C_2O_4} \text{ present in 25.0 cm}^3 = \frac{\frac{0.0400 \times 26.75}{1000}}{2} = 5.35 \times 10^{-4} \text{ mol}$$

(c) (i)

$$n_{Na_2C_2O_4} \text{ in 25.0 cm}^3 \text{ of } \mathbf{FA\,1} = 1.27 \times 10^{-3} - 5.35 \times 10^{-4} = 7.35 \times 10^{-4} \text{ mol}$$

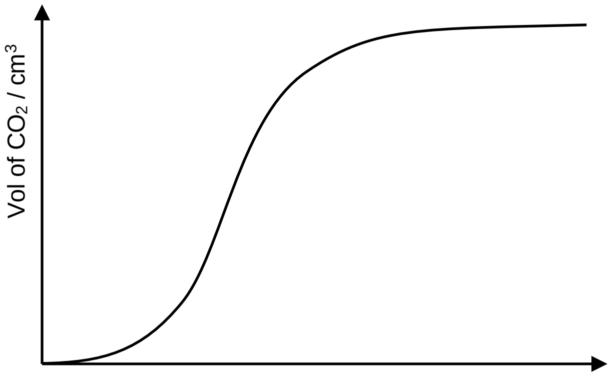
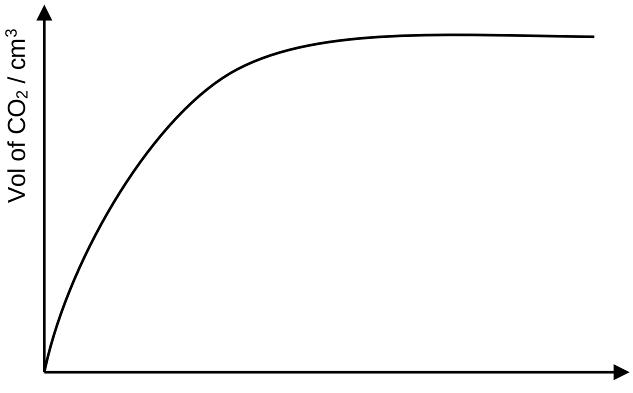
$$m_{Na_2C_2O_4} \text{ in 25.0 cm}^3 \text{ of } \mathbf{FA\,1} = 7.35 \times 10^{-4} \times 134.0 = 9.84 \times 10^{-2} \text{ g}$$

(ii)

$$m_{H_2C_2O_4} \text{ present in 25.0 cm}^3 = 5.35 \times 10^{-4} \times 90.0 = 4.815 \times 10^{-2} \text{ g}$$

$$\text{Percentage by mass of } H_2C_2O_4 \text{ in mixture} = \frac{4.815 \times 10^{-2}}{9.84 \times 10^{-2} + 4.815 \times 10^{-2}} \times 100$$

$$= 32.85 \approx 32.9\ \%$$

	(d)	Heating the solution will ensure the reactants have the required activation energy for effective collisions and reaction to take place. OR Reaction involves 2 negatively charge ions hence it has high activation energy. Rate of reaction/ rate is slow because there is repulsion between MnO_4^- and $C_2O_4^{2-}$.	
	(e)	Results would be more accurate. Lower concentration of **FA 2** would require larger titre volumes (with same uncertainty). Percentage error in volume measurement would be reduced.	
	(f)	**(i)**	 **Fig 1.1** [1] This is an autocatalytic reaction, where the product, Mn^{2+}, acts as a catalyst for the reaction. • At the start, rate is slow as MnO_4^- and $C_2O_4^{2-}$ are negatively charged and repel each other hence frequency of effective collision is slower. (Or No Mn^{2+} forms at the start, hence reaction is slow) • As the titration progresses, increasing amount of MnO_4^- is reduced to Mn^{2+} which acts as a catalyst and speeds up the rate of reaction. • Towards the end of reaction, rate decreases as reactants are used up. 2 bullets – [1], All 3 bullets – [2]
		(ii)	 **Fig 1.2**

(g) **(i)**

1. Fill a burette with $Na_2S_2O_3$.
2. Using a 50 cm^3 measuring cylinder, measure 40.0 cm^3 of $K_2S_2O_8$.
3. Transfer 20.00 cm^3 of $Na_2S_2O_3$ from the burette into a 250 cm^3 conical flask.
4. Using a 25.0 cm^3 measuring cylinder, transfer 25.0 cm^3 of KI and 5.0 cm^3 of starch indicator into the conical flask.
5. Pour the $K_2S_2O_8$ from the measuring cylinder into the conical flask and immediately start the stop watch. Swirl the conical flask and leave it on the table.
6. Stop the stop watch when the colour of the mixture turns blue-black.
7. Record the timing and wash the conical flask and remove any excess water.
8. Repeat steps 2 to 7, using volume indicated in the table below. Add water using a 50 cm^3 measuring cylinder.

Expt	V_{K2S2O8} / cm^3	$V_{\text{deionised water}}$ / cm^3	V_{KI} / cm^3	$V_{Na2S2O3}$ / cm^3	V_{starch} / cm^3	Time taken / s
1	40.0	0.0	25.0	10.00	5.0	
2	30.0	10.0	25.0	10.00	5.0	
3	20.0	20.0	25.0	10.00	5.0	
4	10.0	30.0	25.0	10.00	5.0	

Mark scheme		
i	At least 2 more expts with lower concentration / vol of $S_2O_8^{2-}$ and equally spaced out.	[1]
ii	1 expt has to be at least half or less than half of original vol of $S_2O_8^{2-}$	[1]
iii	V_{total}, V_{KI}, V_{S2O32-}, V_{starch} all kept constant	[1]
iv	Burette used to measure $S_2O_3^{2-}$; measuring cylinder to measure $S_2O_8^{2-}$ and H_2O	[1]
v	$S_2O_8^{2-}$ must be separated from KI and $S_2O_3^{2-}$ before mixing	[1]
vi	Start timing immediately when mixing occurs; stop timing when blue-black appears	[1]
vii	Table with headers and units (penalised only once)	[1]
viii	Precision of burette to 2 d.p., measuring cylinder to 1 d.p.	[1]

(ii) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

(iii)

$$n_{I_2} \text{ produced} = \frac{V_{S_2O_3^{2-}} \times [S_2O_3^{2-}]}{2}$$

$$= \frac{0.020 \times 0.010}{2} = 1.00 \times 10^{-4} \text{ mol [1]}$$

$$[I_2] \text{ produced} = \frac{1.00 \times 10^{-4}}{0.080} = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Rate of } I_2 \text{ formation} = \frac{1.25 \times 10^{-3}}{134} = 9.33 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ [1]}$$

(iv)

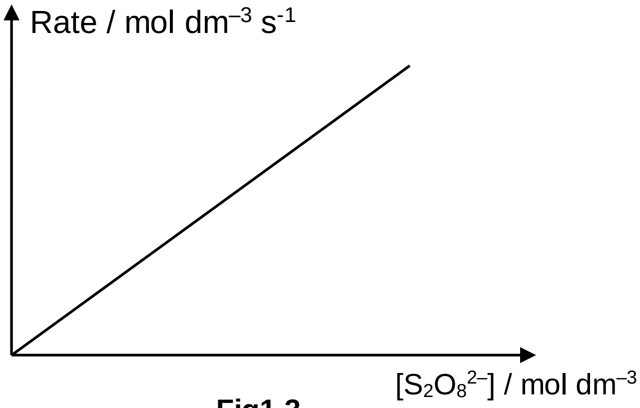


Fig1.3

2 **(a)**

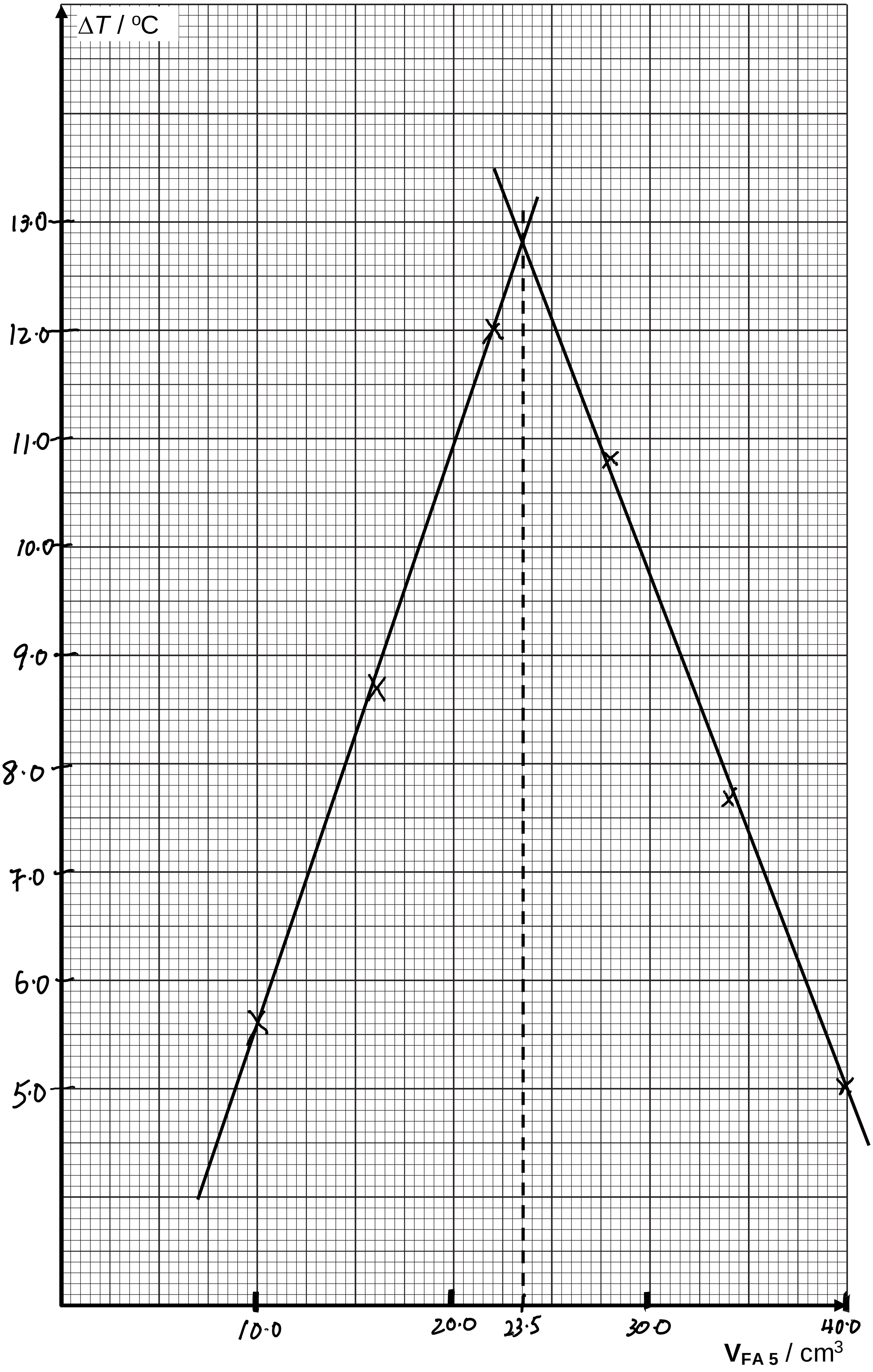
Expt	***V*** $V_{\text{FA 5}}$ / cm^3	$V_{\text{FA 6}}$ / cm^3	T_i / °C	T_{max} / °C	ΔT / °C
1	40.0	10.0	32.5	37.5	5.0
2	34.0	16.0	32.5	40.2	7.7
3	28.0	22.0	32.5	43.2	10.7
4	22.0	28.0	32.5	44.5	12.0
5	16.0	34.0	32.5	41.2	8.7
6	10.0	40.0	32.5	38.0	5.6

Correct headings and units, correct volumes of **FA 6** [1]

Recorded to correct precision: measuring cylinder (1 d.p.); temp (1 d.p.) [1]

Correctly calculates T_{max} and ΔT [1]

(b) **(i)**



Linear scale chosen to cover at least ½ of graph (no odd scale) + correct axes label (header/units) [1]

Plots all points within ½ small sq [1]

Draw two lines of best-fit to <u>intersect clearly</u> [1]

		(ii)	volume of **FA 5** = ...23.5 cm^3 Reads correctly value of **FA 5** from intercept to nearest ½ sq [1]
	(c)	**(i)**	n_{HCl} in **FA 5** = $\frac{23.5 \text{ x } 2.00}{1000}$ = 0.0470 mol
		(ii)	[**FA 6**] = $\frac{0.0470}{\frac{50.0-23.5}{1000}} = 1.77 \text{ mol dm}^{-3}$
	(d)	1. Increase in total volume does not affect accuracy as there is no change in temperature rise, T, as volume increased proportionately with a corresponding increase in the amt of water / heat produced. 2. Accuracy increased with more experiments carried out as more data points helps to draw more accurate best fit lines / get a more accurate intercept.	

3

Table 3.1

		test	observations		
			FA 7	**FA 8**	**FA 9**
(a)	**(i)**	Add 2 or 3 drops of aqueous iodine.	blue-black / black / dark blue	no observable change / yellow / brown	no observable change / yellow / brown
	(ii)	Add 2 or 3 drops of acidified potassium manganate(VII) and **allow to stand for two minutes.**	no observable change / remains purple / pink	purple / pink / $KMnO_4$ / MnO_4^- decolourise	no observable change / remains purple / pink
	(iii)	Add a 3 cm depth of Sandell's solution and place the tube in the hot water bath for two minutes.	no observable change / solution remains blue	blue solution turns brick red / orange / red brown / orangebrown / yellowbrown / brown ppt	no observable change / solution remains blue

(iv) Starch in **FA 7** reacted with iodine to form a blue-black iodine-starch complex

Aldehyde in **FA 8** is oxidised by $KMnO_4$ / Sandell's solution to carboxylic acid.

(v) Add 1 cm^3 of Tollens' reagent to separate test tubes containing **FA 7**, **FA 8** and **FA 9** and warm in a water bath.

Silver mirror / grey / black ppt appears for solution containing aldehyde (**FA 8)**.

Table 3.2

		test	observations	
			FA 10	**FA 11**
(b)	**(i)**	Add a few drops of aqueous silver nitrate.	No observable change / no ppt / solution remains blue / solution turns more pale (blue)	brown ppt (dissolve in excess)
	(ii)	Add a few drops of aqueous barium nitrate or aqueous barium chloride, then	White ppt	No ppt / no observable change
		add dilute nitric acid.	Ppt insoluble in excess acid / no observable change / white ppt remains	No observable change
	(iii)	Add a few drops of aqueous iodine.	white / cream ppt in yellow / brown solution	Brown solution decolourised
	(iv)	Add a 1 cm depth of aqueous iron(II) sulfate.	No observable change / no ppt / solution remains blue / solution turns more pale (blue)	Green ppt formed (turns brown)
	(v)	Add a 1 cm depth of **FA 11**.	Light blue ppt formed	

		(vi)	Identify the ions in **FA 10** and **FA 11**.
			FA 10 cation Cu^{2+} anion SO_4^{2-} **FA 11** anion OH^-
		(vii)	Equation for **(b)(iii)** : $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI (s) + I_2 (aq)$ Note: $I_2 + I^- \Leftrightarrow I_3^-$ Equation for **(b)(v)** : $Cu^{2+} (aq) + 2OH^- (aq) \rightarrow Cu(OH)_2 (s)$

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CHEMISTRY
9729/01

Paper 1 Multiple Choice

Thursday 19 September 2019
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, subject class 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 booklet.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

Instructions on how to fill in the Optical Mark Sheet
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.

Example:

Student	**Examples of Registration No.**	**Shade:**
	1805648	85648

This document consists of **12** printed pages.

[Turn over

1 When a sports medal with a total surface area of 150 cm^2 was evenly coated with silver by electrolysis, its mass increased by 0.216 g.

How many atoms of silver were deposited per cm^2 on the surface of the medal?

A 8.0×10^{18} **B** 1.8×10^{19} **C** 1.2×10^{21} **D** 4.1×10^{22}

2 Which species is deflected to the greatest extent in an electric field?

A e^- **B** H^+ **C** He^{2+} **D** F^-

3 In an experiment, 50.0 cm^3 of a 0.10 mol dm^{-3} solution of **M**$^{3+}$ salt reacted exactly with 25.0 cm^3 of 0.10 mol dm^{-3} aqueous sodium sulfite.

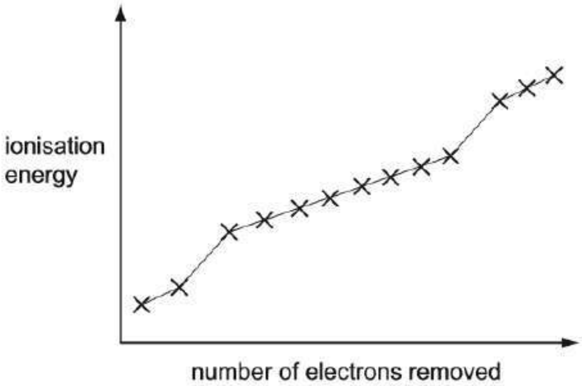
The half-equation for oxidation of sulfite ion is shown below.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

What is the final oxidation number of **M**?

A +1 **B** +2 **C** +4 **D** +5

4 The graph shows the first thirteen successive ionisation energies for element **E**.



What can be deduced about element **E** from the graph?

A It is in Period 3 of the Periodic Table.

B It is a d−block element.

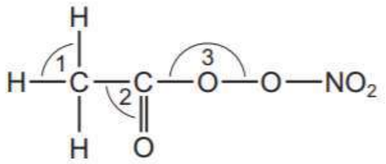
C It is in Group 2 of the Periodic Table.

D It is aluminium.

5 What is the order of increasing radii for the three species shown?

	smallest	⟶	largest
A	Ar	Ca^{2+}	K^+
B	Ar	K^+	Ca^{2+}
C	Ca^{2+}	K^+	Ar
D	K^+	Ar	Ca^{2+}

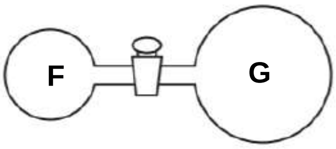
6 Organic nitrates in photochemical smog can cause breathing difficulties. The diagram shows an example of an organic nitrate molecule.



What is the order of increasing bond angles?

A 1 < 2 < 3 **B** 2 < 1 < 3 **C** 3 < 1 < 2 **D** 3 < 2 < 1

7 Two glass vessels **F** and **G** are connected by a closed valve.



F contains helium at 20 °C at a pressure of 1×10^5 Pa. **G** has been evacuated, and has three times the volume of **F**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to 100 °C.

What is the final pressure in the system?

A 3.18×10^4 Pa **B** 4.24×10^4 Pa **C** 1.25×10^5 Pa **D** 5.09×10^5 Pa

8 Carbon monoxide burns readily in oxygen to form carbon dioxide.

What can be deduced from this information?

1 The +4 oxidation state of carbon is more stable than the +2 state.

2 The standard enthalpy change of formation of carbon dioxide is less negative than that of carbon monoxide.

3 The value of the equilibrium constant for the following reaction is likely to be high.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

A 1, 2 and 3 **B** 2 and 3 **C** 1 and 3 **D** 1 only

9 Two reactions and their enthalpy changes are shown.

$$2C(s) + 2H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H^\ominus = +52.2 \text{ kJ mol}^{-1}$$

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H^\ominus = -175.8 \text{ kJ mol}^{-1}$$

These data can be used to calculate the enthalpy change for the reaction shown.

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g) \qquad \Delta H^\ominus_1$$

What is the value of $\Delta H^\ominus_1$?

A -228.0 kJ mol^{-1} **B** -123.6 kJ mol^{-1} **C** $+123.6$ kJ mol^{-1} **D** $+228.0$ kJ mol^{-1}

10 Butanedioate ions can be dehydrogenated to form trans-butenedioate ions. The enzyme fumarase speeds up this reaction.

How does fumarase speed up this reaction?

A Fumarase increases the kinetic energy of the reactants.

B Fumarase increases the frequency of collisions between reactants.

C Fumarase lowers the activation energy of the dehydrogenation reaction.

D Fumarase is specific for this dehydrogenation reaction.

11 The reaction between ethanedioate ions and acidified manganate(VII) ions as shown below takes place very slowly in the cold but can be accelerated with heat or with addition of Mn^{2+} catalyst.

$$2MnO_4^{-} + 5C_2O_4^{2-} + 10H^{+} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

The reaction rate for the reaction can be measured by noting the time elapsed for the purple colour of the manganate(VII) ions to disappear.

The following results were obtained.

Expt	Volume / cm^3				Time / s
	$C_2O_4^{2-}$(aq)	MnO_4^{-}(aq)	Mn^{2+}(aq)	water	
1	20	30	5	25	30
2	20	30	10	20	15
3	20	15	10	35	15
4	20	20	20	20	10

Which conclusions can be drawn about the reaction?

1 The reaction is first order with respect to Mn^{2+} (aq).

2 MnO_4^{-} is involved in the rate-determining step.

3 The unit of rate constant is $mol^{-1}\,dm^{3}\,s^{-1}$.

A 1 only **B** 1 and 2 **C** 2 and 3 only **D** 1, 2 and 3

12 In which reactions does NH_3 behaves as a Lewis base?

1 $2NH_3 \longrightarrow NH_2^{-} + NH_4^{+}$

2 $HSO_4^{-} + NH_3 \longrightarrow SO_4^{2-} + NH_4^{+}$

3 $Ag^{+} + 2NH_3 \longrightarrow [Ag(NH_3)_2]^{+}$

A 1 only **B** 1 and 2 **C** 2 and 3 **D** 1, 2 and 3

13 The numerical values of the solubility products of three metal sulfides are tabulated below.

compound	numerical value of solubility product
CuS	8.5×10^{-45}
Ag_2S	1.6×10^{-49}
Bi_2S_3	1.1×10^{-73}

What is the order of increasing molar solubility of the three metal sulfides in water?

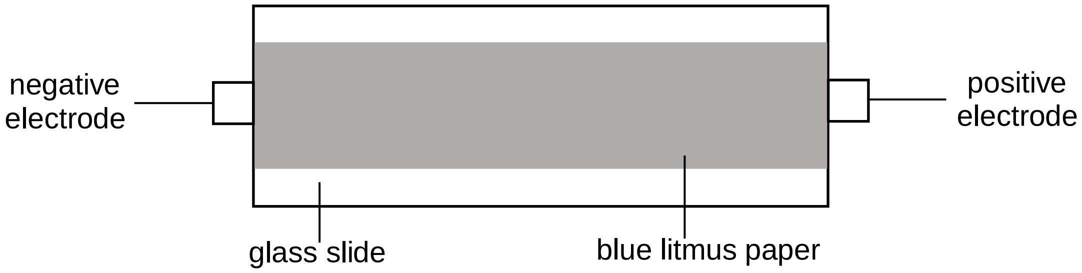
A $Bi_2S_3 < Ag_2S < CuS$

B $CuS < Ag_2S < Bi_2S_3$

C $Ag_2S < Bi_2S_3 < CuS$

D $CuS < Bi_2S_3 < Ag_2S$

14 A piece of blue litmus paper was soaked in concentrated NaC*l* solution and supported on a glass slides. The paper was connected to a direct current supply as shown in the diagram below.



What are the observations near the negative electrode and the positive electrode after the current had flown for some time?

	negative electrode	**positive electrode**
A	blue	red
B	red	blue
C	blue	bleached
D	bleached	blue

15 Which statement does **not** describe the chemical properties of Period 3 compounds?

A SiO_2 is formed from the hydrolysis of $SiCl_4$.

B Al_2O_3 is soluble in both acid and base.

C Equimolar of Na_2O and SO_3 can be mixed in water to give a pH neutral solution.

D The acidity of Period 3 chlorides in water decreases from $NaCl$ to PCl_5.

16 A 5.00 g sample of an anhydrous Group 2 metal nitrate loses 3.29 g in mass when heated strongly. What is the identity of the metal?

A magnesium **B** calcium **C** strontium **D** barium

17 Transition lenses are made of photochromic glass.

Photochromic glass darkens when exposed to bright light

Reaction 1 $Ag^+ + Cl^- \rightleftharpoons Ag + Cl$

Photochromic glass becomes more transparent again when the light is less bright.

Reaction 2 $Cu^+ + Cl \longrightarrow Cu^{2+} + Cl^-$

Reaction 3 $Cu^{2+} + Ag \longrightarrow Cu^+ + Ag^+$

Which statement about these reactions is correct?

A Ag^+ ion are oxidised.

B Cu^+ ion act as catalyst.

C Cu^+ ion act as an oxidising agent.

D The depth of colour of the photochromic glass is related to the concentration of Cl.

18 Which environmental problem is **not** made worse by the release of oxides of nitrogen from car engines?

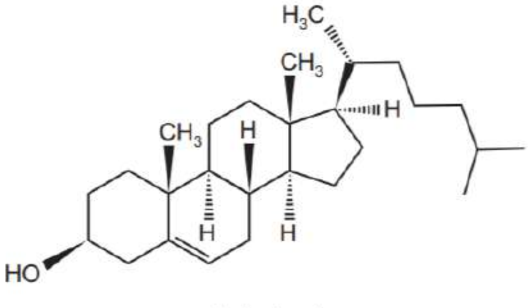
A acidification of lakes

B corrosion of buildings

C photochemical smog

D soil pollution

19 The diagram shows the structure of the naturally-occurring molecule cholesterol.



cholesterol

Which statements about cholesterol are correct?

1 The molecule contains a secondary alcohol group.

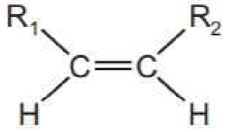
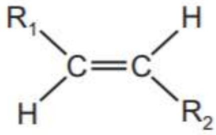
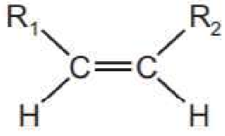
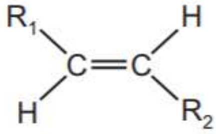
2 The molecule have two π bonds.

3 All carbon atoms in the four rings lie in the same plane.

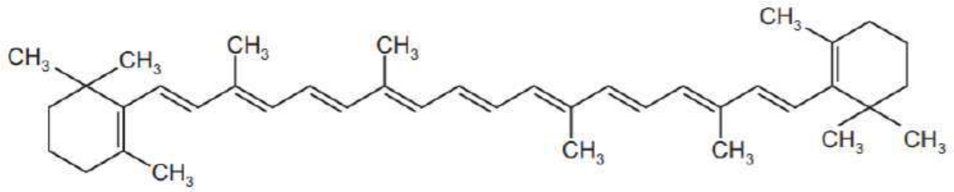
A 1, 2 and 3 **B** 1 and 2 **C** 1 and 3 **D** 1 only

20 The presence of 11−cis retinal, $C_{20}H_{28}O$, in cells in the eye is important for vision. The structure of retinal includes an aldehyde group, a cyclohexene ring and a long aliphatic side chain, in which a carbon-carbon double bond exists between carbons numbered 11 and 12.

Which pair of statements about 11−cis retinal could be correct?

	total number of C=C double bonds	arrangement around adjacent carbons C11 and C12
A	5	
B	5	
C	6	
D	6	

21 β-carotene is responsible for the orange colour of carrots.



β-carotene

β-carotene is oxidised by hot, concentrated, acidified $KMnO_4$. When an individual molecule of β-carotene is oxidised in this way, many product molecules are formed.

How many of these product molecules contain ketone functional group?

A 4 **B** 6 **C** 8 **D** 11

22 Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

reaction 1 $CH_3CHBrCH_3 + NaCN \longrightarrow CH_3CH(CN)CH_3 + NaBr$

reaction 2 $CH_3CHBrCH_3 + NaI \longrightarrow CH_3CHICH_3 + NaBr$

What factor will explain this result?

A The C−I bond is a stronger bond than the C−Br bond.

B The C−N bond is a stronger bond than the C−I bond.

C The cyanide ion is a stronger nucleophile than the iodide ion.

D The cyanide ion is a weaker nucleophile than the iodide ion.

23 Butanedioic acid occurs in amber, algae, lichens, sugar cane and beets. It may be synthesised in two steps from 1,2−dibromoethane.

$$BrCH_2CH_2Br \xrightarrow[\text{step 1}]{} \mathbf{K} \xrightarrow[\text{step 2}]{} HO_2CCH_2CH_2CO_2H$$

Which reagents could be used for this synthesis?

	step **1**	step **2**
A	HCN(g)	HC*l*(aq)
B	HCO_2Na(aq)	HC*l*(aq)
C	ethanolic KCN	H_2SO_4(aq)
D	NaOH(aq)	acidified $K_2Cr_2O_7$

24 Many, but not all, organic reactions need to be heated before reaction occurs.

Which reaction occurs at a good rate at room temperature (20 °C)?

A $CH_3OH + PCl_5 \longrightarrow CH_3Cl + POCl_3 + HCl$

B $CH_3CH_2Br + KCN \longrightarrow CH_3CH_2CN + KBr$

C $CH_3CH_2OH \longrightarrow C_2H_4 + H_2O$

D $CH_3CH_2CN + 2H_2O \longrightarrow CH_3CH_2CO_2H + NH_3$

25 2.76 g of ethanol were mixed with an excess of aqueous acidified potassium manganate(VII). The reaction mixture was then boiled under reflux for one hour. The organic product was then collected by distillation. The yield of product was 75.0%.

What mass of product was collected?

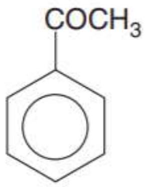
A 1.98 g **B** 2.07 g **C** 2.70 g **D** 4.80 g

26 A compound **N** has all of the following properties:

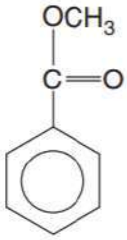
- it is neutral;
- it gives an orange precipitate with 2,4−dinitrophenylhydrazine;
- it evolves white fumes of HCl when treated with PCl_5 in the cold.

Which molecule is compound **N**?

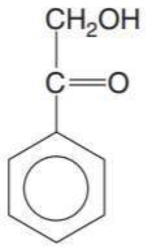
A



B

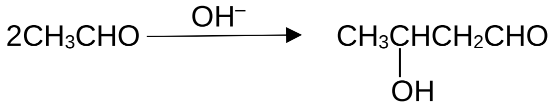


C



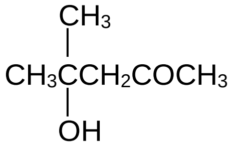
D

27 In the presence of dilute alkali, some aldehydes and ketones undergo the ‘aldol reaction’ where they dimerise to form a hydroxycarbonyl compound (an aldol). For example, ethanal reacts as shown to form 3–hydroxybutanal.



$$2CH_3CHO \xrightarrow{OH^-} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CHO$$

Which carbonyl compound will undergo the aldol reaction to produce the aldol shown below?



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}CH_2COCH_3$$

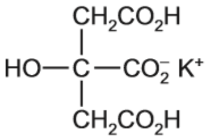
A CH_3COCH_3

B CH_3CH_2CHO

C $(CH_3)_2CHCHO$

D $CH_3CH_2COCH_3$

28 Monopotassium citrate is used as an emulsifying agent in powdered milk. It may be represented by the formula shown.



$$HO—\overset{\displaystyle CH_2CO_2H}{\overset{|}{\underset{\displaystyle CH_2CO_2H}{\underset{|}{C}}}}—CO_2^-\ K^+$$

Which statements about monopotassium citrate are correct?

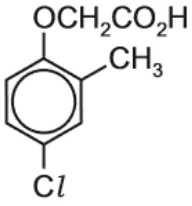
1 It can exist as a pair of enantiomers.

2 It can act as a dibasic acid.

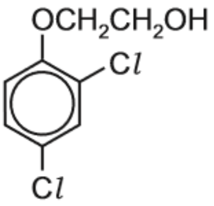
3 It can form esters with both carboxylic acids and alcohols.

A 1, 2 and 3 **B** 1 and 2 **C** 2 and 3 **D** 1 only

29 **L** and **M** are two widely-used selective weed killers.



L



M

Which reagent will distinguish **L** from **M**?

A acidified $AgNO_3$(aq)

B acidified $KMnO_4$(aq)

C Na(s)

D Na_2CO_3(aq)

30 Which pair of compounds is formed when the ester $CH_3OCOC_2H_5$ is boiled with aqueous sodium hydroxide?

A CH_3OH + $C_2H_5CO_2H$

B CH_3ONa + $C_2H_5CO_2Na$

C CH_3OH + $C_2H_5CO_2Na$

D CH_3CO_2Na + C_2H_5OH

NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY **9729/02**
Paper 2 Structured Questions
Monday 16 September 2019
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THE 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 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.

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

For Examiner's Use	
1	/17
2	/9
3	/17
4	/18
5	/14
P2 Total	/75

	Marks	**Weightings**
Paper 1	/30	15 %
Paper 2	/75	30 %
Paper 3	/80	35 %
Paper 4	/55	20 %

Overall Percentage	
Grade	

This document consists of **20** printed pages.

1 **(a)** Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

………………………………………………………………………………………………

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………………………………………………………………………………………………[3]

(b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

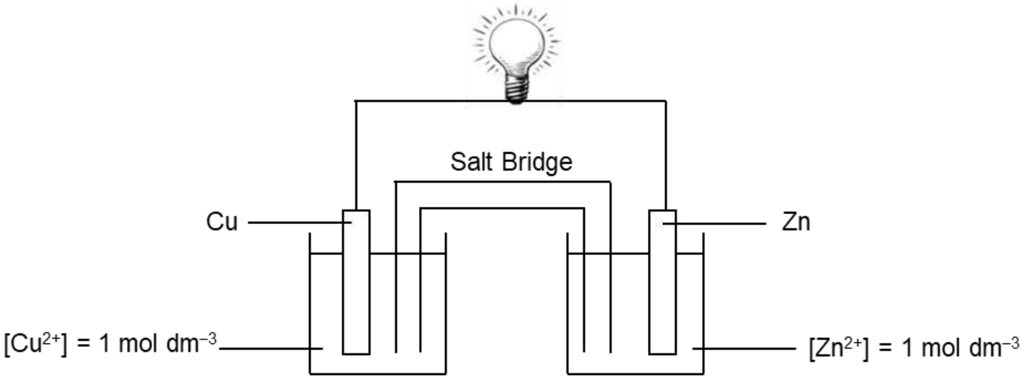

Fig 1.1

(i) Indicate the direction of electron flow **on Fig 1.1**. [1]

(ii) Write the equation for the reaction taking place and calculate $\Delta G^{\ominus}$ for the reaction.

………………………………………………………………………………………

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(II) using a smaller copper electrode

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

…………………………………………………………………………………………… [2]

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm^{-3} solutions of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ using a current of 5.0 A?

[2]

(v) The Nernst equation is an equation that relates the cell potential, E_{cell}, of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{cell}$. It can be simplified and written as

Nernst equation : $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF}\ln Q$

where *R* is the ideal gas constant — *T* is temperature in Kelvin

z is the number of electron transferred — *F* is Faraday's constant

Q is $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ for the *Daniell* cell

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 °C.

[2]

(vi) In another set-up conducted at 25 °C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm^{-3} and 0.002 mol dm^{-3} respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

[2]

[Total: 17]

Question 2 starts on the next page

2 Saccharin is an artificial sweeting agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, $ClSO_3H$. This is also known as aromatic sulfonation process.

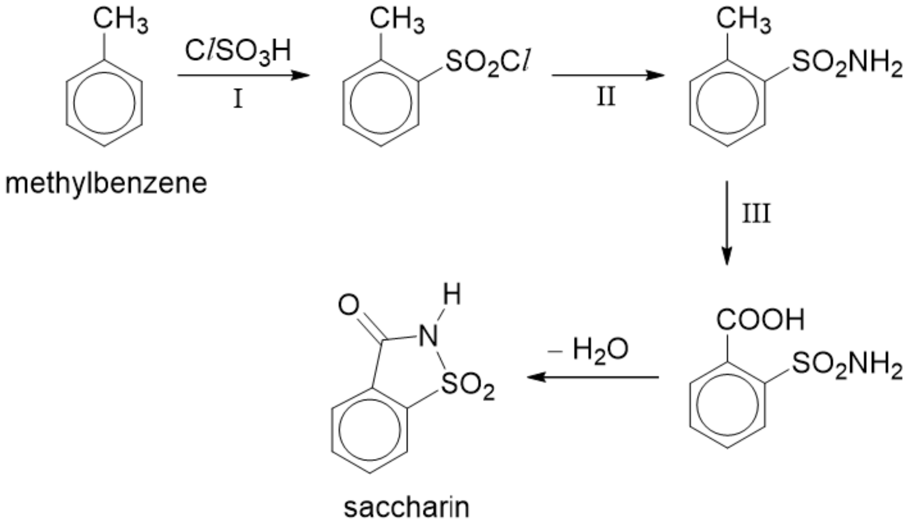

Fig 2.1

(a) Draw a dot-and-cross diagram of chlorosulfonic acid, $ClSO_3H$ and hence state the bond angle for $Cl{-}S{-}O$.

$Cl{-}S{-}O$ bond angle : ……………. [2]

(b) **(i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

Electrophile : ………………….. [1]

(ii) Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

(iii) State the types of reaction that occur during reactions II and III.

reaction II : ……………………………………

reaction III : …………………………………... [2]

(iv) Suggest reagents and conditions for reactions II and III.

reaction II : ………………………………………………..

reaction III : …………………………………................... [2]

[Total : 9]

3 Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

(a) One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4. Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3, express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp}, for NH_4ClO_4.

[2]

(b) A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3. This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

(i) Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation : ……………………………………………………………………………

Overall equation : ……………………………………………………………………………

[2]

(ii) Describe how you would recognise the endpoint of the titration.

……………………………………………………………………………………………. [1]

(iii) The 25.0 cm^3 sample of solution **X** required 30.00 cm^3 of potassium manganate(VII) for complete reaction.

Calculate the concentration of perchlorate ions in the river water.

[3]

(iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for **(b)(iii)**, you may assume the concentration of perchlorate ions in the river water is 2.5×10^{-6} mol dm^{-3}.

[1]

(v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	5×10^{-6} mol dm^{-3}	1×10^{-4} mol dm^{-3}	1.5×10^{-4} mol dm^{-3}
pike	5×10^{-7} mol dm^{-3}	2×10^{-6} mol dm^{-3}	1×10^{-5} mol dm^{-3}
catfish	1×10^{-7} mol dm^{-3}	1×10^{-6} mol dm^{-3}	5×10^{-5} mol dm^{-3}

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write “nil” if there is no effect.

types of fish	health effect(s)
stickleback	
pike	
catfish	

[2]

(c) Perchlorate ions can be metabolized in the tissue of stickleback fish.
The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

The following results was obtained.

Time/ hour	$[ClO_4^-]$ / $\times 10^{-9}$ mol dm^{-3}
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

(i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.

[3]

(ii) Using your graph in **c(i)**, determine the rate constant, *k*. Include units in your answer.

[2]

(iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

[1]

[Total : 17]

4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^-. The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

$CO_2(g) \rightleftharpoons CO_2(aq)$ $K_{CO2} = 3.44 \times 10^{-2}$

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ $K_{H2CO3} = 2.00 \times 10^{-3}$

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$ K_{a1}

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$ K_{a2}

Fig 4.1 shows the molar fraction of H_2CO_3, HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

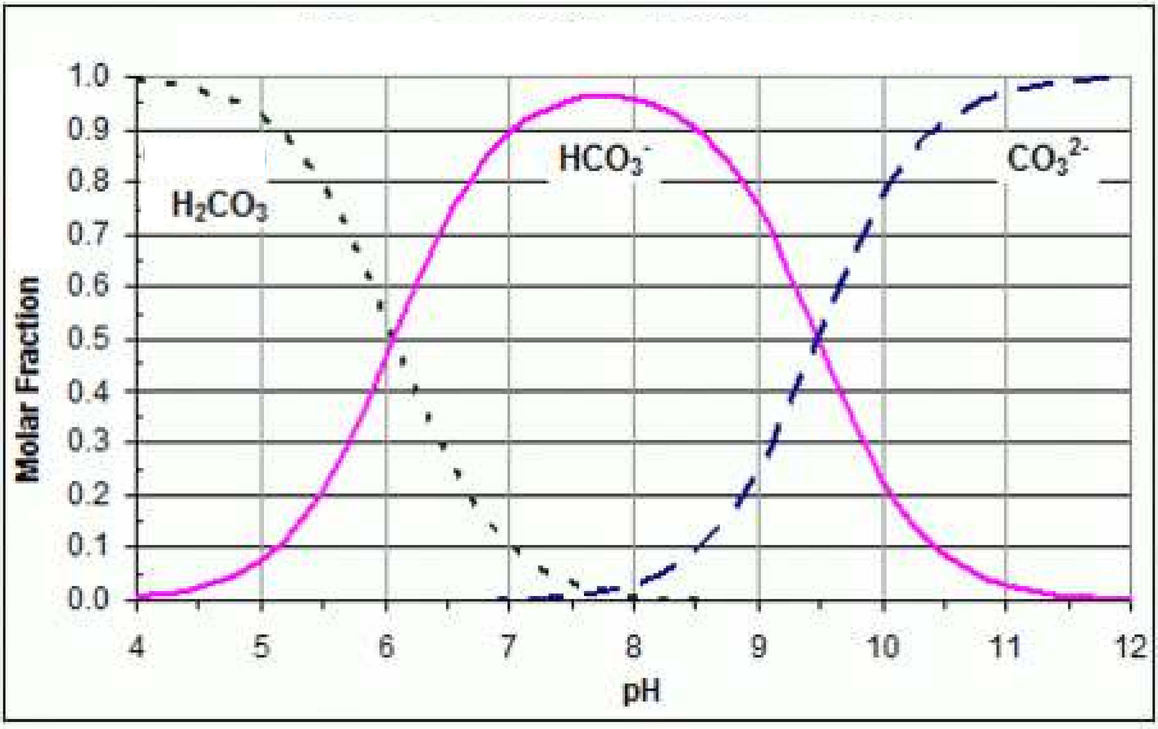

Fig 4.1

For Examiner's Use

(a) **(i)** With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

pH of maximum buffering capacity : ……… and ……… [1]

(ii) Hence deduce the values for K_{a1} and K_{a2}.

[2]

(iii) Explain why the calculated value of K_{a1} is larger than K_{a2}?

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………………………………………………………………………………………………….[1]

(iv) Aquatic organisms survive within specific pH range.
Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

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………………………………………………………………………………………………….[3]

(v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

[3]

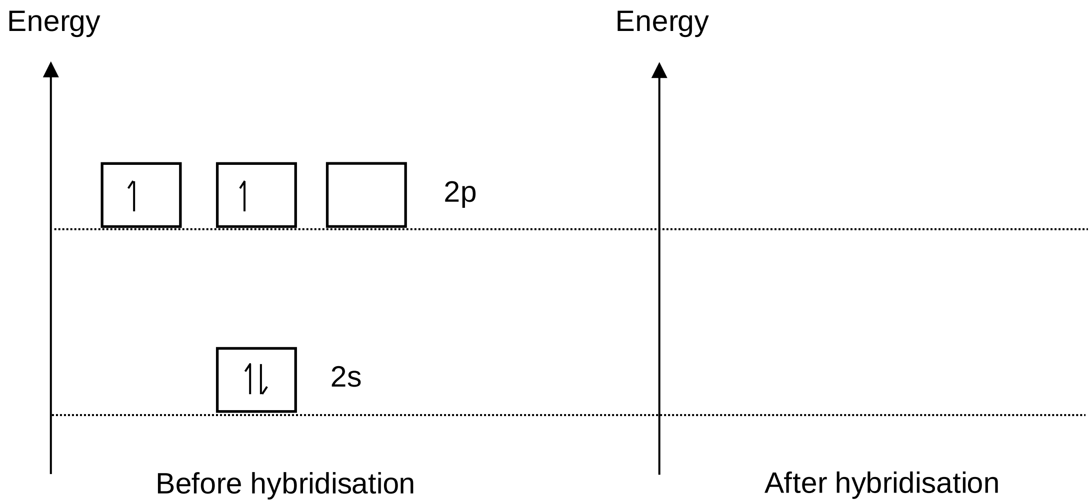
(vi) The concentration of dissolved O_2 is found to be 2.5×10^{-4} mol dm^{-3}.
With the aid of a diagram, show how oxygen can dissolve in water.

[1]

(b) **(i)** Draw the labelled diagram to show the orbitals that form the C=O bond in CO_2, and state the type of hybridisation involved.

[2]

(ii) Indicate the energy level of the orbitals involved in the σ(sigma) and π(pi) bonding of CO_2 on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.



[2]

(c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid $CaCO_3$ to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in Fig 4.2.

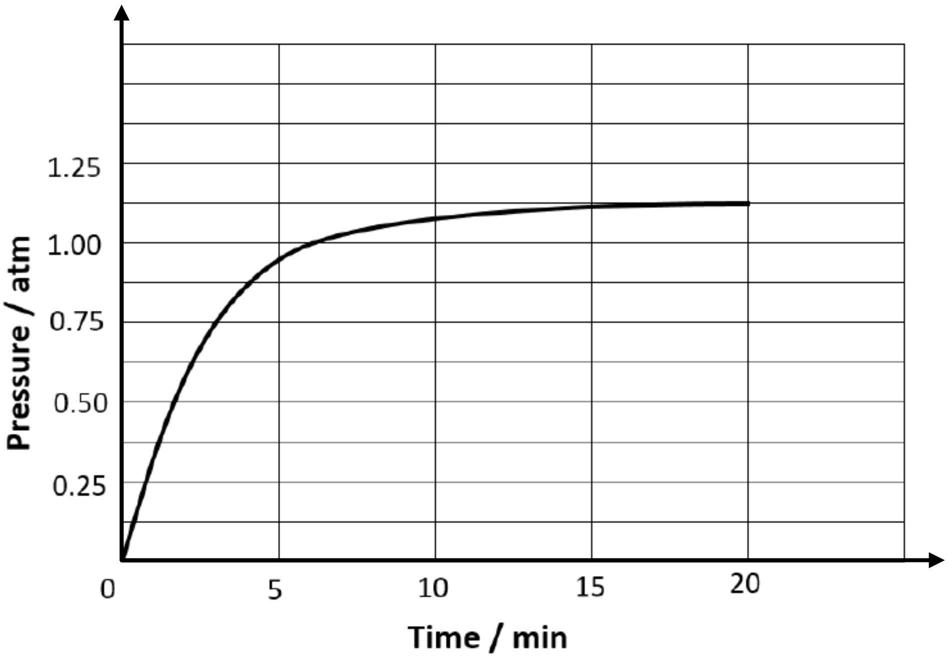


Fig 4.2

(i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $CaCO_3(s)$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]

(ii) After 20 minutes, some $CO_2(g)$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

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…………………………………………………………………………………………….[2]

[Total : 18]

5 (a) Alkene can undergo oxidation with ozone, O_3, to give carbonyl compounds. This reaction is known as *ozonolysis*.

Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O, and compound **L**, C_3H_6O.

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2.

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

(i) Suggest the structures of compounds **J**, **K** and **L**. [3]

Compound **J**	Compound **K**	Compound **L**

(ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using [O] to represent the oxidising agent.

[1]

(iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.

[1]

(b) Cycloalkenes can undergoes *syn* and *anti* addition as shown in Fig 5.1.

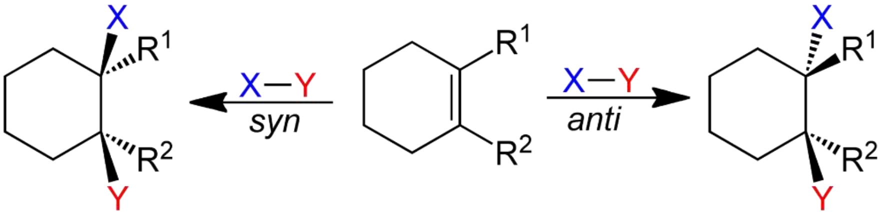


Fig 5.1

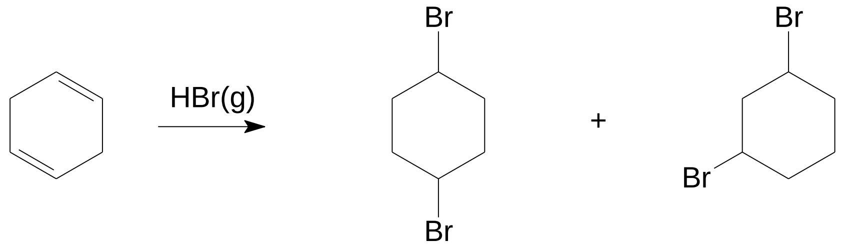
An example of *syn* addition is the oxidation of alkene to diol.
An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2−dimethylcyclohexene with the following reagents.

cold alkaline $KMnO_4$	
Br_2 in CCl_4	

[2]

(c) Fig 5.2 shows the reaction of cyclohexa−1,4−diene with HBr(g).



Cyclohexa−1,4,−diene 1,4−dibromocyclohexane 1,3−dibromocyclohexane

Fig 5.2

(i) 1,4−dibromocyclohexane exhibits cis-trans isomerism.

Draw the structures of the stereoisomers.

cis isomer	trans isomer

[2]

(ii) 1,3−dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.

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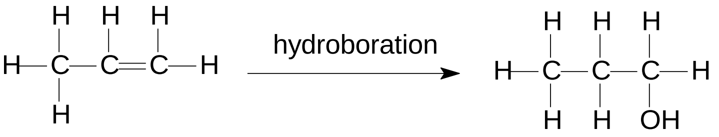
…………………………………………………………………………………………[2]

(d) Hydroboration can be used to convert an alkene to an alcohol.



Hydroboration involves a two-step reaction as shown in Fig 5.3:

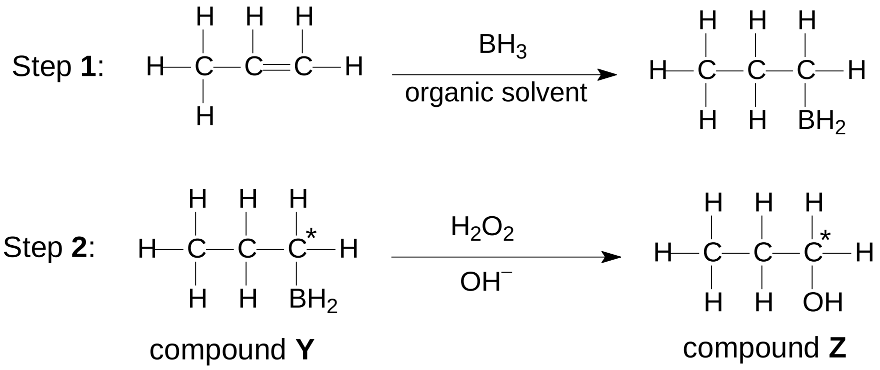


Fig 5.3

The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

(i) Step **1** is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step **1**.

[1]

(ii) State the oxidation number of the carbon atoms labelled * in compound **Y** and **Z**, and hence deduce the role of H_2O_2 in step **2**.

Oxidation number of C* in **Y** is ....

Oxidation number of C* in **Z** is ....

Role of H_2O_2: ……………………………………………..

[2]

[Total : 14]

NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY **9729/03**

Paper 3 Free Response

Wednesday 18 September 2019

2 hours

Candidates answer on separate paper.
Additional Materials: Answer Paper
Data Booklet

READ THE 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 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.

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 from this section.

1 Potassium is an element found in Period 4 of the Periodic Table.

(a) **(i)** Write an equation for the second ionisation energy of potassium. [1]

(ii) Fig 1.1 shows the second ionisation energy for the consecutive elements from Period 3 and Period 4.

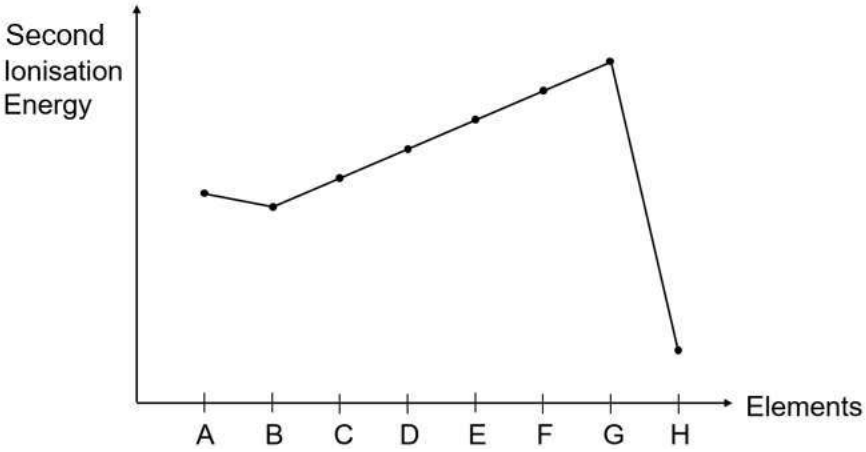


Fig 1.1

Suggest which of the above elements, **A** to **H**, is potassium. [2]

(b) When 0.400 g of potassium dichromate(VI), $K_2Cr_2O_7$, was heated using a strong flame, a yellowish green solid mixture was obtained and a gas was evolved. The gas collected ignited a glowing splint. Upon adding water to the yellowish green solid, part of the solid dissolved to give a yellow solution of K_2CrO_4, leaving a green solid.

(i) State the identity of the gas. [1]

(ii) The green solid that remained was collected and dried. It weighed 0.052 g and was found to be 68.4% chromium by mass and contains only chromium and oxygen.

Determine the chemical formula of the green solid. [2]

(iii) Using your answers to **b(i)** and **b(ii)**, write the equation for the decomposition of potassium dichromate(VI). [1]

(c) State **two** physical properties of chromium that differs from calcium.
Explain the reasons for those differences. [2]

(d) Vanadate(V) ion, VO_3^-, changes into pale yellow oxovanadium(V) ions, VO_2^+, when acid is added. Upon addition of excess zinc, the pale yellow solution changes to blue, to green and finally to violet.

(i) With the aid of an equation, explain the type of reaction that occurs when vanadate(V) ion changes into oxovanadium(V) ions. [2]

(ii) Explain why vanadium is able to exhibit variable oxidation states. [1]

(iii) With the aid of the *Data Booklet*, deduce the final oxidation state of vanadium in the violet solution. [3]

Solid vanadium(V) oxide, V_2O_5, is used as a catalyst for reaction 1.

reaction 1: $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$

(iv) State the type of catalysis and outline the mode of action when V_2O_5 is used for reaction 1. [3]

(v) NO_2 can also act as a catalyst for reaction 1.

Write two equations to show how NO_2 acts as a catalyst in reaction 1. [2]

[Total : 20]

2 Lithium oxide, Li_2O, is used in traditional ceramic glazing to create a blue hue with copper on ceramics.

(a) Using the data below and any appropriate data from the *Data Booklet*, construct a labelled energy level diagram to calculate the standard enthalpy change of formation of $Li_2O(s)$.

	/ kJ mol^{-1}
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
lattice energy of lithium oxide	–2863
standard enthalpy change of atomisation of lithium	+159

[5]

(b) Lithium oxide is produced during the thermal decomposition of lithium peroxide, Li_2O_2, at 450 °C.

$$Li_2O_2(l) \longrightarrow Li_2O(s) + \frac{1}{2}O_2(g)$$

(i) Given that the standard enthalpy change of formation of $Li_2O_2(l)$ is –606 kJ mol^{-1} and using your answer in **(a)**, calculate the enthalpy change for the thermal decomposition of Li_2O_2. [1]

(ii) Explain why the thermal decomposition of Li_2O_2 is feasible. [2]

(c) Table 2.1 gives the melting points of two lithium ionic compounds.

compound	melting point / °C
Li_2O	1400
Li_2O_2	195

Table 2.1

Explain the difference in the melting points. [2]

(d) Similar to lithium peroxide, Li_2O_2, lithium nitrate, $LiNO_3(s)$, undergoes thermal decomposition to produce oxygen and a brown gas.

(i) Write a balance equation, with state symbols, for the thermal decomposition of lithium nitrate. [2]

(ii) Among the Group 1 metal nitrates, only lithium nitrate undergoes thermal decomposition.

Explain why lithium nitrate can undergo thermal decomposition. [2]

(e) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a chelating agent that is widely used to remove transition metal ions such as copper(II) ions from aqueous solutions.

(i) Suggest a synthesis of ethylenediamine tetraacetate, $[EDTA]^{4-}$, starting from methanal and 1,2−diaminoethane ($NH_2CH_2CH_2NH_2$), according to the scheme in Fig. 2.1. Deduce the structure of compound **A**. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

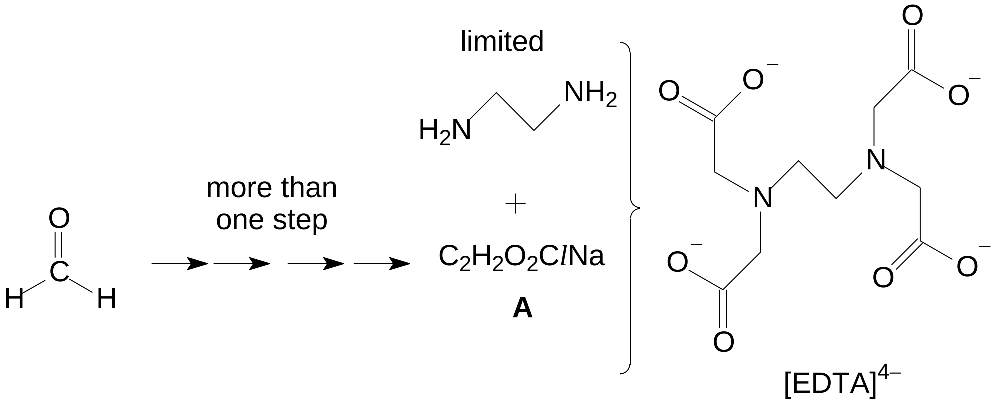


Fig 2.1

[5]

(ii) When aqueous ammonia is added to a solution of $CuSO_4$, a blue precipitate is formed which dissolves in excess aqueous ammonia to give a deep blue solution. On addition of $Na_4(EDTA)$ solid to the mixture, the colour of the solution turns light blue.

Suggest explanations for the above observations, writing equations as appropriate.

[3]

[Total : 22]

3 **(a)** Phenol is a white crystalline solid that is volatile. It is mildly acidic and requires careful handling as it can cause chemical burns.

Table 3.1 shows the physical properties for phenol and its derivatives.

compound	melting point / °C	K_a / mol dm^{-3}
phenol	41	1.12×10^{-10}
2−nitrophenol	46	5.89×10^{-8}
4−nitrophenol	114	7.08×10^{-8}

Table 3.1

(i) Explain the difference in melting points between 2−nitrophenol and 4−nitrophenol. [2]

(ii) Explain the difference in the acidities of phenol and 2−nitrophenol. [2]

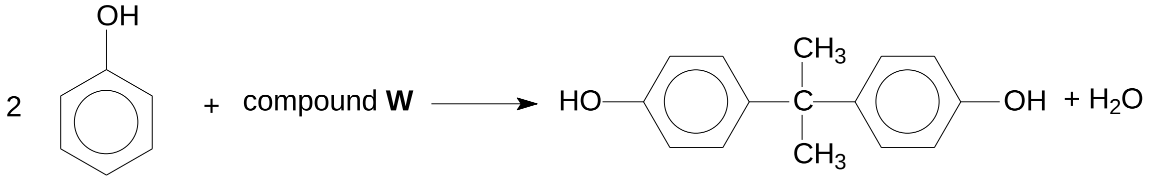
(iii) Suggest how 2,6−dibromo−4−nitrophenol can be synthesised from phenol in a 2−step synthesis. In your synthesis, you should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. [3]

(b) When aqueous neutral $FeCl_3$ is added to a solution containing phenol, a violet solution containing the complex ion $[Fe(C_6H_5O)_6]^{3-}$ is formed.

(i) Draw the structure of the complex ion. [1]

(ii) The violet complex ion $[Fe(C_6H_5O)_6]^{3-}$ is not observed in **both** acidic and alkaline solutions. Suggest explanations for the above observation. [2]

(c) Phenol can react with compound **W** under suitable conditions to give bisphenol-A (BPA).



BPA

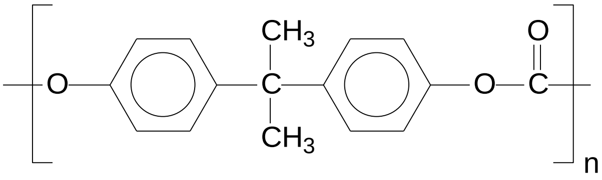
The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

Infra-red absorptions can be used to identity functional groups in organic compounds. For example, phenol shows absorption at 3200−3600 cm^{-1} due to the O−H bond.

The analysis of compound **W** shows absorptions at 1670−1740 cm^{-1}.

Identify the bond present in compound **W** and suggest its structure. [2]

(d) BPA can react with another monomer **X** to produce polycarbonates. Polycarbonates are commonly used in the manufacturing of water bottles.



Polycarbonates

(i) Identify the new functional group formed in the polycarbonates. [1]

(ii) Suggest the structure of monomer **X**. [1]

(iii) Research has shown that BPA can leach into beverages from the polycarbonate water bottles under certain conditions. Exposure to BPA is a concern because of possible health effects of BPA on the brain.

Discuss whether it is safe to consume cold lemon juice stored in a polycarbonate water bottle. [1]

(e) BPA can react with epoxides to form epoxy resins. Fig 3.1 shows the simplified equations for the reaction.

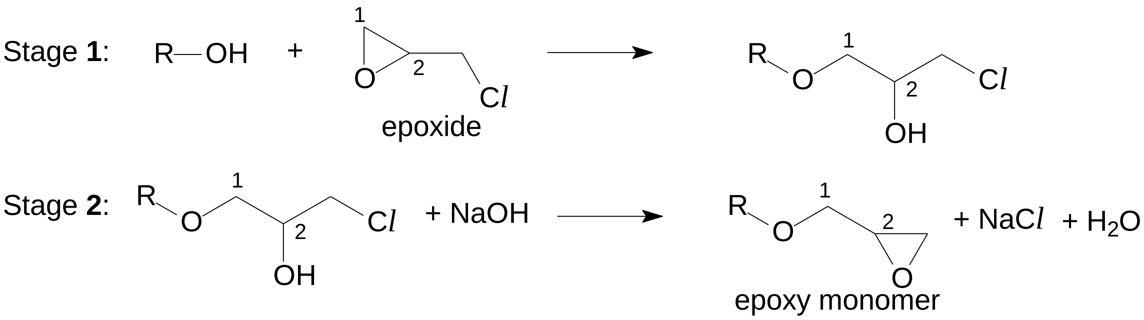


Fig 3.1

(i) For stage **1**, the phenol group of BPA acts as the nucleophile. Suggest why the nucleophile attacks C^1 instead of C^2. [1]

(ii) For stage **2**, state the type of reaction and the role of NaOH in the reaction. [2]

[Total : 18]

Section B

Answer **one** question from this section.

4 **(a)** Diphenylmethanone can be synthesized from methylbenzene in three steps as shown in Fig 4.1.

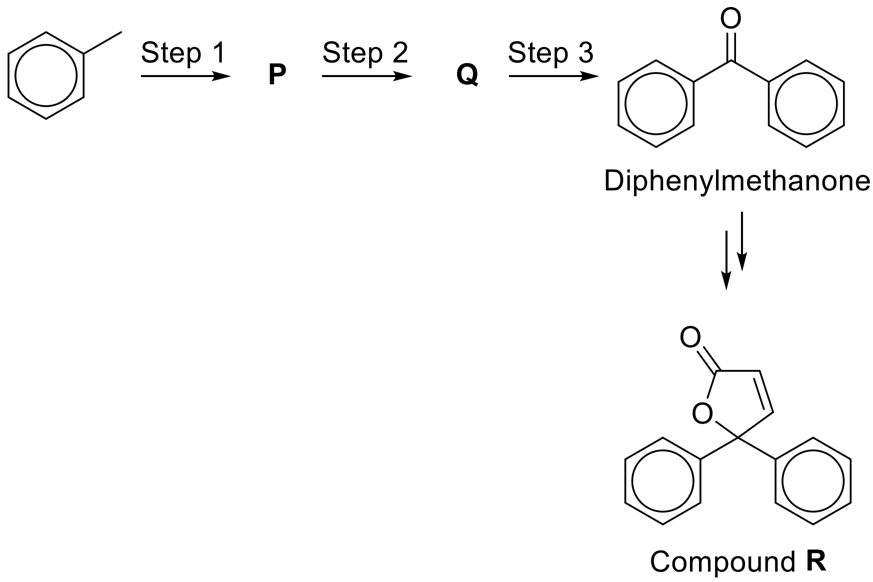
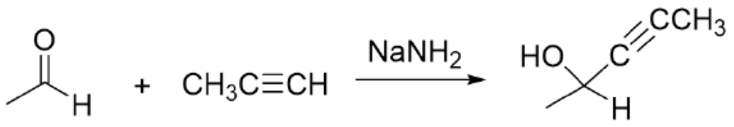


Fig 4.1

(i) Suggest the reagents and conditions for steps **1**, **2** and **3**, and draw the structures for compounds **P** and **Q**. [5]

(ii) When compound **R** is heated with acidified $KMnO_4$, compound **S** is formed as the only organic product. Suggest the structure of compound **S**. [1]

(b) Propyne, $CH_3C\equiv CH$, is a weak acid. It can react with an aldehyde in the presence of trace amount of strong base such as $NaNH_2$.



When propyne reacts with NH_2^-, propynyl ion, $CH_3C\equiv C^-$ is formed.

(i) State the type of reaction that occurred between propyne and ethanal. [1]

(ii) Describe the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(iii) Suggest if the organic product formed from this reaction would rotate plane−polarised light. [2]

(c) The mechanism for the reaction between compounds **T** and **U** is as shown.

Step 1: $\mathbf{T} + \mathbf{U} \rightleftharpoons \mathbf{V}$

Step 2: $\mathbf{T} + \mathbf{V} \rightarrow \mathbf{W}$ (slow)

(i) Write a balanced overall equation for the reaction between compounds **T** and **U**. [1]

(ii) Write an expression for K_c for step 1, stating its units. [2]

(iii) Using the information given in the question and your answer to **c(ii)**, derive the rate equation for the reaction between compounds **T** and **U**. [2]

(iv) A concentration−time graph was plotted for step 1 as shown in Fig 4.2. Equilibrium was established at t_0. At t_1, a change was introduced.

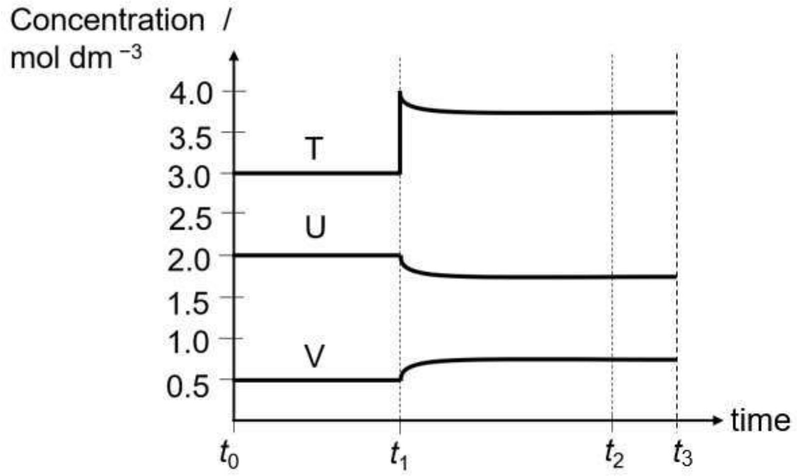


Fig 4.2

State the change that occurred at t_1. Explain the trend observed in the graph from t_1 to t_2. [2]

(v) Suggest whether there would be any change in the individual concentrations of compounds **T**, **U** and **V** when a catalyst is added to the reaction mixture at t_3. [2]

[Total : 20]

5 **(a)** Describe and explain the variation in volatility of the elements in Group 17. [2]

(b) *Use of the Data Booklet is relevant to this question.*

Explain the following observations in terms of the relative thermal stabilities of the hydrides of the Group 17 elements.

compound	HC*l*	HBr	HI
decomposition behaviour	does not decompose even on strong heating	strong heating yields reddish brown fumes of Br_2	purple fumes of I_2 obtained when red-hot rod is plunged into jar of HI

[2]

(c) State and explain the observations when separate solutions of chloride and iodide ions are mixed with aqueous silver nitrate, followed by excess aqueous ammonia. [3]

(d) Carbon monoxide in a sample of polluted air can readily be determined by passing through solid iodine(V) oxide, I_2O_5, to give carbon dioxide and iodine.

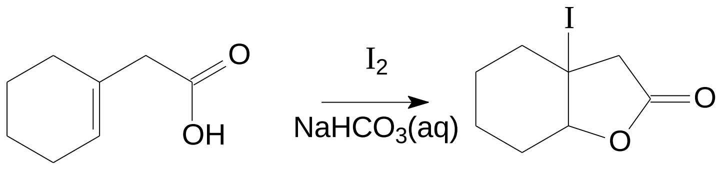
(i) Write a balanced equation for the reaction between carbon monoxide and iodine(V) oxide. [1]

(ii) The iodine produced is dissolved in a suitable solvent and titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$.

1 dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate to discharge the iodine colour.

Calculate the mass of carbon monoxide in this sample of polluted air. [2]

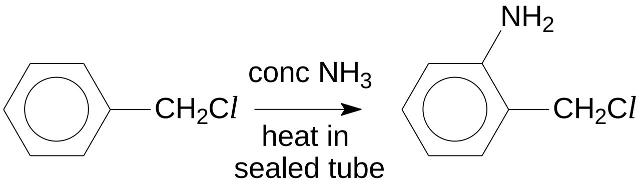
(e) In the presence of aqueous sodium hydrogencarbonate, iodine does not add across the C=C bond of compound **D** as might be expected. Instead, the following reaction occurs.



compound **D**

The first step of the mechanism involves a fast acid-carbonate reaction. Describe the mechanism for this electrophilic addition reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(f) A student attempted to make compound **E** from (chloromethyl)benzene as shown.



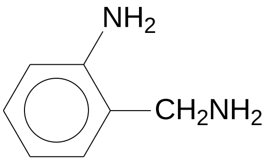
(chloromethyl)benzene compound **E**

However, a different product with molecular formula C_7H_9N was obtained.

(i) Draw the displayed formula of the product obtained from the reaction. [1]

(ii) Explain why compound **E** was not obtained. [1]

(g) The pK_b values of the two amine groups in compound **F** are 3.4 and 9.1.



compound **F**

(i) Copy the structure of compound **F** to your answer booklet and assign the pK_b values to the two amine groups. Explain your answer. [2]

(ii) Calculate the initial pH of 0.100 mol dm^{-3} of compound **F**. [2]

(h) Explain the observations when Br_2(aq) is added to the two samples.

sample	phenylamine	phenylamine dissolved in excess sulfuric acid
observations	orange Br_2 (aq) decolourises and white precipitate forms	orange Br_2 (aq) remains

[2]

[Total : 20]

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NATIONAL JUNIOR COLLEGE
SH 2 Year – End Practical Examination
Higher 2

CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/04

Paper 4 Practical

Tuesday 20 August 2019

Candidate answer on the Question paper.

2 hours 30 minutes

READ THE INSTRUCTIONS FIRST
Write your identification number and name. Circle 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, 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.

At the end of the examination, submit the question paper.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift		
1	**2**	**3**

Laboratory			
CM41	**CM42**	**CM43**	**CM44**
PH31	**PH32**	**PH33**	▨
BI23	**BI24**	▨	▨

For Examiner's Use	
1	**/ 12**
2	**/ 21**
3	**/ 14**
4	**/ 8**
Total	**/ 55**

This document consists of **19** printed pages and **1** blank page.

1 Determination of the solubility product of calcium iodate(V)

When solid calcium iodate(V) is added to water to form a saturated solution, an equilibrium between the undissolved salt and its aqueous ions is established.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^{-}\,(aq)$$

The solubility product, K_{sp} , of calcium iodate(V) is expressed as follows.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^{-}(aq)]^2$$

The solubility product can be found by determining the equilibrium concentration of IO_3^{-} ions in a saturated solution of calcium iodate(V) through a redox titration.

Iodate(V) ions, IO_3^{-}, react with iodide ions according to the following equation.

$$IO_3^{-}\,(aq) + 5I^{-}(aq) + 6H^{+}\,(aq) \longrightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine produced in this reaction may be titrated against sodium thiosulfate using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^{-}(aq)$$

In this question, you will prepare a saturated solution of calcium iodate(V) to carry out the redox titration. Using the experimental results, you will determine the solubility product of calcium iodate(V).

You are provided with:
FA 1 is solid calcium iodate(V), $Ca(IO_3)_2$

FA 2 is 0.05 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 0.50 mol dm^{-3} potassium iodide, KI

FA 4 is 0.50 mol dm^{-3} sulfuric acid, H_2SO_4

FA 5 is starch indicator

Preparation of a saturated solution of calcium iodate (V), FA 6

(a) Procedure

1. Use a 100 cm^3 measuring cylinder to transfer 80.0 cm^3 of deionised water into a 250 cm^3 beaker.
2. Transfer all **FA 1** from the weighing bottle into the beaker. Stir for 1 to 2 minutes and leave to stand for **5 minutes**. There will be some $Ca(IO_3)_2$ solids left undissolved.
3. Use a 0.2 °C division thermometer, record the temperature of the solution in the beaker.
4. To remove the undissolved solids, filter the saturated solution into another clean and **dry** 250 cm^3 beaker using a **dry** filter paper and **dry** funnel. Label this solution as **FA 6**.

Titration

(b) **Procedure**

(i) **1.** Fill a burette with **FA 2**.

2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.

3. Use a 10 cm^3 measuring cylinder to add 5.0 cm^3 of **FA 3**, followed by 5.0 cm^3 of **FA 4** to the same conical flask and swirl quickly.

4. Titrate the iodine in the conical flask with **FA 2** until the brown colour of the iodine becomes pale yellow.

5. Add about 10 drops of starch solution to the flask and continue adding **FA 2** 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

[4]

(ii) From your titres, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

10.0 cm^3 of **FA 6** produced an amount of iodine which required ……...… cm^3 of **FA 2**.
[1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** part.

(i) Calculate the number of moles of $S_2O_3^{2-}$ in the volume of **FA 2** recorded in **1b(ii)**, and hence determine the molar concentration of IO_3^- ions in **FA 6**.

number of moles of $S_2O_3^{2-}$ =……………………………..

concentration of IO_3^- ions in **FA 6** =……………………………..

[2]

(ii) Determine the molar concentration of Ca^{2+} in **FA 6** and hence, calculate the solubility product, K_{sp}, of calcium iodate(V), stating the units.

concentration of Ca^{2+} ions in **FA 6** = ……………………………..

solubility product of $Ca(IO_3)_2$ = ……………………………..

[2]

(d) Explain why it was necessary to use the **dry** apparatus (e.g. beaker, filter paper and funnel) in the preparation of **FA 6**, and what effect failing to do it would have on the titre values?

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……[1]

(e) A literature value for the solubility product of calcium iodate(V) is found to be 6.15×10^{-6} at 20 °C.

State a possible reason for the difference in the K_{sp} value that you have calculated and suggest an improvement that might allow a value closer to the literature value to be obtained.

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……[2]

[Total: 12]

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2 **Determination of the enthalpy change of neutralisation, ΔH_n**

FA 7 is a solution of HC*l* of unknown concentration

FA 8 is a solution of 1.0 mol dm^{-3} of NaOH

In this question, you will carry out a series of experiments where different volumes of **FA 7** and **FA 8** are mixed together.

You will determine the temperature change of the reaction mixture, ΔT, of each experiment and then analyse your results graphically in order to determine the

- concentration of HC*l* in **FA 7**
- 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 7 and FA 8**

(i) **Experiment 1**

1. Place a Styrofoam cup inside a second Styrofoam cup held in a 250 cm^3 beaker to prevent it from tipping over.

2. Using a measuring cylinder, transfer 20.0 cm^3 of **FA 7** into the Styrofoam cup.

3. Measure the temperature of **FA 7** in the Styrofoam cup. Record the initial temperature of the solution of **FA 7** as $T_{FA\,7}$.

4. Rinse and dry the thermometer.

5. Measure 50.0 cm^3 of **FA 8** using another measuring cylinder. Record the initial temperature of the solution of **FA 8** as $T_{FA\,8}$.

6. Transfer the **FA 8** into the cup containing **FA 7**. Stir and record the maximum temperature of the reaction as T_{max}.

7. Rinse and dry the Styrofoam cup and thermometer.

Experiment 2

Repeat steps 2 to 7 using 50.0 cm^3 of **FA 7** and 20.0 cm^3 **FA 8**.

Experiments 3 to 6

Carry out **four** further experiments to investigate how the T_{max} changes with different volumes of **FA 7** and **FA 8**. In each case, the total volume of the reaction mixture must be 70.0 cm^3 and the volume of each reagent should not be less than 20.0 cm^3.

In an appropriate format in the space provided on next page, record

- all measurements of volumes used,
- all temperatures measured, $T_{weighted\ initial}$ and ΔT

$$\Delta T = T_{max} - T_{weighted\ initial}$$

$$T_{weighted\ initial} = \frac{(\text{Volume of FA 7} \times T_{FA\,7}) + (\text{Volume of FA 8} \times T_{FA\,8})}{\text{Volume of FA 7} + \text{Volume of FA 8}}$$

Results

[4]

(ii) Plot a graph of ΔT (*y*–axis) against volume of **FA 7** used (*x*–axis) on the grid in Fig. 2.1 using the data you have obtained in **2a(i)**.

Fig. 2.1

[3]

(iii) Draw two best-fit straight lines, the first should be drawn using the plotted points where ΔT is increasing and the second should be drawn using the plotted points where ΔT is decreasing. Extrapolate (extend) both lines until they intercept.

[1]

(iv) From your graph in Fig. 2.1, determine the maximum temperature change, ΔT_{max}, and the volume, V_{max}, of **FA 7** required to obtain this.

ΔT_{max} = ……………………………°C $V_{\mathbf{max}}$ = ………………………………cm^3 [2]

(b) **Calculation**
Show your working and appropriate significant figures in the final answer to **each** part.

Using your answers in **2a(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of HCl in **FA 7**.

concentration of HCl in **FA 7** = …………………………….. [2]

(ii) the heat change for the neutralisation reaction 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]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_n.

ΔH_n = …………………………….. [1]

(c) In another similar experiment, 1.0 mol dm^{-3} aqueous ammonia was used instead of 1.0 mol dm^{-3} NaOH. A graph of change in temperature, ΔT, against volume of **FA 7** was plotted.

Suggest how would the ΔT_{max} and volume, V_{max}, of **FA 7** from this experiment be compared to your result obtained in **2a(iv)** .

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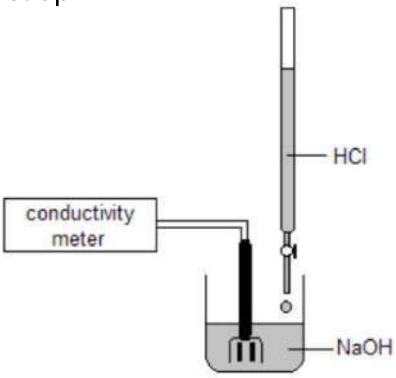
(d) A student employed another method to determine the concentration of the HC*l* in **FA 7** through the use of conductometry. Conductometry is the measurement of the electrolytic conductivity to monitor the progress of a chemical reaction due to ions being produced or reacted away. The equivalence point can then be determined for the acid – base reaction by plotting the conductivity against the volume of the HC*l* added.

$$H^+ + OH^- \longrightarrow H_2O$$

The following apparatus were set up.



The student measured the conductivity of the solution in the beaker with each addition of a small fixed volume of HC*l* and obtained the following graph.

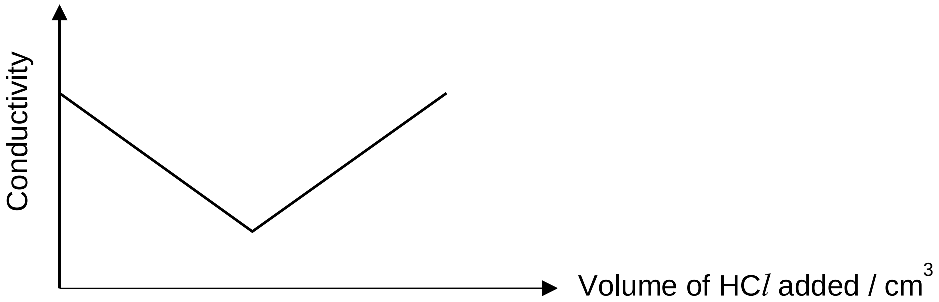


Fig. 2.2

(i) Indicate on the graph (Fig. 2.2), the point which marks the volume of HC*l* needed for complete reaction. [1]

(ii) Explain the shape of the graph in Fig. 2.2.

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(iii) With reference to your experiment in **2(a)**, suggest which method (calorimetry or conductometry) is more accurate for the determination of the concentration of HC*l* in **FA 7**.

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[Total: 21]

3 Identification of ions

FA 9 is a solution containing a mixture of two salts.

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.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated. If there is no observable change, write **no observable change**.

No additional or confirmatory tests for ions present should be attempted.

Table 3.1

	Test	*Observation*
(a)	Place about 3 cm depth of **FA 9** in a test-tube, add equal volume of aqueous sodium hydroxide. Warm the contents in the tube.	
(b)	Filter the mixture from **3(a)** and collect the filtrate in a test-tube. Label the filtrate as **FA 10** and retain it for tests **3(c)** and **3(d)**. Leave the residue in the filter paper and observe it again after 5 minutes.	
(c)	Place 2 cm depth of **FA 10** in a test-tube and add nitric acid until no further change is seen. Label the solution as **FA 11** and retain it for test **3(e)**.	
(d)	Place 1 cm depth of **FA 10** in a test-tube. Add half a spatula of zinc powder. Warm the contents in the tube cautiously.	

	Test	*Observation*
(e)	Place 2 cm depth of **FA 11** in a test-tube, add equal depth of aqueous ammonia. Add excess dilute nitric acid followed by aqueous silver nitrate.	
(f)	Place 1 cm depth of **FA 9** in a test-tube. Add dilute hydrochloric acid followed by aqueous barium chloride.	

[6]

(g) **(i)** Identify the **two** cations and **two** anions present in **FA 9**.

cation 1: ………………………… cation 2: …………………………

anion 1: ………………………… anion 2: …………………………

[4]

(ii) Write equations, with state symbols, to illustrate the observations in **3(c)**.

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……………………………………………………………………………………………….[2]

(iii) Predict what will happen when solid ammonium nitrate is added to **FA 9** followed by aqueous ammonia.

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……………………………………………………………………………………………….[2]

[Total : 14]

4 Planning

Determination of the hardness of water in a sample.

Hard water is water that has high mineral content and is formed when water percolates through deposits of limestone, chalk and gypsum, which are largely made of calcium carbonates, bicarbonates and sulfates. The hardness of water is measured in terms of the molar concentration of Ca^{2+} in mol dm^{-3}.

In a particular sample of water, the hardness is caused by the presence of calcium chloride. The amount of Ca^{2+}, and hence the concentration of Ca^{2+}, can be determined by precipitation with an excess of oxalic acid.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$$

You are to design an experiment to determine the hardness of water in a sample.

You are provided with

- sample of water with estimated hardness of 0.02 mol dm^{-3}
- 0.1 mol dm^{-3} of oxalic acid $H_2C_2O_4$
- electronic balance
- common laboratory apparatus

(a) Given the K_{sp} of calcium oxalate is 2.7×10^{-9} mol^2 dm^{-6}, predict what will be observed when 25.0 cm^3 of the water sample is mixed with equal volume of the 0.1 mol dm^{-3} of oxalic acid solution.

[2]

(b) Your plan should include a step-by-step description of the method, including

- the sequence of steps to ensure that the maximum amount of precipitate is recovered,
- the use of appropriate apparatus,
- the recordings using the letters A, B, C etc to represent the measurement taken and present it with an appropriate table format,
- the processing of the results to determine the molar concentration of Ca^{2+} in the water sample.

[A_r: C, 12.0; Ca, 40.1; H, 1.0; O, 16.0]

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…………………………………………………………………………………………[6]

[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 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

Answer Keys to 2019 SH2 H2 Chemistry Prelim MCQ

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

1 Amount of Ag deposited = $\frac{0.216}{107.9}$ = 0.002002 mol

Amount of Ag per cm^2 = $\frac{0.002002}{150}$ = 0.00001335 mol per cm^2

No of Ag atom per cm^2 = $0.00001335 \times 6.02 \times 10^{23} = 8.034 \times 10^{18}$ atom per cm^2

Ans: **A**

2 Angle of deflection $\propto \frac{\text{charge}}{\text{mass}}$

Mass of electron is approximately $\frac{1}{2000}$ the mass of a proton, hence electron has the largest angle of deflection.

Ans: **A**

3 Amount of SO_3^{2-} = $\frac{25.0}{1000} \times 0.10 = 0.0025$ mol
Amount of electron transferred = $0.0025 \times 2 = 0.005$ mol
Amount of M^{3+} reacted = $\frac{50.0}{1000} \times 0.10 = 0.005$ mol
Mol ratio $M^{3+} : e^- = 1 : 1$

During **reduction**, 1 mol of M^{3+} gains 1 mol of e^-.
Oxidation state of M^{3+} **decreases by 1 unit** from **+3** to **+2**.

Ans: **B**

4 The sharp rise between 2nd and 3rd I.E. shows that there are 2 valence electron in the outermost shell. Hence it is in Group 2.

The next inner quantum shell contains 8 electrons, for d-block element, the next inner quantum shell should contain 3s, 3p and 3d electrons, which would be more than 8.

It cannot be a Period 3 Group 2 element as Mg only has 12 electrons.

Ans: **C**

5 The species are isoelectronic (same number of electrons) with same shielding effect.
Nuclear charge increases from Ar < K^+ < Ca^{2+}
Hence nuclear attraction towards valence electrons increases from Ar < K^+ < Ca^{2+}.

Ca^{2+} would have the smaller radius while Ar has the largest radius.

Ans: **C**

6 Bond angle 1 is 109.5° (4b.p. 0l.p. → tetrahedral)

Bond angle 2 is 120° (3b.p. 0l.p. → trigonal planar)

Bond angle 3 is 104.5° (2b.p. 2l.p. → bent)

Ans: **C**

7 $p_1V_1 = nRT_1$
$p_2V_2 = nRT_2$

$$\frac{p_1V_1}{p_2V_2} = \frac{T_1}{T_2}$$

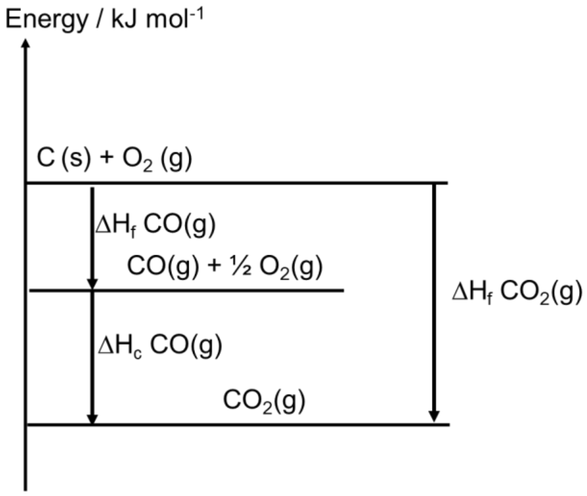
$$\frac{(1\times10^5)\times V_1}{p_2\times4V_1} = \frac{(20+273)}{(100+273)}$$

$p_2 = 31830$ Pa

Ans: **A**

8 $CO(g) + ½ O_2(g) \rightarrow CO_2(g)$

Combustion is an exothermic process, this means that energy level of CO_2 is lower than CO. Hence option 1 is correct.

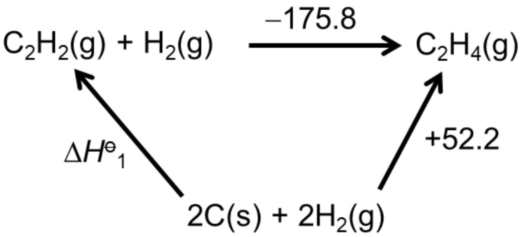


Option 2 is wrong. ΔH_f CO_2(g) should be more negative than that of CO(g).

Since the combustion spontaneous (burns readily), the K_c for the equilibrium would be a very large value.

Ans: **C**

9



$\Delta H^{\ominus}_1 = 52.2 + 175.8 = +228$ kJ mol^{-1}

Ans: **D**

10 Option A is wrong. Increase in temperature would increase the kinetic energy.

Option B is wrong. Catalyst increases the frequency of **<u>effective</u>** collision.

Option D is a correct statement but does not explain “how” fumarase speed up the reaction.

Option C is correct. Fumarase is an enzyme that provides alternative reaction pathway with lower activation energy.

Ans: **C**

11 Rate of reaction = $\frac{change\ in\ vol\ of\ MnO_4^{-}}{time\ taken}$

Expt	Volume / cm^3				Time / s	rate
	$C_2O_4^{2-}$(aq)	MnO_4^-(aq)	Mn^{2+}(aq)	water		
1	20	30	5	25	30	1
2	20	30	10	20	15	2
3	20	15	10	35	15	1
4	20	20	20	20	10	2

Comparing expt 1 & 2, [$C_2O_4^{2-}$] and [MnO_4^-] is kept constant but when [Mn^{2+}] × 2, rate × 2. Hence it is first order w.r.t. Mn^{2+}. Option 1 is correct.

Comparing expt 2 & 3, [$C_2O_4^{2-}$] and [Mn^{2+}] is kept constant but when [MnO_4^-] ÷ 2, rate ÷ 2. Hence it is first order w.r.t. MnO_4^-.

We cannot determine the order of reaction w.r.t. $C_2O_4^{2-}$.

Rate = k[Mn^{2+}] [MnO_4^-] [$C_2O_4^{2-}$]^x

The slow step would involve one Mn^{2+} and one MnO_4^- ion and **maybe** $C_2O_4^{2-}$ ion. Option 2 is correct.

We cannot deduce the order of reaction w.r.t. $C_2O_4^{2-}$ and hence we cannot conclude the units of the rate constant.

Ans: **B**

12 Lewis base is an electron pair donor.

In reaction 1 and 2, NH_3 donates electron pair to H^+.

In reaction 3, NH_3 donates electron pair to Ag^+.

Ans: **D**

13 $CuS (s) \rightleftharpoons Cu^{2+} (aq) + S^{2-} (aq)$
s s

$K_{sp} = s^2$
$s = \sqrt{(8.5 \times 10^{-45})}$
$= 9.22 \times 10^{-23}$ mol dm^{-3}

$Ag_2S (s) \rightleftharpoons 2Ag^+ (aq) + S^{2-} (aq)$
2s s

$K_{sp} = (2s)^2(s)$
$4s^3 = 1.6 \times 10^{-49}$
$s = 3.42 \times 10^{-17}$ mol dm^{-3}

$Bi_2S_3 (s) \rightleftharpoons 2Bi^{3+} (aq) + 3S^{2-} (aq)$
2s 3s
$K_{sp} = (2s)^2(3s)^3$
$108s^5 = 1.1 \times 10^{-73}$
$s = 1.00 \times 10^{-15}$ mol dm^{-3}

Ans: **B**

14 At cathode (−ve electrode):
Species present: Na^+ and H_2O
[R] $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Blue litmus remains blue

At anode (+ve electrode):
Species present: Cl^- (concentrated) and H_2O
Note: Concentrated Cl^- will be oxidized in preference over H_2O.
[O] $2Cl^- \rightarrow Cl_2 + 2e^-$
Chlorine bleaches the litmus paper.

Ans: **C**

15 Statement A is correct. $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

Statement B is correct. Al_2O_3 is amphoteric oxide that can react with both acid and base to give soluble products.

Statement C is correct.
$Na_2O + H_2O \rightarrow 2NaOH$
$SO_3 + H_2O \rightarrow H_2SO_4$
$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Statement D is wrong. Acidity of Period 3 chlorides in water **<u>increase</u>** from $NaCl$ to PCl_5. pH of the resultant solution decreases from pH 7 to pH 1.

Ans: **D**

16 $M(NO_3)_2(s) \rightarrow MO(s) + 2NO_2(g) + ½\ O_2(g)$

Mass loss is due to NO_2 and O_2.
We can assume 3.29 g of $N_2O_5(g)$ is loss.

$M(NO_3)_2(s) \rightarrow MO(s) + N_2O_5(g)$
Amount of $N_2O_5 = \frac{3.29}{14.0\times2+16.0\times5} = 0.03046$ mol

Amount of $M(NO_3)_2 = 0.03046$ mol

M_r of $M(NO_3)_2 = \frac{5.00}{0.03046} = 164.1$

A_r of M = 164.1 – 2×(14.0+16.0×3) = 40.1
M is calcium.

Ans: **B**

17 Statement A is wrong. Ag^+ is reduced.

Statement B is correct. Cu^+ is used up in reaction 2 and regenerated in reaction 3.

Statement C is wrong. Cu^+ acts as a reducing agent in reaction 2.

Statement D is wrong. The depth of colour should be related to concentration of Ag(s).

Ans: **B**

18 Oxides of nitrogen can contribute to

- formation of smog through reaction with other air pollutants. PAN is a major component of smog which is harmful to plants and humans.

$$\text{Hydrocarbons} + O_2 + NO_2 + \text{light} \rightarrow \text{peroxyacetyl nitrate (PAN)}$$

- formation of ozone at lower atmosphere. **High concentration of ozone at lower atmosphere causes respiratory problems.**

$$NO_2 \rightarrow NO + O$$
$$O + O_2 \rightarrow O_3$$

- NO_2 **acts as a catalyst for the oxidation** of SO_2 to SO_3, $SO_2 + ½\ O_2 \rightarrow SO_3$

$$NO_2 + SO_2 \rightarrow SO_3 + NO$$
$$NO + ½\ O_2 \rightarrow NO_2 \text{ (regenerated)}$$

SO_3 dissolves in rainwater to cause acid rain (H_2SO_4).

Ans: **D**

19 Option 1 is correct. The molecule contains a secondary alcohol group.

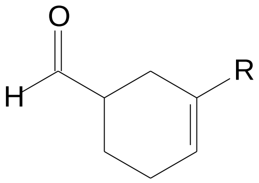
Option 2 is wrong. The C=C bond consists of one σ and one π bond.

Option 3 is wrong. Most of the C atoms are sp^3 hybridized with tetrahedral geometry. This shows that the C atoms are not in the same plane.

Ans: **D**

20 The C=C bond between C11 and C12 is in a cis arrangement.

Considering the following structure with aldehyde and cyclohexene ring,



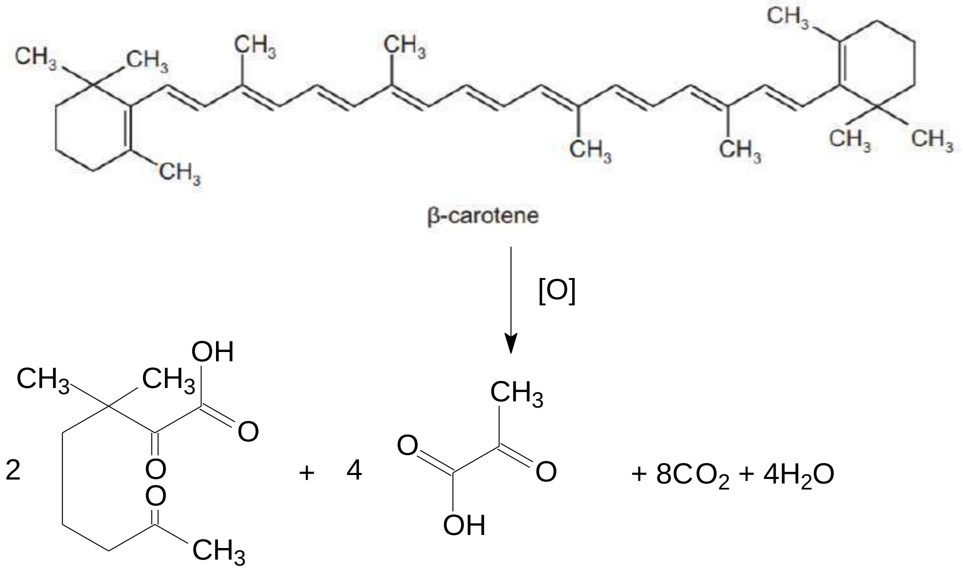
The long aliphatic side chain has a formula of $C_{13}H_{19}$.

When drawing out, there will need to have 4 C=C in the long aliphatic side chain.

Total number of C=C in the molecule = 5

Ans: **A**

21

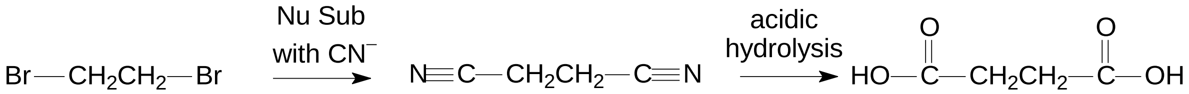


Ans: **B**

22 The example shows that CN^- can undergo nucleophilic substitution with C−Br at a faster rate than I^-. Option C is the best explanation.

Ans: **C**

23



$$\text{Br—CH}_2\text{CH}_2\text{—Br} \xrightarrow[\text{with CN}^-]{\text{Nu Sub}} \text{N}{\equiv}\text{C—CH}_2\text{CH}_2\text{—C}{\equiv}\text{N} \xrightarrow[\text{hydrolysis}]{\text{acidic}} \text{HO—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—CH}_2\text{CH}_2\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH}$$

Ans: **C**

24 Reaction A can occur at room temperature.

Reaction B requires heating with ethanolic KCN for nucleophilic substitution.

Reaction C requires heating with concentrated H_2SO_4 for elimination.

Reaction D requires heating for hydrolysis.

Ans: **A**

25 Ethanol, C_2H_5OH (M_r = 46.0), reacts with hot acidified $KMnO_4$ to gives ethanoic acid, CH_3COOH (M_r = 60.0).

Amount of ethanol = $\frac{2.76}{46.0}$ = 0.06 mol
Theoretical yield of ethanoic acid = 0.06 × 60.0 = 3.6 g
Mass of 75% yield of ethanoic acid = 0.75 × 3.6 = 2.7 g

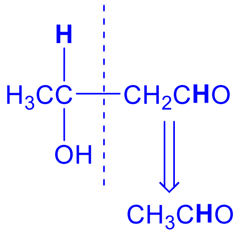
Ans: **C**

26 Compound N

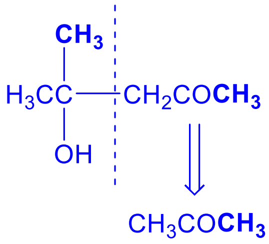
- does not contain carboxylic acid/phenol/amine
- contains a carbonyl group that undergoes condensation reaction with 2,4−DNPH
- contains an alcohol or carboxylic acid group that undergoes substitution with PCl_5

Ans: **C**

27 From the question, the following pattern is observed:



Replacing the bold –H with –CH_3 and working backwards,



Ans: **A**

28 Statement 1 is wrong. There is no chiral carbon in the compound.

Statement 2 is correct. There are two carboxylic functional group.

Statement 3 is correct. Tertiary alcohol group can react with carboxylic acid to form ester. Carboxylic acid groups can react with alcohol to form ester.

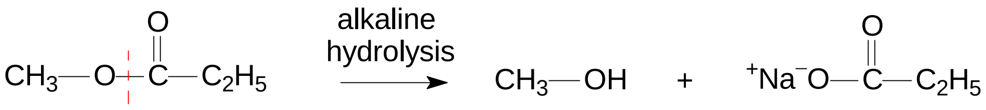
Ans: **C**

29

	L	M
Acidified $AgNO_3$(aq)	No ppt	No ppt
Acidified $KMnO_4$(aq)	Purple $KMnO_4$ turns colourless	Purple $KMnO_4$ turns colourless
Na(s)	Effervescence of H_2(g)	Effervescence of H_2(g)
Na_2CO_3(aq)	Effervescence of CO_2(g)	No effervescence of CO_2(g)

Ans: **D**

30



$$CH_3-O-\overset{\overset{\large O}{\|}}{C}-C_2H_5 \xrightarrow{\text{alkaline hydrolysis}} CH_3-OH + {}^{+}Na\,{}^{-}O-\overset{\overset{\large O}{\|}}{C}-C_2H_5$$

Ans: **C**

Suggested Answer for SH2 H2 Chemistry 2019 Prelim Paper 2

1 **(a)** Brass is a mixture of copper and zinc. When a piece of brass is placed in dilute hydrochloric acid, only one of the metals present dissolves.

Explain the observation and write an equation for the reaction that occurs.

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

$2H^+ + 2e^- \rightleftharpoons H_2 \quad E^\ominus = 0.00\ V$

For reaction between Zn and H^+,

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$

$= 0.00 - (-0.76)$

$= +0.76V$ (reaction is feasible)

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$ OR $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

For reaction between Cu and H^+,

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$

$= 0.00 - (0.34)$

$= -0.34V$ (reaction is not feasible)

Note: It is essential to calculate $E^\ominus_{cell}$ between metal and H^+ to conclude whether the reaction is feasible. Some answers suggest Zn is more likely to be oxidized than Cu but that does not explain why Cu do not react with H^+.

(b) Copper and zinc are the two electrodes in a *Daniell* cell. The cell is set up as shown in Fig 1.1.

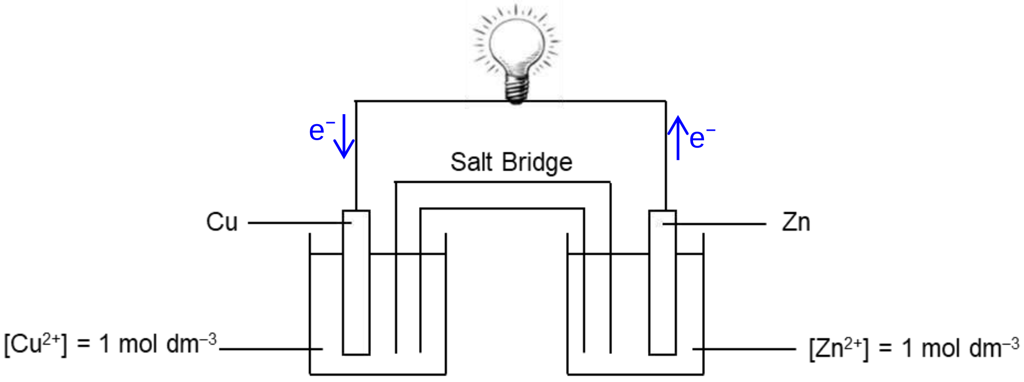


Fig 1.1

(i) Indicate the direction of electron flow **on Fig 1.1**. [1]

Note:

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^\ominus = +0.34V$

Cu^{2+}/Cu half cell undergoes [R] and gain e^-

Zn^{2+}/Zn half cell undergoes [O] and lose e^-

Electrons flow from the anode (oxidation) to the cathode (reduction).

(ii) Write the equation for the reaction taking place and calculate $\Delta G^\ominus$ for the reaction.

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$$
$$= +0.34 - (-0.76)$$
$$= +1.10V$$

$$\Delta G^\ominus = -nFE^\ominus_{cell}$$
$$= -2 \times 96500 \times 1.10$$
$$= -2.12 \times 10^5 \text{ J mol}^{-1}$$

[3]

(iii) Discuss the effect of the following changes on the cell potential of the above cell.

(I) adding excess amount of aqueous ammonia into the Zn^{2+}/Zn half-cell

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76V$

When excess amount of aqueous ammonia is added to Zn^{2+}/Zn half-cell, $[Zn(NH_3)_4]^{2+}$ complex ion will be formed.In order to partially offset the decrease in $[Zn^{2+}]$, oxidation of Zn is favoured to form more Zn^{2+}. Hence $E(Zn^{2+}/Zn)$ becomes more negative.

$E_{cell} = E^\ominus(Cu^{2+}/Cu) - E(Zn^{2+}/Zn)$

E_{cell} will become more positive.

(II) using a smaller copper electrode

Size of electrode will not affect the $E^\ominus$ of the reduction half-equation and E_{cell} since there is no shift in the position of the equilibrium.

Note: Solid does not affect position of equilibrium.

(iv) How many hours will it take for this galvanic cell to plate 15.0 g of metallic copper from 1 mol dm^{-3} solutions of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ using a current of 5.0 A?

[R] $Cu^{2+} + 2e^- \rightarrow Cu$

Amount of Cu $= \frac{15.0}{63.5} = 0.2362$ mol

Amount of electrons = 0.4724 mol

$Q = It = n_eF$

$$t = \frac{0.4724 \times 96500}{5.0}$$
$$= 9117s$$
$$= 2.53h$$

[2]

(v) The Nernst equation is an equation that relates the cell potential, E_{cell}, of an electrochemical reaction to the standard cell potential, $E^{\ominus}_{cell}$. It can be simplified and written as

Nernst equation : $E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF} \ln Q$

where *R* is the ideal gas constant | *T* is temperature in Kelvin

z is the number of electron transferred | *F* is Faraday's constant

Q is $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ for the *Daniell* cell

Using the above equation, calculate Q for the overall redox reaction of the *Daniell* cell when it reaches equilibrium at 25 °C.

At equilibrium, $E_{cell} = 0$

$$E^{\ominus}_{cell} = \frac{RT}{zF} \ln Q$$

$$1.10 = \frac{8.31 \times 298}{2 \times 96500} \ln Q$$

$$Q = 1.71 \times 10^{37}$$

[2]

(vi) In another set-up conducted at 25 °C, the concentration of Cu^{2+} ions and Zn^{2+} ions have been adjusted to 0.125 mol dm^{-3} and 0.002 mol dm^{-3} respectively.

Using the Nernst equation, calculate the e.m.f. of this cell.

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{zF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10 - \frac{8.31 \times 298}{2 \times 96500} \ln \frac{[0.002]}{[0.125]}$$

$$= 1.15\text{V}$$

[2]

[Total: 17]

For Examiner's Use

2 Saccharin is an artificial sweeting agent used in some soft drinks and produced in various ways. Fig 2.1 shows the original route by *Remsen and Fahlberg*, starting with methylbenzene undergoing electrophilic substitution reaction using chlorosulfonic acid, $ClSO_3H$. This is also known as aromatic sulfonation process.

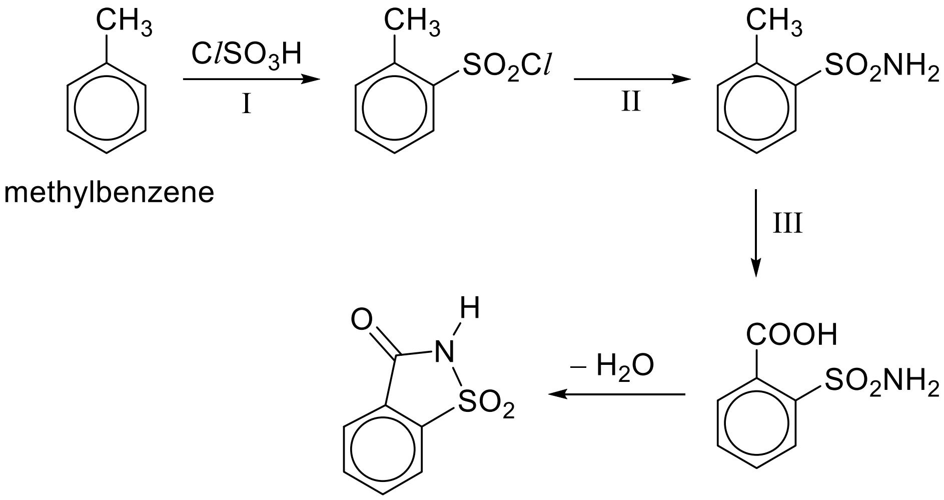
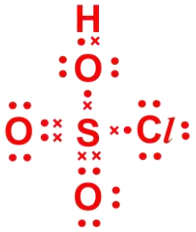


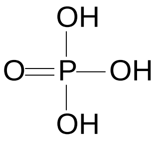
Fig 2.1

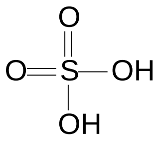
(a) Draw a dot-and-cross diagram of chlorosulfonic acid, $ClSO_3H$ and hence state the bond angle for Cl−S−O.

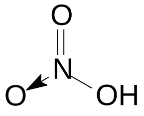


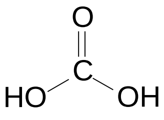
Cl−S−O bond angle : 109.5°

Note: All acid compounds are covalent molecule. They only dissociate into ions in aqueous state. Acids containing H&O atoms lose H^+ from the O−H bonds when ionize in water. Examples of acid molecule structures:







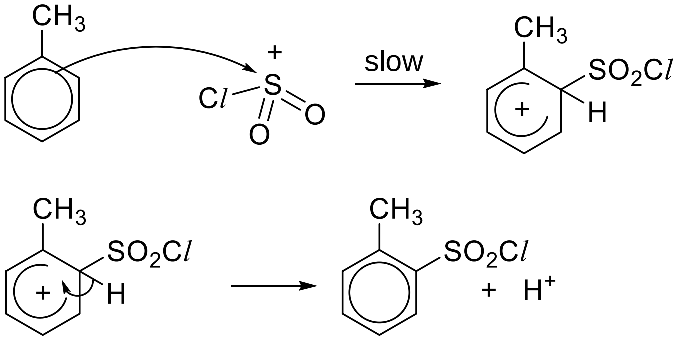


[2]

(b) **(i)** Reaction I of the aromatic sulfonation process involves the formation of an electrophile. Identify the electrophile.

Electrophile : $^+SO_2Cl$ [1]

(ii) Hence, describe the mechanism for reaction I of the reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



Note:
arrow from benzene π electron to S atom of the electrophile to form arenium cation
arrow from C−H bond to center of arenium cation to regenerate aromaticity and lose H^+ [2]

(iii) State the types of reaction that occur during reactions II and III.

reaction II : nucleophilic substitution / condensation

reaction III : oxidation [2]

(iv) Suggest reagents and conditions for reactions II and III.

reaction II : excess ethanolic NH_3, heat in sealed tube (behave like C−C*l*)
(also accept NH_3(g) r.t.p. as it could react similar to acyl chloride)

reaction III : $KMnO_4$, dilute H_2SO_4, heat [2]

[Total : 9]

3 Perchlorate (ClO_4^-) compounds are used as oxidisers in some fireworks to aid the combustion reaction. These perchlorates can contaminate bodies of water near fireworks displays. Elevated concentrations of perchlorate in water can affect wildlife and it may also affect human health if it contaminates drinking water.

(a) One common perchlorate present in fireworks is ammonium perchlorate, NH_4ClO_4. Given that the solubility of ammonium perchlorate is 30.6 g per 100 cm^3, express its solubility in mol dm^{-3} and hence, calculate the solubility product, K_{sp}, for NH_4ClO_4.

$$\text{Solubility, s} = \frac{30.6}{117.5} \times 10 = 2.60 \text{ mol dm}^{-3}$$

$$K_{sp} \text{ of } NH_4ClO_4 = [NH_4^+][ClO_4^-] = (s)(s) = (2.60)^2$$

$$= 6.78 \text{ mol}^2 \text{ dm}^{-6}$$

[2]

(b) A group of NJC students conducted a study to determine the perchlorate content of the water in the Singapore River before and after the fireworks display in the National Day Parade Rehearsal.

They followed the methodology described below one week before the rehearsal:

- Collect a 100.0 cm^3 sample of the river water and acidify it with 10 cm^3 of 1 mol dm^{-3} sulfuric acid.
- The resulting solution is added to an excess of 50 cm^3 of 5×10^{-5} mol dm^{-3} iron(II) sulfate solution. The mixture is then made up to 250 cm^3. This is solution **X**.
- A 25.0 cm^3 sample of solution **X** is pipetted into a conical flask.

The 25.0 cm^3 solution is titrated against 1×10^{-6} mol dm^{-3} potassium manganate(VII) to determine the amount of remaining iron(II) ions in the sample.

(i) Write the half equation for the conversion of perchlorate ions to chlorine in the acidic medium and hence the overall equation for the reaction between perchlorate and iron(II) ions.

Half equation : [R] $2ClO_4^- + 16H^+ + 14e^- \rightarrow Cl_2 + 8H_2O$

Overall equation : $2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

[2]

(ii) Describe how you would recognise the endpoint of the titration.
Mixture turns first permanent pink [1]

(iii) The 25.0 cm^3 sample of solution **X** required 30.00 cm^3 of potassium manganate(VII) for complete reaction.

Calculate the concentration of perchlorate ions in the river water.

Amt of $MnO_4^- = \frac{30}{1000} \times 1 \times 10^{-6} = 3.0 \times 10^{-8}$ mol

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Amt of Fe^{2+} in 25 $cm^3 = 5 \times 3.0 \times 10^{-8} = 1.50 \times 10^{-7}$ mol

Amt of Fe^{2+} in 250 $cm^3 = 1.50 \times 10^{-6}$ mol

Amt of Fe^{2+} that reacted with $ClO_4^- = (\frac{50}{1000} \times 5 \times 10^{-5}) - 1.50 \times 10^{-6}$
$= 1.0 \times 10^{-6}$ mol

$2ClO_4^- + 16H^+ + 14Fe^{2+} \rightarrow Cl_2 + 14Fe^{3+} + 8H_2O$

Amt of $ClO_4^- = \frac{1.0 \times 10^{-6}}{14} \times 2 = 1.429 \times 10^{-7}$ mol

$[ClO_4^-] = \frac{1.429 \times 10^{-7}}{(^{100}/_{1000})} = 1.43 \times 10^{-6}$ mol dm^{-3}

[3]

(iv) Given that the perchlorate concentration in the Singapore River increased by 20% in the 24 hours after the fireworks display for the National Day Parade rehearsal, calculate the concentration of perchlorate ions in the river 24 hours after the fireworks display.

If you did not manage to work out an answer for **(b)(iii)**, you may assume the concentration of perchlorate ions in the river water is 2.5 × 10^{-6} mol dm^{-3}.

$[ClO_4^-] = 120\% \times 1.43 \times 10^{-6}$
$= 1.71 \times 10^{-6}$ mol dm^{-3}

OR

$[ClO_4^-] = 120\% \times 2.5 \times 10^{-6}$
$= 3.00 \times 10^{-6}$ mol dm^{-3}

[1]

(v) Table 3.1 shows the health effects on fishes due to varying concentration of perchlorate ion in the river.

types of fish	abnormalities in skeletal growth	increased angiogenesis	myocardial infarction
stickleback	5×10^{-6} mol dm^{-3}	1×10^{-4} mol dm^{-3}	1.5×10^{-4} mol dm^{-3}
Pike	5×10^{-7} mol dm^{-3}	2×10^{-6} mol dm^{-3}	1×10^{-5} mol dm^{-3}
catfish	1×10^{-7} mol dm^{-3}	1×10^{-6} mol dm^{-3}	5×10^{-5} mol dm^{-3}

Table 3.1

Using your answer in **b(iv)**, predict the type of health effect(s) experienced by each type of fish 24 hours after the fireworks display. Write "nil" if there is no effect.

types of fish	health effect(s)
stickleback	Nil
pike	abnormalities in skeletal growth
catfish	abnormalities in skeletal growth and increased angiogenesis

[2]

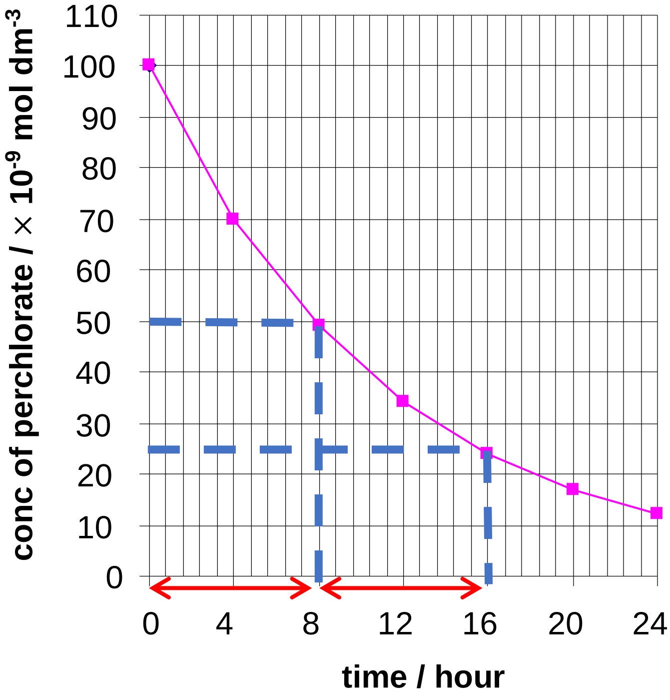
(c) Perchlorate ions can be metabolized in the tissue of stickleback fish. The fish tissue concentration of perchlorate ions was investigated for one of the stickleback fish found in the Singapore River.

The following results was obtained.

Time/ hour	[C*l*O_4^-] / × 10^{-9} mol dm^{-3}
0	100
4	70
8	49
12	34
16	24
20	17
24	12

Table 3.2

(i) Plot the data from Table 3.2 on the grid provided and use your graph to prove that the order of reaction with respect to perchlorate is one.



Clearly labelled axis
Construction line for $t_{½}$
All points plotted correctly
Constant half-life of 8 hours, hence first order wrt perchlorate ions. [3]

(ii) Using your graph in **c(i)**, determine the rate constant, *k*. Include units in your answer.

For first order reaction, $t_{1/2} = \frac{\ln 2}{k}$

$k = 0.0866\ h^{-1}$

[2]

(iii) Hence, estimate the time taken for the perchlorate ions to reach 1% of its initial concentration.

$$\left(\frac{1}{2}\right)^n = \left(\frac{1}{100}\right)$$

n = 6.64

Time taken = 6.64 × 8 = 53.15 hours.

OR

need 7 half-lifes to reach 0.78%, time taken = 7 × 8 = 56 hours

[1]

[Total : 17]

4 Alkalinity refers to the capability of water to neutralize acid. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0.

In the ocean, dissolved carbon dioxide from the atmosphere is in equilibrium with seawater concentrations of carbonic acid, H_2CO_3 and hydrogen carbonate, HCO_3^-. The ocean has a very large buffering capacity made possible with the presence calcium carbonate rocks in lakes and streams.

Relevant chemical equations and equilibrium constants at 293K that affects the ocean's pH and buffering capacity are shown below.

$CO_2(g) \rightleftharpoons CO_2(aq)$	$K_{CO2} = 3.44 \times 10^{-2}$
$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$	$K_{H2CO3} = 2.00 \times 10^{-3}$
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	K_{a1}
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	K_{a2}

Fig 4.1 shows the molar fraction of H_2CO_3, HCO_3^- and CO_3^{2-} in a sample of river water at 293K.

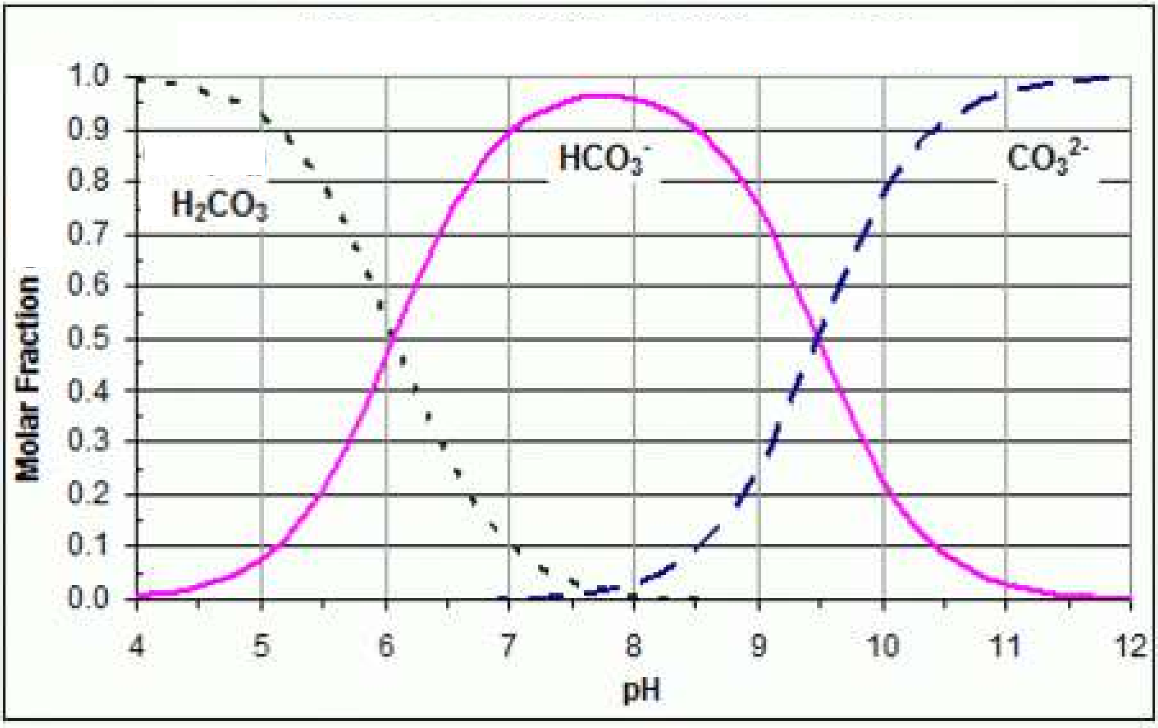


Fig 4.1

(a) **(i)** With reference to Fig 4.1, state the two pH values where the mixture are at its maximum buffering capacity.

pH of maximum buffering capacity : 6 and 9.5 [1]

(ii) Hence deduce the values for K_{a1} and K_{a2}.

pH = pK_{a1} = 6 (where $[H_2CO_3]$ and $[HCO_3^-]$ are equal])
$K_{a1} = 1 \times 10^{-6}$ mol dm^{-3}

pH = pK_{a2} = 9.5 (where $[HCO_3^-]$ and $[CO_3^{2-}]$ are equal])
$K_{a2} = 3.16 \times 10^{-10}$ mol dm^{-3}

[2]

(iii) Explain why the calculated value of K_{a1} is larger than K_{a2}?
It is **easier/less energy required** to dissociate/ give out a **positively charge H^+** ion from a **neutral molecule**, H_2CO_3, than from a negatively charged HCO_3^- ion. Thus position of equilibrium lie more to the right for K_{a1}.

(iv) Aquatic organisms survive within specific pH range.
Suggest with equations, how the hydrogen carbonate and carbonate system in natural water ensures the survival of aquatic organisms.

Large reservoir of CO_3^{2-} neutralises **small amount** of H^+ added.

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ **with full arrow**

Large reservoir of HCO_3^- neutralises **small amount** of OH^- added

$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$ **with full arrow**

Hence **pH of the buffer** solution remains **approximately the same.**

(v) Table 4.1 gives the corresponding component of the gas in atmosphere. Determine the concentration of carbon dioxide in mol dm^{-3} in the atmosphere and hence determine the concentration of carbon dioxide dissolved in pure water at room temperature and pressure.

component in dry air	volume ratio of gas in dry air / ppm
oxygen	209 500
nitrogen	780 840
carbon dioxide	399
argon	9300

Table 4.1

[ppm refers to parts per million]

In 1 dm^3 of air,

$$\text{vol. of } CO_2(g) = \frac{399}{1000000} \times 1 = 3.99 \times 10^{-4} \text{ dm}^3$$

$$\text{amount of } CO_2(g) = \frac{3.99 \times 10^{-4}}{24} = 1.663 \times 10^{-5} \text{ mol}$$

$$\text{concentration of } CO_2(g) = 1.663 \times 10^{-5} \text{ mol dm}^{-3}$$

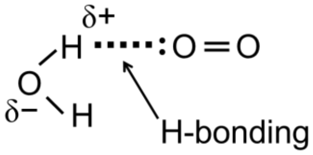
$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{[CO_2(g)]}$$

$$3.44 \times 10^{-2} = \frac{[CO_2(aq)]}{1.663 \times 10^{-5}}$$

$$[CO_2(aq)] = 5.71 \times 10^{-7} \text{ mol dm}^{-3}$$

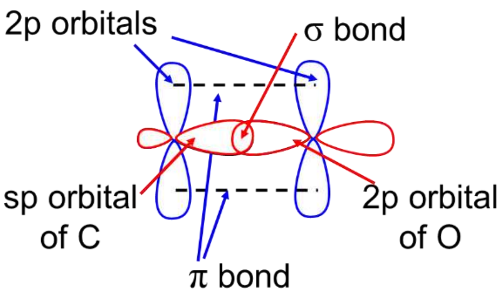
[3]

(vi) The concentration of dissolved O_2 is found to be 2.5×10^{-4} mol dm^{-3}. With the aid of a diagram, show how oxygen can dissolve in water.



- Lone pair electron on oxygen of O_2
- δ+ on H and δ− on O of H_2O
- Label hydrogen bonding between lone pair of O (from O_2) and the δ+ on H [1]

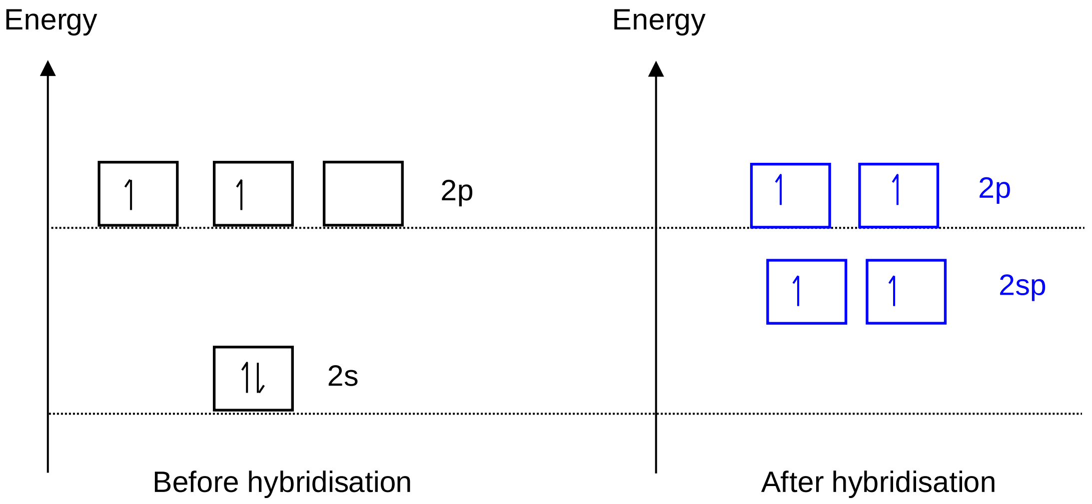
(b) **(i)** Draw the labelled diagram to show the orbitals that form the C=O bond in CO_2, and state the type of hybridisation involved.



sp hybridisation

For your information: O atom in CO_2 is actually sp^2 hybridised. For O atom, sp^2 hybrid orbital is used for sigma bonding and the unhybridised p orbital for pi bonding. However, for A level H2 Chemistry, we only study hybridisation for central atom and we can assume that terminal O atoms do not undergo hybridisation. [2]

(ii) Indicate the energy level of the orbitals involved in the σ(sigma) and π(pi) bonding of CO_2 on the energy level diagram provided. You should use boxes to represent the orbitals and half arrows to represent electrons.



- Correct label of the orbitals
- Energy level of the 2 2sp hybrid orbital in between energy level of p and s orbitals
- Energy of the 2 unhybridised p orbital at the same energy level
- Correct number of electrons in each orbitals. [2]

(c) Calcium carbonate is an important compound that ensures the alkalinity of river water. When calcium carbonate is heated, it decomposes according to the equation below.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of solid $CaCO_3$ to a rigid 1 dm^3 container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100K. As the container was heated, the total pressure of the $CO_2(g)$ in the container was measured over time. The data are plotted in Fig 4.2.

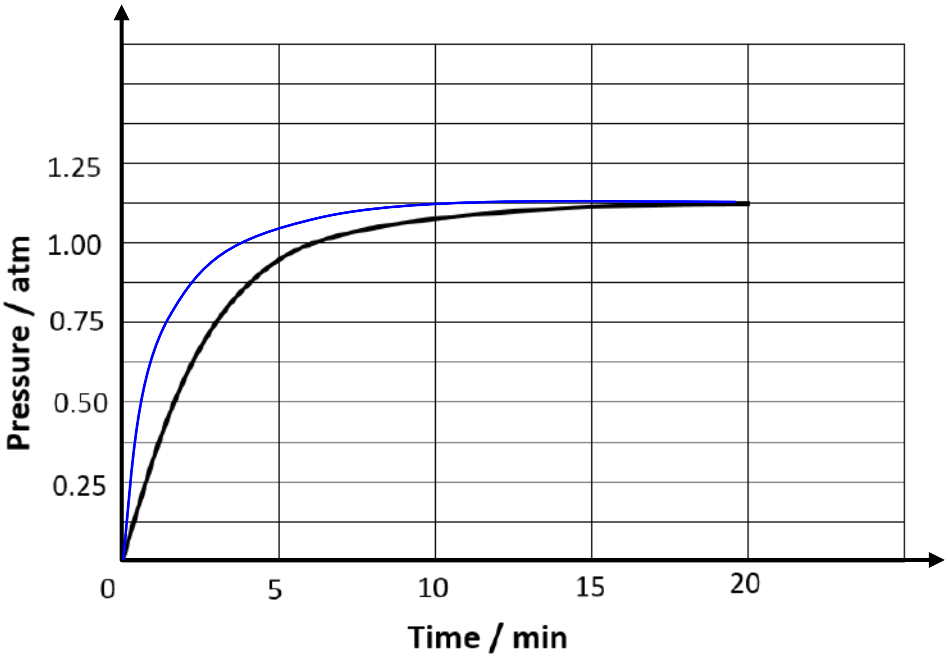


Fig 4.2

(i) The student repeated the experiment, but this time the student crushed another 50.0 g sample of $CaCO_3(s)$ into powdered form. Sketch the resultant graph **on the same axis provided in Fig 4.2**. [1]

steeper gradient but same final pressure

(ii) After 20 minutes, some $CO_2(g)$ was injected into the container, initially raising the pressure to 2.5 atm while keeping the temperature constant. Would the final pressure inside the container be less than, greater than, or equal to its initial pressure at 20 minutes? Explain your reasoning.

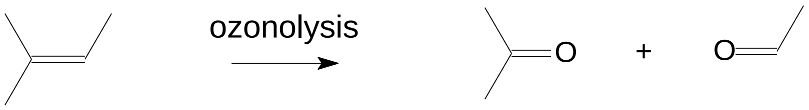
$K_p = P_{CO_2}$

***K_p* changes only when temperature changes**. Since ***K_p* only dependent on P_{CO2} in the equation.** The final pressure after adding more CO_2 will still be **1.125atm / equal to its initial pressure at 20 minutes**.

[2]

[Total : 18]

5 **(a)** Alkene can undergo oxidation with ozone, O_3, to give carbonyl compounds. This reaction is known as *ozonolysis*.



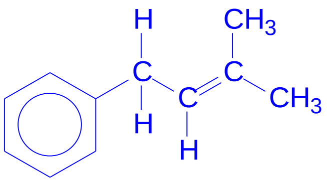
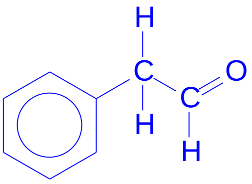
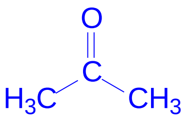
Alkene **J**, $C_{11}H_{14}$, undergoes *ozonolysis* to give compound **K**, C_8H_8O, and compound **L**, C_3H_6O.

Compound **K** gives a brick red precipitate when warmed with alkaline Cu^{2+} tartrate complex.

Compound **L** gives a yellow precipitate when warmed with alkaline I_2.

Alkene **J** gives compound **L** and benzoic acid, $C_6H_5CO_2H$, as the only organic products when heated with acidified $KMnO_4$.

(i) Suggest the structures of compounds **J**, **K** and **L**. [3]

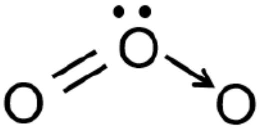
		
Compound **J**	Compound **K**	Compound **L**

(ii) Write an equation for the reaction of alkene **J** with $KMnO_4$, using [O] to represent the oxidising agent.

$C_{11}H_{14} + 6[O] \longrightarrow C_3H_6O + C_6H_5COOH + CO_2 + H_2O$

[1]

(iii) Draw the structure of O_3 to illustrate its shape and show any dative covalent bond it may contain.



bent and dative bond

[1]

For Examiner's Use

(b) Cycloalkenes can undergoes *syn* and *anti* addition as shown in Fig 5.1.

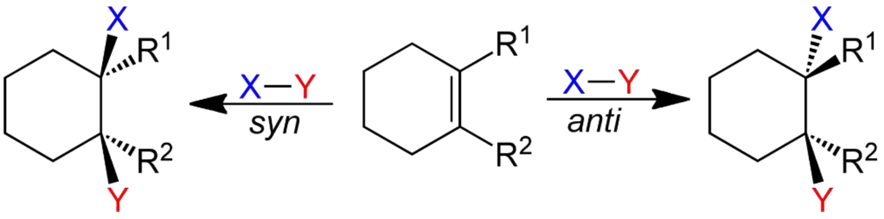
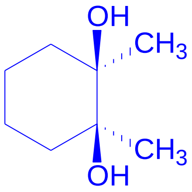
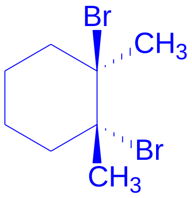


Fig 5.1

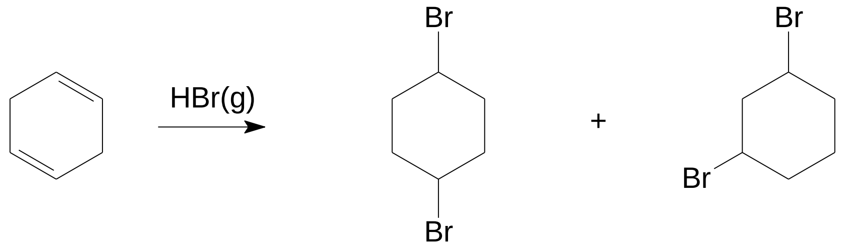
An example of *syn* addition is the oxidation of alkene to diol.
An example of *anti* addition is the bromination of alkene.

Using information from Fig 5.1, suggest the structure of the product for the reaction of 1,2–dimethylcyclohexene with the following reagents.

cold alkaline $KMnO_4$	
Br_2 in CCl_4	

[2]

(c) Fig 5.2 shows the reaction of cyclohexa–1,4–diene with HBr(g).

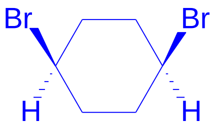
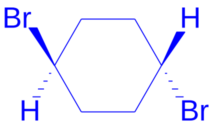


Cyclohexa–1,4,–diene 1,4–dibromocyclohexane 1,3–dibromocyclohexane

Fig 5.2

(i) 1,4–dibromocyclohexane exhibits cis-trans isomerism.

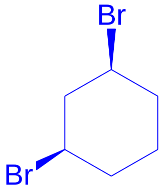
Draw the structures of the stereoisomers.

cis isomer	trans isomer
 	

[2]

(ii) 1,3−dibromocyclohexane contains two chiral carbons. This gives rise to only three stereoisomers, of which two are optically active.

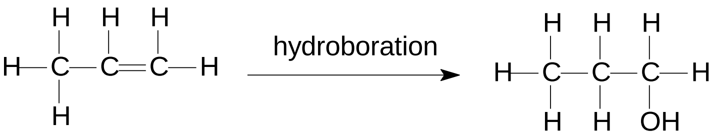
Suggest the structure of the *optically inactive* stereoisomer and explain why it has no optical activity.



This stereoisomer contains an internal plane of symmetry. **The rotation of plane polarised light by each chiral carbon is completely cancelled out by the other chiral carbon.**

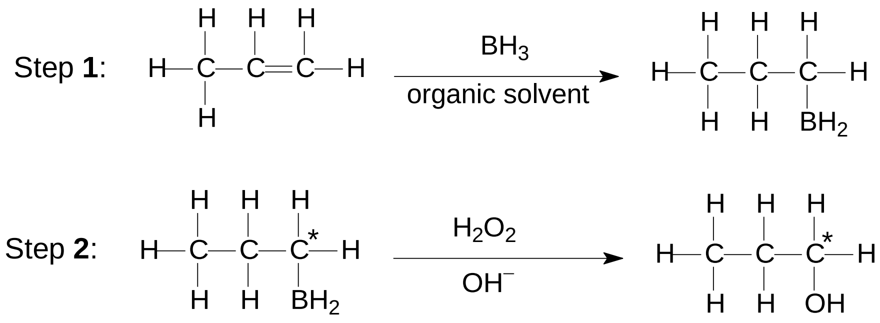
[2]

(d) Hydroboration can be used to convert an alkene to an alcohol.



$$CH_3CH=CH_2 \xrightarrow{\text{hydroboration}} CH_3CH_2CH_2OH$$

Hydroboration involves a two-step reaction as shown in Fig 5.3:



$$\text{Step 1: } CH_3CH=CH_2 \xrightarrow[\text{organic solvent}]{BH_3} CH_3CH_2CH_2BH_2$$

$$\text{Step 2: } CH_3CH_2C^{*}H_2BH_2 \xrightarrow[OH^-]{H_2O_2} CH_3CH_2C^{*}H_2OH$$

compound **Y** compound **Z**

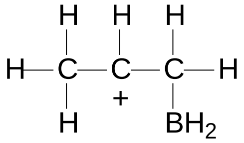
Fig 5.3

The electronegativity data for some elements are given in Table 5.1.

element	B	C	H	O
electronegativity	2.0	2.5	2.1	3.6

Table 5.1

(i) Step **1** is an electrophilic addition reaction. Draw the structure of the carbocation intermediate involved in step **1**.



Note: Based on the data on electronegativity, B is δ+ and H is δ– (B is less electronegative than H). Thus BH_2^+/BH_3 is the electrophile.

[1]

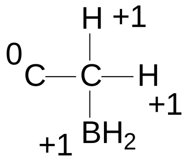
(ii) State the oxidation number of the carbon atoms labelled * in compound **Y** and **Z**, and hence deduce the role of H_2O_2 in step **2**.

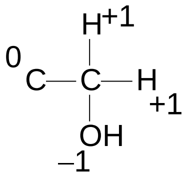
Oxidation number of C* in **Y** is −3

Oxidation number of C* in **Z** is −1

Role of H_2O_2: as oxidising agent

Note:
Oxidation number of C atom in organic compound is obtained by looking at the atoms surrounding the C atom.





H and B atoms are less electronegative than C atom, the single bonded H and B atoms would be assigned an oxidation number of +1 relative to the C atom.
O is more electronegative than C, the single bonded O is assigned O.N of −1 relative to the C.

[2]

[Total : 14]

Suggested Answer for SH2 H2 Chemistry 2019 Prelim Paper 3

Section A

Answer **all** the questions from this section.

1 Potassium is an element found in Period 4 of the Periodic Table.

(a) **(i)** Write an equation for the second ionisation energy of potassium. [1]

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

Must show state symbol

(ii) Fig 1.1 shows the second ionisation energy for the consecutive elements from Period 3 and Period 4.

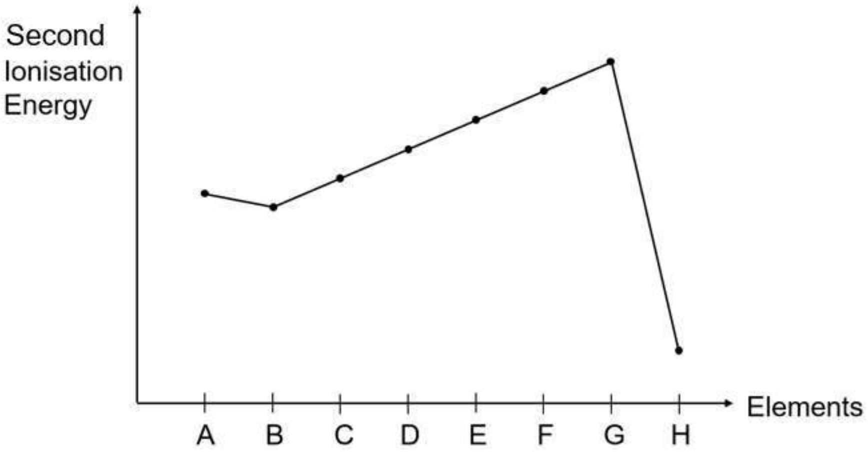


Fig 1.1

Suggest which of the above elements, **A** to **H**, is potassium. [2]

The second electron of potassium is removed from the **3p subshell (inner quantum shell)** as compared to the second electron of calcium which is removed from the **4s subshell (outer quantum shell)**. **Much more energy is required** to remove the second electron from K as compared to Ca. Hence **element G is potassium**.

Note: It is insufficient to mention that 2nd I.E. of K is much higher than 1st I.E. as the comparison with 1st I.E. is not reflected in Fig 1.1

(b) When 0.400 g of potassium dichromate(VI), $K_2Cr_2O_7$, was heated using a strong flame, a yellowish green solid mixture was obtained and a gas was evolved. The gas collected ignited a glowing splint. Upon adding water to the yellowish green solid, part of the solid dissolved to give a yellow solution of K_2CrO_4, leaving a green solid.

(i) State the identity of the gas. [1]

Oxygen gas.

(ii) The green solid that remained was collected and dried. It weighed 0.052 g and was found to be 68.4% chromium by mass and contains only chromium and oxygen.

Determine the chemical formula of the green solid. [2]

	Cr	O
Mass	$\frac{68.4}{100} \times 0.052 =$ 0.03557	$\frac{31.6}{100} \times 0.052 =$ 0.01643
A_r	52.0	16.0
Moles	0.000684	0.001027
÷ by smallest no.	1	1.5
Mol ratio	2	3

Hence chemical formula is Cr_2O_3

(iii) Using your answers to **b(i)** and **b(ii)**, write the equation for the decomposition of potassium dichromate(VI). [1]

$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

(c) State **two** physical properties of chromium that differs from calcium.
Explain the reasons for those differences. [2]

TM has **higher density** due to **larger atomic mass and smaller radius giving rise to dense close-packed structure** (allowing more small size but heavy atoms to be packed within a specific volume.)

TM has **higher melting point** due to **more delocalised electrons contributed from 3d and 4s subshells**, resulting in **stronger metallic bonding**.

TM has **higher electrical/heat conductivities** due to **more delocalised electrons contributed from 3d and 4s subshells**.

Note: Variable oxidation states and reactions to give coloured complexes are **chemical** properties.

(d) Vanadate(V) ion, VO_3^-, changes into pale yellow oxovanadium(V) ions, VO_2^+, when acid is added. Upon addition of excess zinc, the pale yellow solution changes to blue, to green and finally to violet.

(i) With the aid of an equation, explain the type of reaction that occurs when vanadate(V) ion changes into oxovanadium(V) ions. [2]

$VO_3^- + 2H^+ \rightarrow VO_2^+ + H_2O$

Acid-base reaction

(ii) Explain why vanadium is able to exhibit variable oxidation states. [1]

Because of the **close proximity** in energy of the 4s and 3d electron in V, it is able to **lose electrons from both the 3d and 4s subshells**, hence it can exhibit variable oxidation states.

(iii) With the aid of the *Data Booklet*, deduce the final oxidation state of vanadium in the violet solution. [3]

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^\ominus = -0.76\ V$

$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \quad E^\ominus = +1.00\ V$

Reaction between VO_2^+ and Zn,

$E^\ominus = +1.00 - (-0.76)$

$= +1.76\ V > 0$ (reaction is feasible)

$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O \quad E^\ominus = +0.34\ V$

Reaction between VO^{2+} and Zn,

$E^\ominus = +0.34 - (-0.76)$

$= +1.10\ V > 0$ (reaction is feasible)

$V^{3+} + e^- \rightleftharpoons V^{2+} \quad E^\ominus = -0.26\ V$

Reaction between V^{3+} and Zn,

$E^\ominus = -0.26 - (-0.76)$

$= +0.50\ V > 0$ (reaction is feasible)

$V^{2+} + 2e \rightleftharpoons V \quad E^\ominus = -1.20\ V$

Reaction between V^{2+} and Zn,

$E^\ominus = -1.20 - (-0.76)$

$= -0.44\ V < 0$ (reaction is NOT feasible)

Hence final oxidation state of V is +2

Note: It is important to show that V^{2+} do not undergo further reduction when excess Zn is present.

Solid vanadium(V) oxide, V_2O_5, is used as a catalyst for reaction 1.

reaction 1: $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

(iv) State the type of catalysis and outline the mode of action when V_2O_5 is used for reaction 1. [3]

Heterogeneous catalysis is involved in the reaction:

Reactants are **adsorbed** on the surface of the catalyst; the reactant molecules are **brought closer together with correct orientation** and the **bonds to be broken are weakened, thus E_a for the reaction is lowered**.

The products formed **desorb** and leave the surface of the catalyst.

(v) NO_2 can also act as a catalyst for reaction 1.

Write two equations to show how NO_2 acts as a catalyst in reaction 1. [2]

$NO_2 + SO_2 \rightarrow SO_3 + NO$

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

Note: Eqns can be found under Org Book 1 > Alkane > Environmental pollutants. NO_2 is acting as a homogeneous catalyst and it should produce a gaseous intermediate during catalysis.

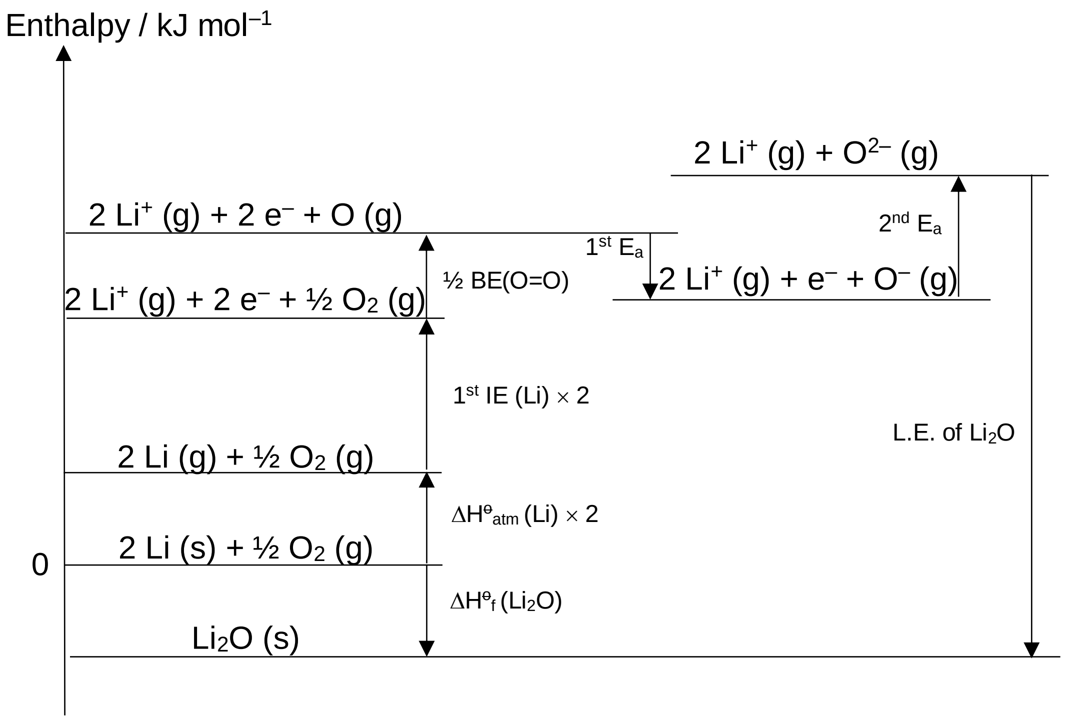
[Total : 20]

2 Lithium oxide, Li_2O, is used in traditional ceramic glazing to create a blue hue with copper on ceramics.

(a) Using the data below and any appropriate data from the *Data Booklet*, construct a labelled energy level diagram to calculate the standard enthalpy change of formation of $Li_2O(s)$.

	/ kJ mol^{-1}
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
lattice energy of lithium oxide	–2863
standard enthalpy change of atomisation of lithium	+159

[5]



- **State symbol**
- **Balanced equation**
- **Correct enthalpy change**

By Hess' Law,

$\Delta H^{\circ}_{f}(Li_2O) = 2[\Delta H^{\circ}_{atm}(Li)] + 2[1^{st}\ IE\ (Li)] + \Delta H_{atm}(O_2) + 1^{st}\ E_a\ (O) + 2^{nd}\ Ea\ (O) + L.E.$

$= 2(+159) + 2(+519) + ½\ (+496) + (–141) + (+798) + (–2863)$

$= –602$ kJ mol^{-1}

(b) Lithium oxide is produced during the thermal decomposition of lithium peroxide, Li_2O_2, at 450 °C.

$$Li_2O_2(l) \longrightarrow Li_2O(s) + \frac{1}{2}O_2(g)$$

(i) Given that the standard enthalpy change of formation of $Li_2O_2(l)$ is –606 kJ mol^{-1} and using your answer in **(a)**, calculate the enthalpy change for the thermal decomposition of Li_2O_2. [1]

enthalpy change for the thermal decomposition of Li_2O_2

$= \sum\Delta H^\ominus_f$ (products) – $\sum\Delta H^\ominus_f$ (reactants)

$= \Delta H^\ominus_f (Li_2O) + \Delta H_f (O_2) - \Delta H^\ominus_f (Li_2O)$

$= (-602) + 0 - (-606)$

$= +4$ kJ mol^{-1}

(ii) Explain why the thermal decomposition of Li_2O_2 is feasible. [2]

$\Delta G = \Delta H - T\Delta S$

The increase in the entropy ($\Delta S > 0$) from the production of O_2 gas and the elevated temperature readily offset the slightly endothermic enthalpy change causing ΔG to be negative, hence the reaction is feasible.

(c) Table 2.1 gives the melting points of two lithium ionic compounds.

compound	melting point / °C
Li_2O	1400
Li_2O_2	195

Table 2.1

Explain the difference in the melting points. [2]

$|L.E| \propto \frac{q_+ \times q_-}{r_+ + r_-}$

Both Li_2O and Li_2O_2 have the **same Li^+ cation**, but different anion. Since $\mathbf{O_2^{2-}}$ in Li_2O_2 has a **larger ionic radius** as compared to the $\mathbf{O^{2-}}$ in Li_2O with a **smaller ionic radius**, the **magnitude of the lattice energy of Li_2O_2** is **smaller** **(or lattice energy of Li_2O_2 is less exothermic)** than that of Li_2O. Hence, **less energy is need to overcome the weaker ionic bond** in Li_2O_2 resulting in lower melting point.

(d) Similar to lithium peroxide, Li_2O_2, lithium nitrate, $LiNO_3(s)$, undergoes thermal decomposition to produce oxygen and a brown gas.

(i) Write a balance equation, with state symbols, for the thermal decomposition of lithium nitrate. [2]

$2LiNO_3(s) \rightarrow Li_2O(s) + 2NO_2(g) + ½O_2(g)$

(ii) Among the Group 1 metal nitrates, only lithium nitrate undergoes thermal decomposition.

Explain why lithium nitrate can undergo thermal decomposition. [2]

Although Li$^+$ ion has a singly positively charge, but it has the **smallest ionic radius** among the Group 1 metal ions. Therefore, Li$^+$ ion, with a **high** $\frac{\textbf{charge}}{\textbf{size}}$ **ratio, polarises/distorts the electron cloud of NO$_3^-$ anion** and **weakens the N–O bond** in NO$_3^-$. Hence, LiNO$_3$ undergoes thermal decomposition, but not other Group 1 metal nitrate.

(e) Ethylenediamine tetraacetate, [EDTA]$^{4-}$, is a chelating agent that is widely used to remove transition metal ions such as copper(II) ions from aqueous solutions.

(i) Suggest a synthesis of ethylenediamine tetraacetate, [EDTA]$^{4-}$, starting from methanal and 1,2−diaminoethane ($NH_2CH_2CH_2NH_2$), according to the scheme in Fig. 2.1. Deduce the structure of compound **A**. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

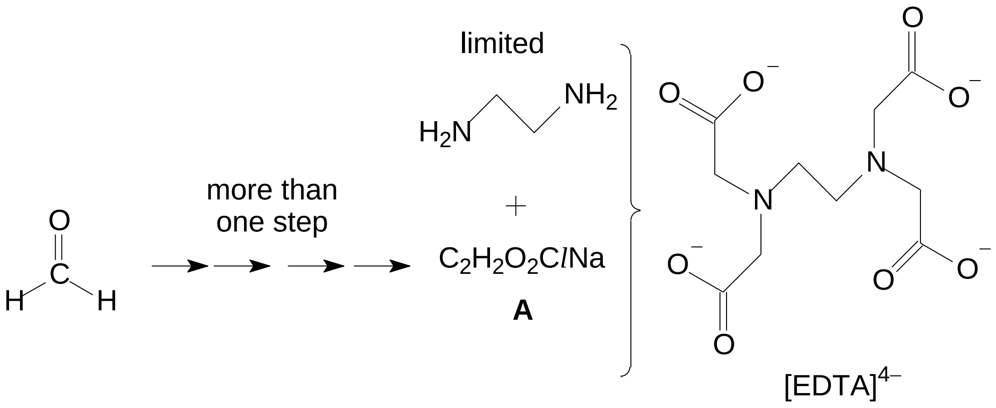
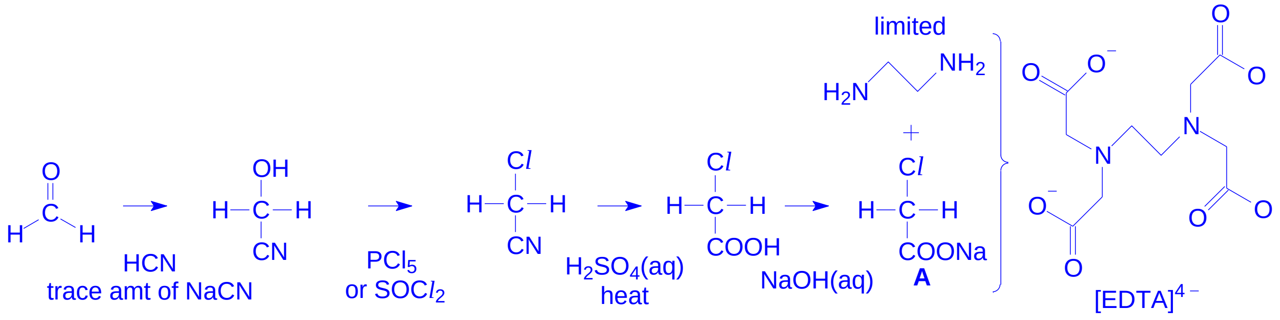


Fig 2.1

[5]



(ii) When aqueous ammonia is added to a solution of $CuSO_4$, a blue precipitate is formed which dissolves in excess aqueous ammonia to give a deep blue solution. On addition of $Na_4(EDTA)$ solid to the mixture, the colour of the solution turns light blue.

Suggest explanations for the above observations, writing equations as appropriate. [3]

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Precipitation of $Cu(OH)_2(s)$ occurs.

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$ ---- Eqm (1)

blue soln   blue ppt

Blue ppt dissolves due to formation of tetraamine copper(II) complex

$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$

blue ppt   deep blue

or

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$

deep blue

$[Cu(H_2O)_6]^{2+}$decreases causing the eqm (1) to shift left and $Cu(OH)_2$ (s) dissolves.

Ligand exchange results in the deep blue solution turning to light blue

$[Cu(NH_3)_4]^{2+}(aq) + [EDTA]^{4-}(aq) \rightleftharpoons [Cu(EDTA)]^{2-}(aq) + 4NH_3(aq)$

deep blue soln   light blue soln

[Total : 22]

3 **(a)** Phenol is a white crystalline solid that is volatile. It is mildly acidic and requires careful handling as it can cause chemical burns.

Table 3.1 shows the physical properties for phenol and its derivatives.

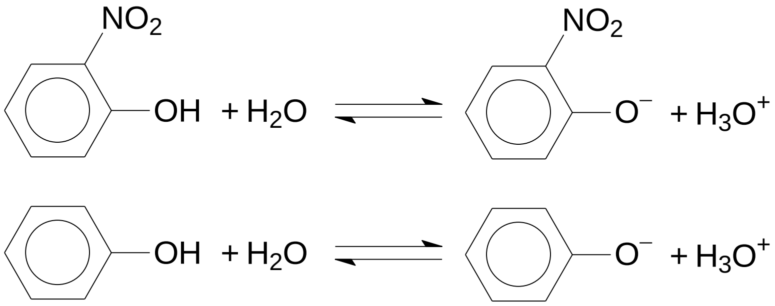
compound	melting point / °C	K_a / mol dm^{-3}
phenol	41	1.12×10^{-10}
2−nitrophenol	46	5.89×10^{-8}
4−nitrophenol	114	7.08×10^{-8}

Table 3.1

(i) Explain the difference in melting points between 2−nitrophenol and 4−nitrophenol. [2]

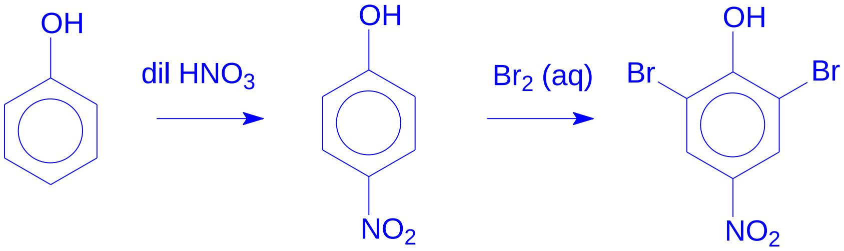
2−nitrophenol can exhibit **intramolecular H-bonding** and hence there are **less extensive intermolecular H-bonding** as compared to 4−nitrophenol. **Less energy is needed to overcome the weaker intermolecular forces of attractions between molecules of 2−nitrophenol**, hence its melting point is lower than 4−nitrophenol.

(ii) Explain the difference in the acidities of phenol and 2−nitrophenol. [2]



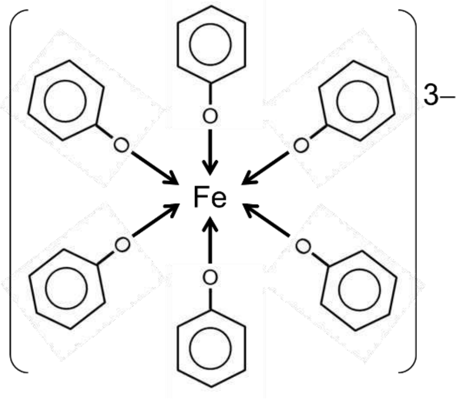
Electron-withdrawing –NO_2 groups decrease the intensity of the negative charge/disperse negative charge on the conjugate base and **stabilises it**, thus the **dissociation** of 2−nitrophenol into H^+ and conjugate base is **more favourable (or position of equilibrium shifts to the right)**. Hence 2−nitrophenol is more acidic than phenol.

(iii) Suggest how 2,6−dibromo−4−nitrophenol can be synthesised from phenol in a 2−step synthesis. In your synthesis, you should state the reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. [3]



(b) When aqueous neutral $FeCl_3$ is added to a solution containing phenol, a violet solution containing the complex ion $[Fe(C_6H_5O)_6]^{3-}$ is formed.

(i) Draw the structure of the complex ion. [1]

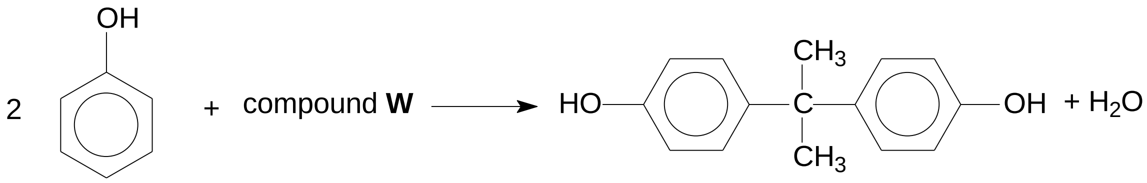


(ii) The violet complex ion $[Fe(C_6H_5O)_6]^{3-}$ is not observed in **both** acidic and alkaline solutions. Suggest explanations for the above observation. [2]

In acidic solution, the **phenoxide ligands gain H^+** to become phenol, there are no phenoxide ligands.

In alkaline solution, Fe^{3+} would react with OH^- to **give $Fe(OH)_3$ red brown ppt instead.**

(c) Phenol can react with compound **W** under suitable conditions to give bisphenol-A (BPA).



BPA

The use of the table of characteristic infra-red absorption frequencies for some selected bonds in the *Data Booklet* is relevant to this question.

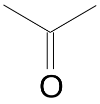
Infra-red absorptions can be used to identity functional groups in organic compounds. For example, phenol shows absorption at 3200−3600 cm^{-1} due to the O−H bond.

The analysis of compound **W** shows absorptions at 1670−1740 cm^{-1}.

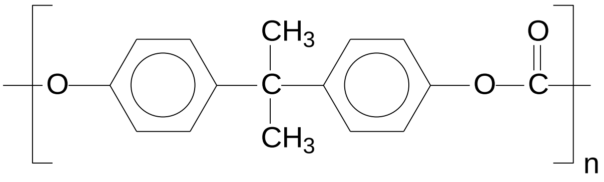
Identify the bond present in compound **W** and suggest its structure. [2]

Bond present is C=O

Based on the balanced equation, we can conclude that compound **W** has molecular formula of C_3H_6O. Compound **W** is propanone.



(d) BPA can react with another monomer **X** to produce polycarbonates. Polycarbonates are commonly used in the manufacturing of water bottles.

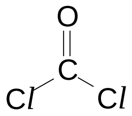


polycarbonates

(i) Identify the new functional group formed in the polycarbonates. [1]

Ester

(ii) Suggest the structure of monomer **X**. [1]



Note: Phenol reacts with acyl chloride to form ester

(iii) Research has shown that BPA can leach into beverages from the polycarbonate water bottles under certain conditions. Exposure to BPA is a concern because of possible health effects of BPA on the brain.

Discuss whether it is safe to consume cold lemon juice stored in a polycarbonate water bottle. [1]
Yes it is likely to be safe. **Complete hydrolysis of polymer into monomer BPA did not occur** and it would require **presence of concentrated acid and heating at high temperature.**

OR

No it is unsafe, eventhough rate of hydrolysis is slow, **some hydrolysis might occur and small amount of BPA** could be released into the lemon juice.

(e) BPA can react with epoxides to form epoxy resins. Fig 3.1 shows the simplified equations for the reaction.

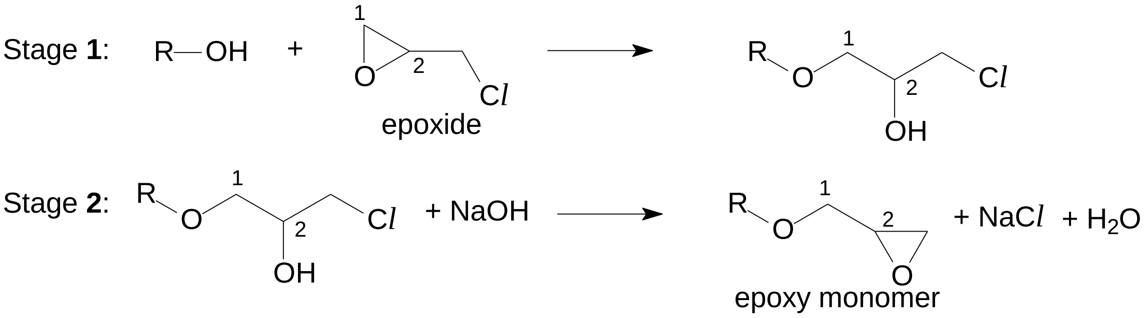


Fig 3.1

(i) For stage **1**, the phenol group of BPA acts as the nucleophile. Suggest why the nucleophile attacks C^1 instead of C^2. [1]
C^1 is less steric hindered than C^2.

(ii) For stage **2**, state the type of reaction and the role of NaOH in the reaction. [2]

Nucleophilic substitution

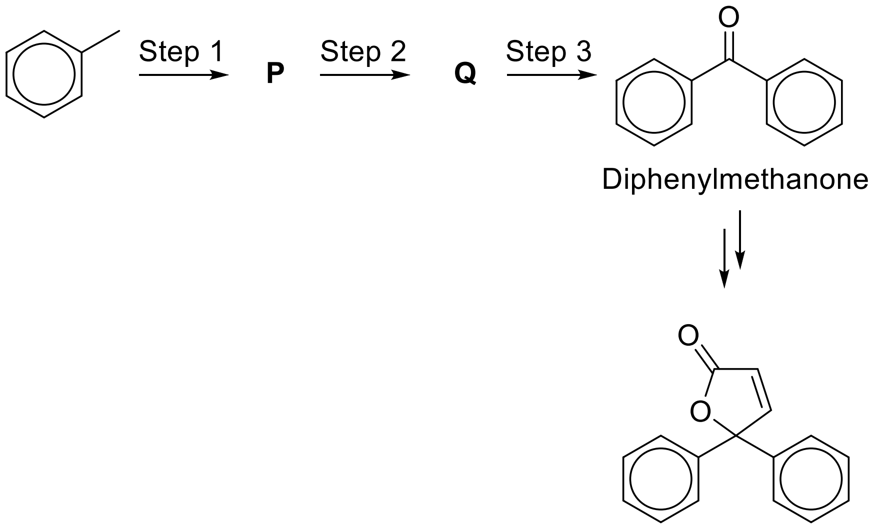
NaOH acts as a base.

[Total : 18]

Section B

Answer **one** question from this section.

4 **(a)** Diphenylmethanone can be synthesized from methylbenzene in three steps as shown in Fig 4.1.



Compound **R**

Fig 4.1

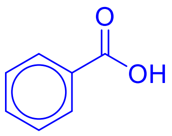
(i) Suggest the reagents and conditions for steps **1**, **2** and **3**, and draw the structures for compounds **P** and **Q**. [5]

Step 1: $KMnO_4$, H_2SO_4(aq), heat

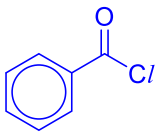
Step 2: anhydrous $SOCl_2$ or anhydrous PCl_3 or anhydrous PCl_5

Step 3: anhydrous $FeCl_3$, benzene

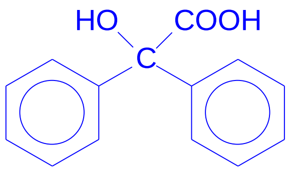
P:



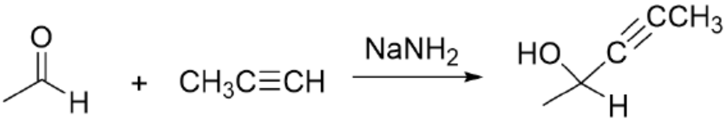
Q:



(ii) When compound **R** is heated with acidified $KMnO_4$, compound **S** is formed as the only organic product. Suggest the structure of compound **S**. [1]



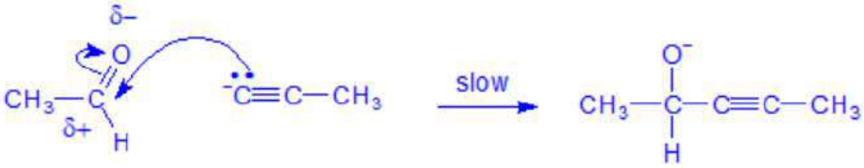
(b) Propyne, $CH_3C{\equiv}CH$, is a weak acid. It can react with an aldehyde in the presence of trace amount of strong base such as $NaNH_2$.



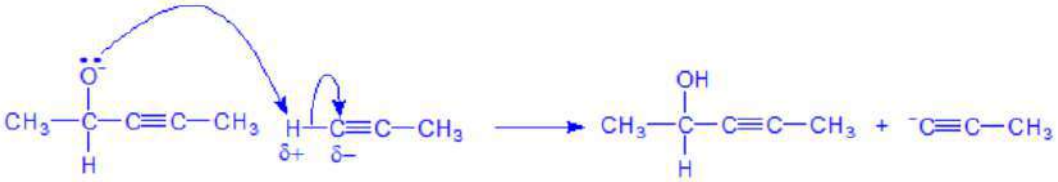
When propyne reacts with NH_2^-, propynyl ion, $CH_3C{\equiv}C^-$ is formed.

(i) State the type of reaction that occurred between propyne and ethanal. [1]
Nucleophilic addition

(ii) Describe the mechanism for this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]
Step 1:



Step 2:



(iii) Suggest if the organic product formed from this reaction would rotate plane−polarised light. [2]
Trigonal planar carbonyl C is **attacked by the nucleophile from either side of the plane with equal probability**. The **two enantiomers are formed in equal amount**. The product is a racemic mixture where the **rotation of plane−polarised light by one enantiomer is completely cancelled out by the other enantiomer**. Hence the organic product formed **would not rotate plane−polarised light.**

(c) The mechanism for the reaction between compounds **T** and **U** is as shown.

Step 1: $\mathbf{T} + \mathbf{U} \rightleftharpoons \mathbf{V}$
Step 2: $\mathbf{T} + \mathbf{V} \rightarrow \mathbf{W}$ (slow)

(i) Write a balanced overall equation for the reaction between compounds **T** and **U**. [1]
$2\mathbf{T} + \mathbf{U} \longrightarrow \mathbf{W}$

(ii) Write an expression for K_c for step 1, stating its units. [2]
$K_c = \frac{[V]}{[T][U]}$ units = $mol^{-1}dm^3$

(iii) Using the information given in the question and your answer to **c(ii)**, derive the rate equation for the reaction between compounds **T** and **U**. [2]

$[V] = K_c[T][U]$

Rate = $k[T][V]$

$= k[T](K_c[T][U]) = kK_c[T]^2[U]$ or $k'[T]^2[U]$

(iv) A concentration−time graph was plotted for step 1 as shown in Fig 4.2. Equilibrium was established at t_0. At t_1, a change was introduced.

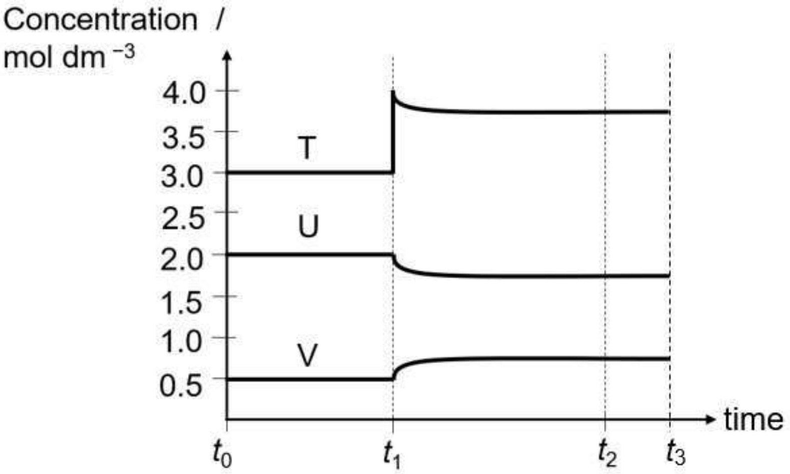


Fig 4.2

State the change that occurred at t_1. Explain the trend observed in the graph from t_1 to t_2. [2]

Concentration of **T** was increased at t_1.

By Le Chatelier's Principle, the equilibrium position will shift to the right to partially decrease the concentration of **T** and **U** and cause partial increase in concentration of **V**.

(v) Suggest whether there would be any change in the individual concentrations of compounds **T**, **U** and **V** when a catalyst is added to the reaction mixture at t_3. [2]

Catalyst increases both the rate of forward and backward reaction by the same extent but not the equilibrium position. Hence, there will be no change in K_c. The proportion of compound T, U and V remains unchanged.

[Total : 20]

5 (a) Describe and explain the variation in volatility of the elements in Group 17. [2]

Down the Group, *volatility* of the halogens *decreases*.

Cl_2, Br_2 and I_2 are non-polar molecules with weak temporary dipole- induced dipole interactions (td-id) between the molecules.

Down the Group, the total no. of electrons in the molecules or relative molecular mass increases, size of electron cloud increases and is thus more easily distorted.

Increasing amount of energy is required to overcome the increasingly stronger td-id intermolecular forces.

(b) *Use of the Data Booklet is relevant to this question.*

Explain the following observations in terms of the relative thermal stabilities of the hydrides of the Group 17 elements.

compound	HC*l*	HBr	HI
decomposition behaviour	does not decompose even on strong heating	strong heating yields reddish brown fumes of Br_2	purple fumes of I_2 obtained when red-hot rod is plunged into jar of HI

[2]

Thermal stability of the hydrogen halides decreases down the Group.
The thermal stability of the hydrogen halide depends on the strength of the **H-X bond**.
BE(H−C*l*) = 431 kJ mol^{-1}, BE(H−Br) = 366 kJ mol^{-1}, BE(H−I) = 298 kJ mol^{-1}.
and hence less energy is needed to overcome the bond and the HX decomposes more readily.

(c) State and explain the observations when separate solutions of chloride and iodide ions are mixed with aqueous silver nitrate, followed by excess aqueous ammonia. [3]
White AgC*l* ppt, soluble in excess NH_3
Yellow AgI ppt, insoluble in excess NH_3

In the presence of excess NH_3, $Ag^+(aq)$ forms complex with NH_3, thus decreasing $[Ag^+]$.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \text{ ....(1)}$$

When $[Ag^+]$ decreases, ionic products for silver chloride & silver iodide decrease, but since silver chloride has a larger K_{sp} than silver iodide, ionic product of silver chloride becomes less than its K_{sp} and it dissolves in aqueous ammonia while silver iodide does not.

(d) Carbon monoxide in a sample of polluted air can readily be determined by passing through solid iodine(V) oxide, I_2O_5, to give carbon dioxide and iodine.

(i) Write a balanced equation for the reaction between carbon monoxide and iodine(V) oxide. [1]
$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$

(ii) The iodine produced is dissolved in a suitable solvent and titrated with aqueous sodium thiosulfate, $Na_2S_2O_3$.

1 dm^3 sample of air produced iodine that required 20.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate to discharge the iodine colour.

Calculate the mass of carbon monoxide in this sample of polluted air. [2]

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

No. of moles of $S_2O_3^{2-} = 0.10 \times \frac{20}{1000}$

$= 2.00 \times 10^{-3}$

$2S_2O_3^{2-} \equiv I_2 \equiv 5CO$

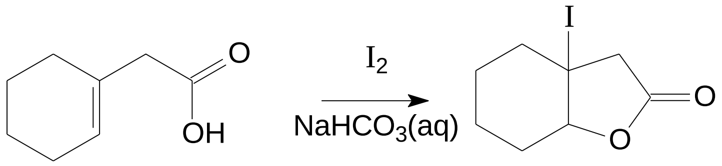
No. of moles of $I_2 = 1.00 \times 10^{-3}$

No. of moles of $CO = 5.00 \times 10^{-3}$

Mass of CO $= 5.00 \times 10^{-3} \times 28.0$

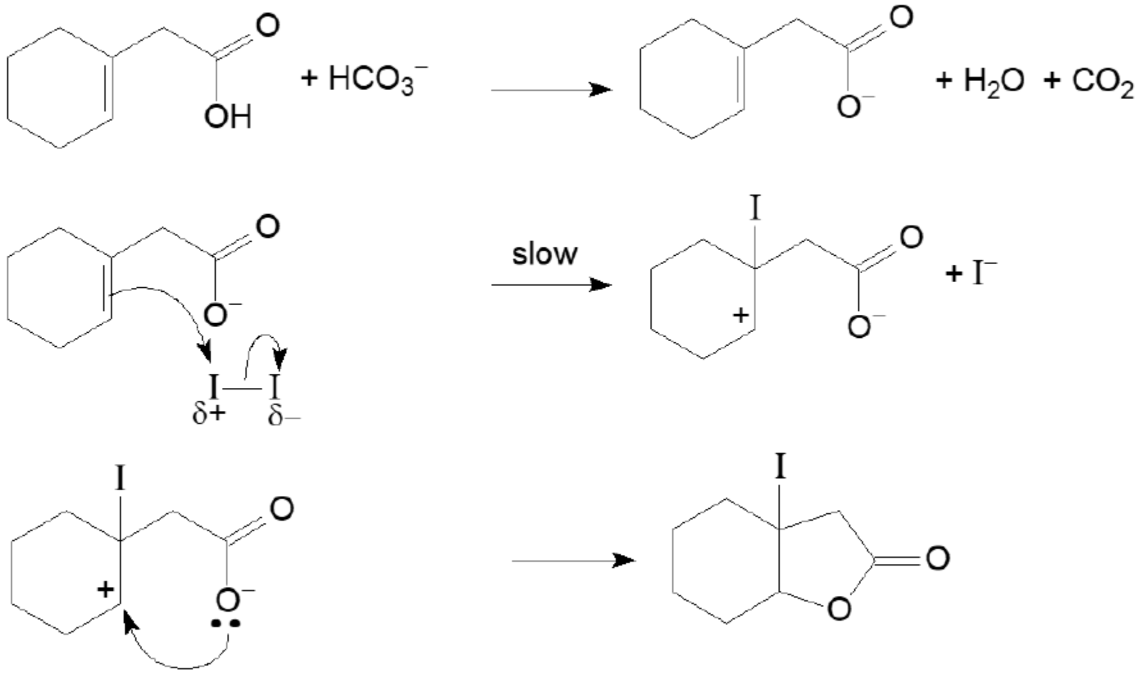
$= 0.140$ g

(e) In the presence of aqueous sodium hydrogencarbonate, iodine does not add across the C=C bond of compound **D** as might be expected. Instead, the following reaction occurs.

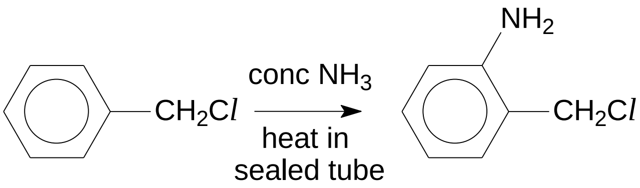


compound **D**

The first step of the mechanism involves a fast acid-carbonate reaction. Describe the mechanism for this electrophilic addition reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]



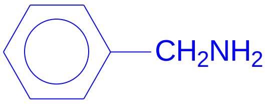
(f) A student attempted to make compound **E** from (chloromethyl)benzene as shown.



(chloromethyl)benzene compound **E**

However, a different product with molecular formula C_7H_9N was obtained.

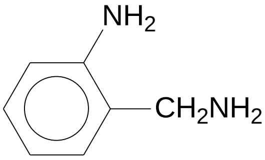
(i) Draw the displayed formula of the product obtained from the reaction. [1]



(ii) Explain why compound **E** was not obtained. [1]

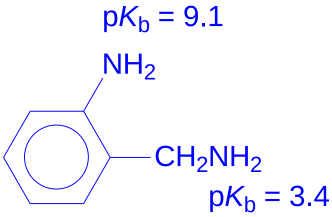
NH_3 is an electron rich nucleophile. NH_3 undergoes nucleophilic substitution at C-C*l* bond instead of attacking the electron rich benzene ring for electrophilic substitution.

(g) The pK_b values of the two amine groups in compound **F** are 3.4 and 9.1.



compound **F**

(i) Copy the structure of compound **F** to your answer booklet and assign the pK_b values to the two amine groups. Explain your answer. [2]



Phenylamine is a weaker base with higher pK_b value. The lone pair electron on N is delocalized into the π electron cloud of the benzene ring. Hence the N atom is less likely to accept an H^+.

(ii) Calculate the initial pH of 0.100 mol dm^{-3} of compound **F**. [2]

Let compound F be **B**

pK_b = 3.4 => $K_b = 10^{-3.4}$

Method 1: Weak base, use ICE and K_b to calculate OH^- dissociated

	B	+ H_2O	$\rightleftharpoons$	BH^+	+ OH^-
Initial / mol dm^{-3}	0.1	-		0	0
Change / mol dm^{-3}	$-x$	-		$+x$	$+x$
Eqm / mol dm^{-3}	$0.1 - x$	-		x	x

$$\text{Base dissociation constant, } K_b = \frac{[BH^+][OH^-]}{[B]} = 10^{-3.4}$$

$$\frac{x^2}{0.1-x} = 10^{-3.4}$$

Since B is a weak base, x << 0.1 and we can assume that $(0.1 - x) \approx 0.1$

$$\frac{x^2}{0.1} = 10^{-3.4}$$

x = 0.006310 mol dm^{-3} = $[OH^-]_{eqm}$

pOH = 2.20

pH = 14 – 2.20 = **11.80 (2d.p.)**

Method 2: Weak base, use formula to calculate OH^- dissociated

Weak base,

$[OH^-] = \sqrt{K_b \times [weak\ base]} = \sqrt{10^{-3.4} \times 0.10}$

$[OH^-]$ = 0.006310 mol dm^{-3}

pOH = 2.20

pH = 14 – 2.20 = **11.80 (2d.p.)**

(h) Explain the observations when Br_2(aq) is added to the two samples.

sample	phenylamine	phenylamine dissolved in excess sulfuric acid
observations	orange Br_2 (aq) decolourises and white precipitate forms	orange Br_2 (aq) remains

[2]

Phenylamine undergoes electrophilic substitution with Br_2(aq) as N atom **donates lone pair of electrons into the ring (OR $-NH_2$ is a strong activating group)** which increases the electron density of the benzene ring, making it more susceptible to the electrophilic attack.

White ppt of 2,4,6-tribromophenylamine is produced.

In the presence of sulfuric acid, $-NH_2$ group, a base, **is protonated to form $-NH_3^+$** (which is a deactivating group), hence the **benzene ring is no longer activated** and cannot react with Br_2(aq).

NATIONAL JUNIOR COLLEGE
SH 2 Year – End Practical Examination
Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY 9729/04

Paper 4 Practical
Candidate answer on the Question paper.

Tuesday 20 August 2019
2 hours 30 minutes

READ THE INSTRUCTIONS FIRST
Write your identification number and name. Circle 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, 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.

At the end of the examination, submit the question paper.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift		
1	**2**	**3**

Laboratory			
CM41	**CM42**	**CM43**	**CM44**
PH31	**PH32**	**PH33**	
BI23	**BI24**		

For Examiner's Use	
1	**/ 12**
2	**/ 21**
3	**/ 14**
4	**/ 8**
Total	**/ 55**

This document consists of **19** printed pages and **1** blank page.

1 Determination of the solubility product of calcium iodate(V)

When solid calcium iodate(V) is added to water to form a saturated solution, an equilibrium between the undissolved salt and its aqueous ions is established.

$$Ca(IO_3)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2IO_3^-\,(aq)$$

The solubility product, K_{sp} , of calcium iodate(V) is expressed as follows.

$$K_{sp} = [Ca^{2+}(aq)]\,[IO_3^-(aq)]^2$$

The solubility product can be found by determining the equilibrium concentration of IO_3^- ions in a saturated solution of calcium iodate(V) through a redox titration.

Iodate(V) ions, IO_3^-, react with iodide ions according to the following equation.

$$IO_3^-\,(aq) + 5I^-(aq) + 6H^+\,(aq) \longrightarrow 3I_2\,(aq) + 3H_2O\,(l)$$

The iodine produced in this reaction may be titrated against sodium thiosulfate using starch solution as indicator. Thiosulfate ions react with iodine according to the following equation:

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

In this question, you will prepare a saturated solution of calcium iodate(V) to carry out the redox titration. Using the experimental results, you will determine the solubility product of calcium iodate(V).

You are provided with:
FA 1 is solid calcium iodate(V), $Ca(IO_3)_2$

FA 2 is 0.05 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$

FA 3 is 0.50 mol dm^{-3} potassium iodide, KI

FA 4 is 0.50 mol dm^{-3} sulfuric acid, H_2SO_4

FA 5 is starch indicator

Preparation of a saturated solution of calcium iodate (V), FA 6

(a) Procedure

1. Use a 100 cm^3 measuring cylinder to transfer 80.0 cm^3 of deionised water into a 250 cm^3 beaker.
2. Transfer all **FA 1** from the weighing bottle into the beaker. Stir for 1 to 2 minutes and leave to stand for **5 minutes**. There will be some $Ca(IO_3)_2$ solids left undissolved.
3. Use a 0.2 °C division thermometer, record the temperature of the solution in the beaker.
4. To remove the undissolved solids, filter the saturated solution into another clean and **dry** 250 cm^3 beaker using a **dry** filter paper and **dry** funnel. Label this solution as **FA 6**.

Titration

(b) **Procedure**

(i) **1.** Fill a burette with **FA 2**.

2. Pipette 10.0 cm^3 of **FA 6** into a conical flask.

3. Use a 10 cm^3 measuring cylinder to add 5.0 cm^3 of **FA 3**, followed by 5.0 cm^3 of **FA 4** to the same conical flask and swirl quickly.

4. Titrate the iodine in the conical flask with **FA 2** until the brown colour of the iodine becomes pale yellow.

5. Add about 10 drops of starch solution to the flask and continue adding **FA 2** 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

Temperature of the solution in the beaker = ………….. °C

	1	**2**	
Final burette reading / cm^3			
Initial burette reading / cm^3			
Volume of FA 2 used / cm^3			

[1]Record the temperature of the solution in the beaker
[1] Records all burette readings to 2 d.p including a(ii). (MMO)
[1] Has at least 2 titre values ± 0.10 cm^3 (MMO)
[1] Table has appropriate headings and units (PDO)

[-1] Incorrect calculation for volume of FA2

[4]

(ii) From your titres, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

Average vol of **FA 2** used = (x.00 +.00)/2 =x.00 cm^3 (round to 2 d.p.) **[1]**

* Do not award marks if inconsistent values used
* Do penalise if no working

10.0 cm^3 of **FA 6** produced an amount of iodine which required ……...… cm^3 of **FA 2**.
[1]

(c) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** part.

(i) Calculate the number of moles of $S_2O_3^{2-}$ in the volume of **FA 2** recorded in **b(ii)**, and hence determine the molar concentration of IO_3^- ions in **FA 6**.

Amt of $S_2O_3^{2-}$ = (ans from b(ii)/1000) x 0.05 = A mol **[1]**

$$\frac{\eta_{IO_3^-}}{\eta_{S_2O_3^{2-}}} = \frac{1}{6}$$

Amt of IO_3^- = $\frac{1}{6}\times A$ = B mol

$[IO_3^-]$ = $B\times\frac{1000}{10.0}$ = c mol dm^{-3} **[1]** **(Allow ecf)**

number of moles of $S_2O_3^{2-}$ =……………………………..

concentration of IO_3^- ions in **FA 6** =……………………………..

[2]

(ii) Determine the molar concentration of Ca^{2+} in **FA 6** and hence, calculate the solubility product, K_{sp}, of calcium iodate(V), stating the units.

$$\frac{\eta_{Ca^{2+}}}{\eta_{IO_3^-}} = \frac{1}{2}$$

$[Ca^{2+}]$= ½ $[IO_3^-]$ = ½ c mol dm^{-3} **[1]** **(Allow ecf)**

K_{sp} = $[Ca^{2+}(aq)]\ [IO_3^-(aq)]^2$

= [½ C] $[C]^2$

= ½ C^3 $mol^3\ dm^{-9}$ **[1] (Allow ecf)**

(Do not award the mark if the units is wrong)

concentration of Ca^{2+} ions in **FA 6** = ……………………………..

solubility product of $Ca(IO_3)_2$ = ……………………………..

[2]

(d) Explain why it was necessary to use the **dry** apparatus (e.g. beaker, filter paper and funnel) in the preparation of **FA 6**, and what effect failing to do it would have on the titre values?

To prevent the dilution of the saturated **FA 6** solution which results in lesser amount of

……………………………………………………………………………………………….

IO_3^- reacted during titration and hence smaller titre value **[1]**

(Do not award mark if there is no mention to the change in the titre value or change in conc of FA 6 or IO_3^-.)

[1]

(e) A literature value for the solubility product of calcium iodate(V) is found to be 6.15 × 10^{-6} at 20 °C.

State a possible reason for the difference in the K_{sp} value that you have calculated and suggest an improvement that might allow a value closer to the literature value to be obtained.

If the **calculated K_{sp} > literature K_{sp} value**, the explanation is as follow:

The experiment is not carried out at 20 °C **[1]**.
$Ca(IO_3)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2IO_3^-\ (aq)$
Hence, the equilibrium position shifted to the right.

Use a thermostatically controlled **water bath maintained at 20 °C** during the preparation of **FA 6** before carrying out the filtration **[1]**.

or

If the **calculated K_{sp} < literature K_{sp} value**, the explanation is as follow:

The **salt has not dissolve to form a saturated solution** or **reach equilibrium with its dissolved ions**. **[1]**

Leave the mixture to stand for longer period and use a thermostatically controlled **water bath to maintain at 20 °C** for the salt solution to reach equilibrium / saturation. **[1]**

[Total: 12]

2 **Determination of the enthalpy change of neutralisation, ΔH_n**

FA 7 is a solution of HC*l* of unknown concentration
FA 8 is a solution of 1.0 mol dm^{-3} of NaOH

In this question, you will carry out a series of experiments where different volumes of **FA 7** and **FA 8** are mixed together.

You will determine the temperature change of the reaction mixture, ΔT, of each experiment and then analyse your results graphically in order to determine the

- concentration of HC*l* in **FA 7**
- 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 7 and FA 8**

(i) **Experiment 1**

1. Place a Styrofoam cup inside a second Styrofoam cup held in a 250 cm^3 beaker to prevent it from tipping over.

2. Using a measuring cylinder, transfer 20.0 cm^3 of **FA 7** into the Styrofoam cup.

3. Measure the temperature of **FA 7** in the Styrofoam cup. Record the initial temperature of the solution of **FA 7** as $T_{FA\,7}$.

4. Rinse and dry the thermometer.

5. Measure 50.0 cm^3 of **FA 8** using another measuring cylinder. Record the initial temperature of the solution of **FA 8** as $T_{FA\,8}$.

6. Transfer the **FA 8** into the cup containing **FA 7**. Stir and record the maximum temperature of the reaction as T_{max}.

7. Rinse and dry the Styrofoam cup and thermometer.

Experiment 2
Repeat steps 2 to 7 using 50.0 cm^3 of **FA 7** and 20.0 cm^3 **FA 8**.

Experiments 3 to 6
Carry out **four** further experiments to investigate how the T_{max} changes with different volumes of **FA 7** and **FA 8**. In each case, the total volume of the reaction mixture must be 70.0 cm^3 and the volume of each reagent should not be less than 20.0 cm^3.

In an appropriate format in the space provided on next page, record

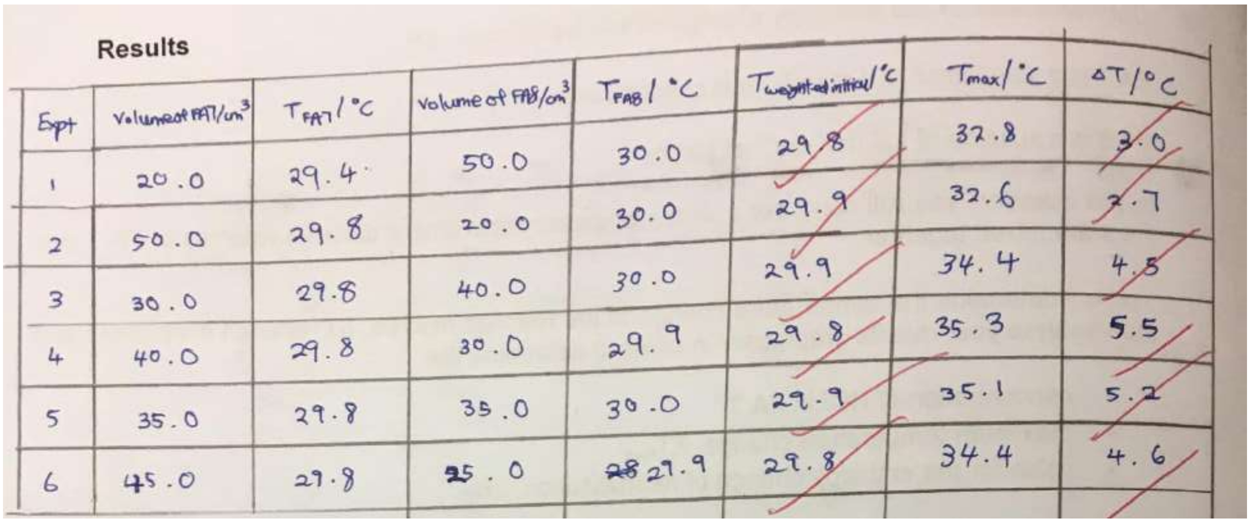
- all measurements of volumes used,
- all temperatures measured, $T_{weighted\ initial}$ and ΔT

$\Delta T = T_{max} - T_{weighted\ initial}$

$$T_{weighted\ initial} = \frac{(Volume\ of\ FA\ 7 \times T_{FA\ 7}) + (Volume\ of\ FA\ 8 \times T_{FA\ 8})}{Volume\ of\ FA\ 7 + Volume\ of\ FA\ 8}$$

Result

Expt	Vol of **FA 7** /cm^3	Vol of **FA 8** /cm^3	T$_{FA 7}$ / ^{o}C	T $_{FA 8}$ / ^{o}C	T$_{weighed\ initial}$ / ^{o}C	T$_{may}$ / ^{o}C	ΔT/ ^{o}C
1							
2							
3							
4							
5							
6							



Results

Expt	Volume of FA7/cm^3	T$_{FA7}$ / °C	Volume of FA8/cm^3	T$_{FA8}$ / °C	T$_{weighted\ initial}$/ °C	T$_{max}$/ °C	ΔT / °C
1	20.0	29.4	50.0	30.0	29.8	32.8	3.0
2	50.0	29.8	20.0	30.0	29.9	32.6	2.7
3	30.0	29.8	40.0	30.0	29.9	34.4	4.5
4	40.0	29.8	30.0	29.9	29.8	35.3	5.5
5	35.0	29.8	35.0	30.0	29.9	35.1	5.2
6	45.0	29.8	25.0	~~28~~ 29.9	29.8	34.4	4.6

[1] Appropriate header with units

[1] Recording to correct precision

[1] Correct calculation of T$_{weighted\ initial}$ and ΔT$_{max}$ in 1 d.p

[1] Proper spread of the choice of the volume used for the other 4 expts

[-1] Missing any of the experiment results

[-1] Missing the recording of T$_{weighted\ initial}$

[-1] Vol of either FA7 or FA8 used is less than 20.0 cm^3

[-1] Recording of data is NOT IN ONE table.

[-1] Missing T$_{FA7}$ and/or T$_{FA8}$

[4]

(ii) Plot a graph of ΔT (y–axis) against volume of **FA 7** used (x–axis) on the grid in Fig. 2.1 using the data you have obtained in **2a(i)**.

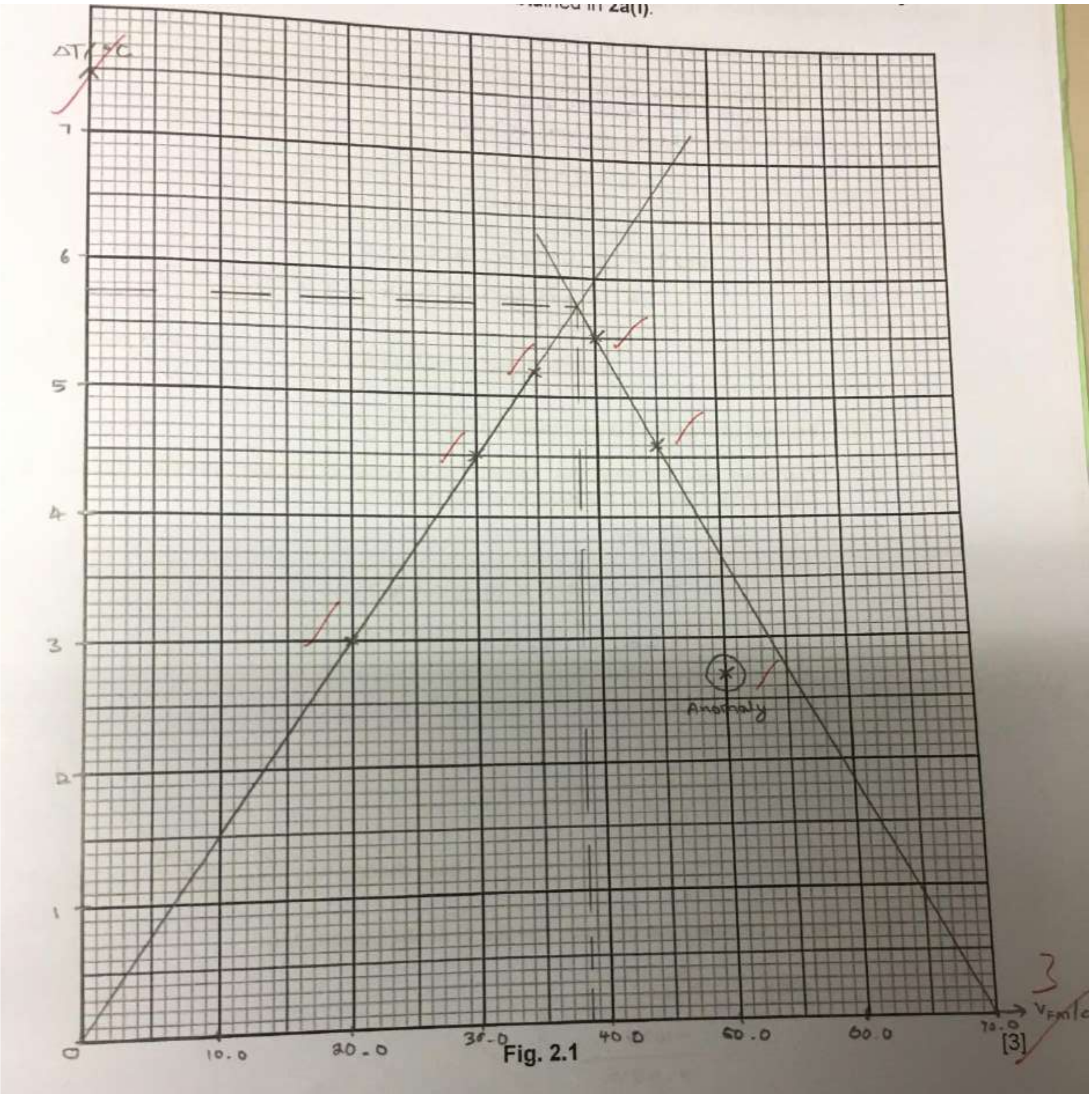


Fig. 2.1 [3]

[1] - Label of the axis with units and appropriate scale
[1] - Points plotted within half a square of 'x'
[1] –The line of best fit must include two points at x= 0 and x = 70
Note: ΔT_{max} should be higher than any of the plotted points.
[-1] if ΔT_{max} is lower than the plotted points .
Plotted points covers more than 50% of grids in both *x* & *y* axis

(iii) Draw two best-fit straight lines, the first should be drawn using the plotted points where ΔT is increasing and the second should be drawn using the plotted points where ΔT is decreasing. Extrapolate (extend) both lines until they intercept. [1]

[1] - Line of best fit to pass through the plotted points

(iv) From your graph in Fig. 2.1, determine the maximum temperature change, ΔT_{max}, and the volume, V_{max}, of **FA 7** required to obtain this.
Correct reading off the ΔT_{max} value from the graph [1] (ignore precision)

Correct reading off the V_{max} value from the graph [1] (ignore precision)

ΔT_{max} = …………………………°C V_{max} = ……………………………cm^3 [2]

(b) Calculation

Show your working and appropriate significant figures in the final answer to **each** part.

Using your answers in **2a(iv)**, calculate

(i) the concentration, in mol dm^{-3}, of HC*l* in **FA 7**.

$V_{NaOH} = 70 - V_{max} = A$ cm^3
Amt of NaOH = A/1000 x 1.0 = B mol **[1]**

Amount of HC*l* = B mol
Conc of HC*l* = B / (V_{max}/1000) = C mol dm^{-3} **[1] (Allow ecf)**

concentration of HC*l* in **FA 7** = …………………………….. [2]

(ii) the heat change for the neutralisation at ΔT_{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}.

$q = mc\Delta T_{max} = 70 \times 4.18 \times \Delta T_{max}$ = D J

heat change = –D J **[1] (Accept if heat change value is positive)**

heat change = …………………………….. [1]

(iii) Hence, calculate the enthalpy change of neutralisation, ΔH_n.

Amount of H_2O = Amount of NaOH = Amount of HC*l* = B mol

ΔH_{neut} = −D / B = −E kJ mol^{-1} **[1] (Must have the <u>negative sign</u> to award the mark)**
(Allow ecf)

ΔH_n = …………………………….. [1]

(c) In another similar experiment, 1.0 mol dm^{-3} aqueous ammonia was used instead of 1.0 mol dm^{-3} NaOH. A graph of maximum change in temperature, ΔT, against volume of **FA 7** was plotted.

Suggest how would the ΔT_{max} and volume, V_{max}, of **FA 7** from this experiment be compared to your result obtained in **2a(iv)** .

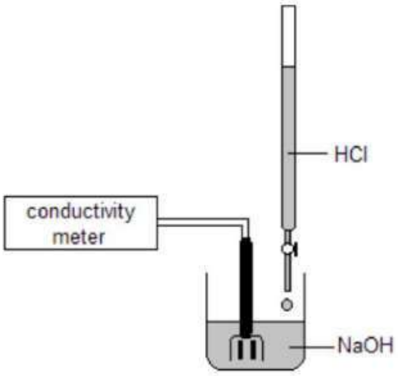
<u>Lower temperature rise, ΔT_{max}</u>, as **<u>some heat released is used to dissociate</u>** the weak ……………………………………………………………………………………
base completely. **[1]**
(Do not accept rate of reaction is less vigorous and heat lost or less water formed or the reaction is less exothermic)

……
V_{max} is the same as same number of moles of HC*l* is needed to react with the aqueous
……
NH_3 since the reacting mole ratio remains the same. **[1]**
……[2]

(d) A student employed another method to determine the concentration of the HC*l* in **FA 7** through the use of conductometry. Conductometry is the measurement of the electrolytic conductivity to monitor the progress of a chemical reaction due to ions being produced or reacted away. The equivalence point can then be determined for the acid – base reaction by plotting the conductivity against the volume of the HC*l* added.

$$H^+ + OH^- \longrightarrow H_2O$$

The following apparatus were set up.



The student measured the conductivity of the solution in the beaker with each addition of a small fixed volume of HC*l* and obtained the following graph.

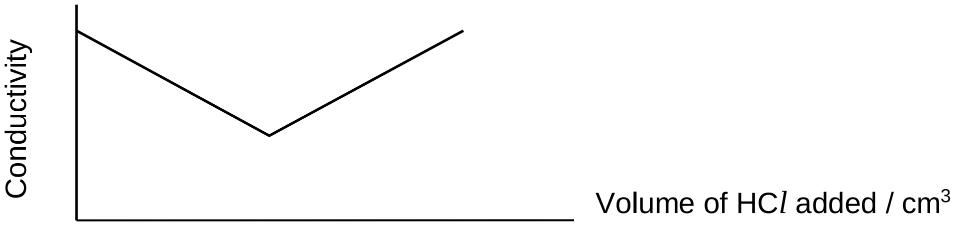
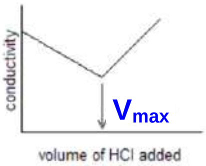


Fig. 2.2

(i) Indicate on the graph (Fig. 2.2), the point which marks the volume of HC*l* needed for complete reaction. [1]

V_{max} is the volume of HC*l* that corresponds to the minimum conductivity **[1]**



(ii) Explain the shape of the graph in Fig. 2.2.

The conductivity decreases as more HC*l* is added. This is due to the **formation of water** from H+ and OH^-, which **decreases the total amount of ions** in water and hence conductivity. **[1]**

The conductivity decreases to the lowest point where the equivalence volume of HC*l* is reached, as **all the NaOH has reacted** with the HC*l* .Thus. that is the **minimum amount of ions** that can be present and gives the lowest conductivity. **[1]**

After the equivalence point, **no more neutralisation** occurs. Any HC*l* that is added **dissociates and contributes to the total amount of ions** in water, thus increasing the conductivity. **[1]**

……………………………………………………………………………………………[3]

(iii) With reference to your experiment in **2(a)**, suggest which method (calorimetry or conductometry) is more accurate for the determination of the concentration of HC*l* in **FA 7**.

Conductometry is more accurate. For conductometry, there is **no heat loss to the surroundings**.

Explanation 1: For **calorimetry, the heat loss to the surroundings** will lower the ΔT_{max} and hence render the volume of HC*l* needed for complete neutralisation inaccurate

Explanation 2: For **calorimetry, the heat loss to the surroundings** will affect each ΔT plotted point, resulting in inaccurate two best-fit straight lines drawn to determine ΔT_{max} and hence volume of HC*l* needed for complete neutralisation will be inaccurate.
[1]

……………………………………………………………………………………………[1]

[Total: 21]

3 Identification of ions

FA 9 is a solution containing a mixture of two salts.

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.

The volumes given below are approximate and should be estimated rather than measured, unless otherwise stated. If there is no observable change, write **no observable change**.

No additional or confirmatory tests for ions present should be attempted.

Table 3.1

	Test	*Observation*
(a)	Place about 3 cm depth of **FA 9** in a test-tube, add equal volume of aqueous sodium hydroxide. Warm the contents in the tube.	White, off-white, buff or light brown ppt. [1] Moist red litmus did not turn blue or no alkaline gas produced. [1] Ppt turned browned or darkened. [1]
(b)	Filter the mixture from **(a)** and collect the filtrate in a test tube. Label the filtrate as **FA 10** and retain it for tests **3(c)** and **3(d)**. Leave the residue in the filter paper and observe it again after 5 minutes.	White, off-white, buff, light brown or brown residue. [awarded once either here or in test (a) but not in both] Colourless filtrate obtained. [1] Residue turned brown or darkened. [awarded once either here or in test (a) but not in both]
(c)	Place 2 cm depth of **FA 10** in a test-tube and add nitric acid until no further change is seen. Label the solution as **FA 11** and retain it for test **3(e)**.	White ppt formed [1] Dissolved in excess nitric acid to give a colourless solution. [1]
(d)	Place 1 cm depth of **FA 10** in a test-tube. Add half a spatula of zinc powder. Warm the contents in the tube cautiously.	Colourless and pungent gas evolved [1] which turned moist red litmus paper blue. [1]
(e)	Place 2 cm depth of <u>**FA 11**</u> in a test-tube, add equal depth of aqueous ammonia. <u>Add</u> excess dilute nitric acid followed by aqueous silver nitrate.	White ppt formed[1] Soluble/dissolved in excess aqueous ammonia to form a colourless solution. [1] On adding HNO_3 acid, no gas evolved[1] White ppt formed [1] Dissolved in excess nitric acid to give a colourless solution. [1] On adding silver nitrate, no ppt observed. [1]

	Test	*Observation*
(f)	Place 1 cm depth of **FA 9** in a test-tube. Add dilute hydrochloric acid followed by aqueous barium chloride.	On adding acid, no observable change/ no gas liberated/ no ppt formed. **[1]** On adding barium chloride, white ppt formed. **[1]**

[6]

[6] – obtain 13 points
[5] – obtain 11 points
[4] – obtain 9 points
[3] – obtain 7 points
[2] – obtain 5 points
[1] – obtain 3 points

(g) **(i)** Identify the **two** cations and **two** anions present in **FA 9.**

cation 1: Mn^{2+} **[1]** cation 2: Zn^{2+} **[1]**

anion 1: SO_4^{2-} **[1]** anion 2: NO_3^- **[1]**

[4]

(ii) Write equations, with state symbols, to illustrate the observations in **3(c)**.

$[Zn(OH)_4]^{2-}(aq) + 2H^+(aq) \rightleftharpoons Zn(OH)_2(s) + 2H_2O(l)$ **[1]**
colourless filtrate white ppt

$Zn(OH)_2(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2H_2O(l)$ **[1]**
white ppt colourless solution

[2]

(iii) Predict what will happen when solid ammonium nitrate is added to **FA 9** followed by aqueous ammonia.

$NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ----(1)

The dissociation of ammonium nitrate produces NH_4^+ which suppressed the dissociation of NH_3 (or causes the position of equilibrium of (1) lies to the left). **[1]**

The concentration of OH^- is too low for the ppt to form or less ppt formed. **[1]**

[2]

[Total : 14]

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4 Planning

Determination of the hardness of water in a sample.

Hard water is water that has high mineral content and is formed when water percolates through deposits of limestone, chalk and gypsum, which are largely made of calcium carbonates, bicarbonates and sulfates. The hardness of water is measured in terms of the molar concentration of Ca^{2+} in mol dm^{-3}.

In a particular sample of water, the hardness is caused by the presence of calcium chloride. The amount of Ca^{2+}, and hence the concentration of Ca^{2+}, can be determined by precipitation with an excess of oxalic acid.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$$

You are to design an experiment to determine the hardness of water in a sample.

You are provided with

- sample of water with estimated hardness of 0.02 mol dm^{-3}
- 0.1 mol dm^{-3} of oxalic acid $H_2C_2O_4$
- electronic balance
- common laboratory apparatus

(a) Given the K_{sp} of calcium oxalate is 2.7×10^{-9} mol^2 dm^{-6} , predict what will be observed when 25.0 cm^3 of the water sample is mixed with equal volume of the 0.1 mol dm^{-3} of oxalic acid solution.

$$[Ca^{2+}] = \tfrac{1}{2}(0.02) = 0.01 \text{ mol dm}^{-3}$$
$$[C_2O_4^{2-}] = \tfrac{1}{2}(0.1) = 0.05 \text{ mol dm}^{-3}$$
$$\textit{ionic product, IP} = [Ca^{2+}][C_2O_4^{2-}]$$
$$= (0.01)(0.05)$$
$$= 5.0 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6} \text{ [1]}$$

Since IP > K_{sp}, calcium oxalate will be precipitated. [1] (Can award this mark based on correct deduction of IP against Ksp even if IP above is calculated wrongly)

[2]

(b) Your plan should include a step-by-step description of the method, including the

- sequence of steps to ensure that the maximum amount of precipitate is recovered,
- the use of appropriate apparatus,
- the recordings using the letters A, B, C etc to represent the measurement taken and present it with an appropriate table format,
- the processing of the results to determine the molar concentration of Ca^{2+} in the water sample.

[A_r: C, 12.0; Ca, 40.1; H, 1.0; O, 16.0]

Forming of precipitate

1. *Pipette out 25.0 cm^3 of the sample water with a 25.0 cm^3 pipette into a dry and clean 250 cm^3 beaker*
2. *Using a burette, transfer 25.0 cm^3 of 0.1 mol dm^{-3} of oxalic acid into the same beaker (as long as oxalic acid is in excess)*
3. *Stir the mixture thoroughly with a glass rod and leave it to stand for a few minutes for equilibrium to be reached*

Recovering of precipitate

4. *Filter the solution into a 250 cm^3 conical flask and collect the residue precipitate into a pre-weighed filter paper.*
5. *Rinse the beaker and glass rod with small volume of deionised water and transfer the washings and continue to filter.*
6. *Wash the precipitate with limited cold deionised water to get rid of aq ions adsorbed on the surface of precipitate.*
7. *Drain off excess water by pressing the solid between filter papers.*
8. *Dry the precipitate in oven at 80 - 100 °C ± 10%.*
9. *Cool and weigh the dried precipitate*
10. *Repeat the heat cool weigh process until mass is constant to ±0.01g*

Mass of filter paper	*/ g*	*A*
Mass of filter paper and residue after first heating	*/ g*	*B*
Mass of filter paper and residue after second heating	*/ g*	*C*
Mass of filter paper and residue after third heating	*/ g*	*C*
Mass of residue	*/g*	*C – A* = E

$$\text{Amount of } CaC_2O_4 = \frac{E}{40.1+2(12.0)+4(16.0)} = F \text{ mol}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s)$$

Amt of Ca^{2+} to form CaC_2O_4 = F mol

$$[Ca^{2+}] \text{ in mol dm}^{-3} = \frac{F}{\left(\frac{25.0}{1000}\right)} = G \text{ mol dm}^{-3}$$

Marks	Requirement	Key marking Points
L-[1]	**Logical flow** of plan	- **Pipetting out water sample into beaker followed by adding fixed solution of oxalic acid into beaker** - **Filtering out precipitate** - **Drying with filter paper and oven or IR lamp (Buchner funnel accepted)** ***Award mark for including all 3 points*.**
A- [1]	Appropriate **apparatus** and their capacities	- **100 cm^3 beaker** - **250 cm^3 beaker** - **250 cm^3 conical flask** - **25.0 cm^3 pipette**
R-[1]	Essential experimental details to ensure **reliable results**	- **Stir mixture with glass rod and leave to stand for a few minutes** - **Repeat heat cool weigh process until mass is constant at ± 0.01g**
P-[1]	Appropriate volumes with **correct precision**	- **25.0 cm^3 of water sample** - **25.0 cm^3 of oxalic acid**
D-[1]	Appropriate table for tabulation of **data**	- **Correct headers and units** - **Letter**
M-[1]	**Manipulation** of data	- **Correct calculation for mass of residue** - **Correct calculation for the conc of Ca^{2+} in water**

[6]

[Total: 8]

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JC2 PRELIM EXAMINATION

CANDIDATE NAME					
CLASS	18J				
CENTRE NUMBER	S	3	0	4	4

INDEX NUMBER				

H2 CHEMISTRY 9729/01

Paper 1 Multiple Choice

26 September 2019

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 **16** 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 50.00 cm^3 of a solution of 0.300 mol dm^{-3} MoO_x^{2-} was reduced to Mo^{3+} using Zn powder. The filtrate required 45.00 cm^3 of 0.200 mol dm^{-3} acidified $KMnO_4$ to revert back to its original form of MoO_x^{2-}.

What is the value of x?

A 1 **B** 2 **C** 3 **D** 4

2 10 cm^3 of an unknown hydrocarbon was combusted in excess oxygen gas. The gaseous mixture contracted by 30 cm^3. The gaseous mixture further contracted by 40 cm^3 when it was passed through aqueous sodium hydroxide. All volumes of gases were measured at room temperature and pressure.

1	cyclopropane
2	butane
3	cyclobutane
4	but-2-ene

What is the hydrocarbon?

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 2, 3 and 4

3 The successive ionisation energies, in kJ mol^{-1}, of elements **X** and **Y** are given below.

X	575	1820	2740	11600	14800	18400	23400
Y	1320	3390	5320	7470	11000	13330	71330

1 The element preceding **X** in the Periodic Table has a higher first ionisation energy.

2 Element **Y** has a lower first ionisation energy than the element preceding it in the Periodic Table.

3 **X** and **Y** forms a compound with the formula $\mathbf{X}_3\mathbf{Y}_2$.

4 Oxide of **X** dissolves in water to give an acidic solution.

Which statements about **X** and **Y** are true?

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 2 and 4 only

4 *Use of Data Booklet is relevant to this question.*

Some isotopes are unstable and undergo beta decay (β-decay).

β-decay is a process where a neutron transforms into a proton by the emission of an electron. The proton is retained in the nucleus.

Which of the following change describes a β-decay?

A $^{40}\text{K} \rightarrow {}^{40}\text{Ca}$

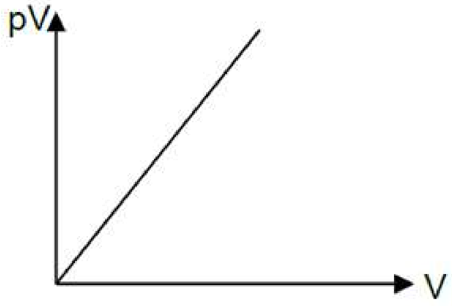
B $^{32}\text{P} \rightarrow {}^{31}\text{P}$

C $^{11}\text{C} \rightarrow {}^{12}\text{C}$

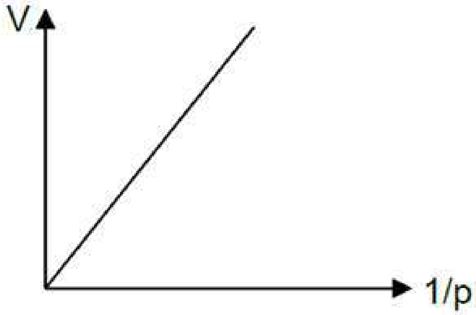
D $^{23}\text{Na} \rightarrow {}^{22}\text{Ne}$

5 Which graph does **not** describe the behaviour of a fixed mass of ideal gas at constant temperature?

A



B



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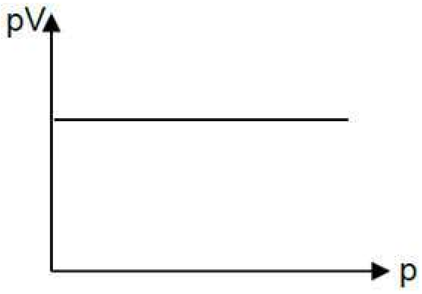

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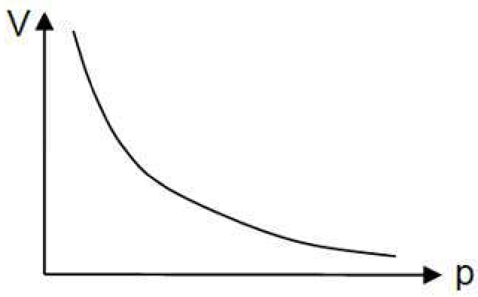


6 Which of the following statements are correct?

1 Covalent compounds can act as electrolytes in water.

2 Ionic bonds and covalent bonds can occur in the same compound.

3 An ionic compound will have the greatest degree of covalent character if both the cation and anion are large.

4 Ionic compounds can conduct electricity in both solid and liquid states.

A 1 and 2 only

B 1 and 4 only

C 3 and 4 only

D 2 and 4 only

7 Which of the following shows a decrease in bond angle from left to right?

A	$SiCl_4$	H_2O	NF_3
B	$AlCl_3$	NH_3	PH_3
C	PCl_3	PF_3	PBr_3
D	CCl_4	SF_6	XeF_4

8 The table below gives the standard enthalpy change of hydrogenation of three compounds to form cyclohexane:

Compound	$\Delta H_{\text{hydrogenation}}$ /kJ mol^{-1}
benzene	−206
1,3,5−cyclohexatriene	−360
cyclohexene	−120

Which of the following statements is correct?

A 1,3,5−cyclohexatriene is more stable than benzene.

B Benzene has a lower energy content than 1,3,5−cyclohexatriene.

C The C=C bond energy in cyclohexene is weaker than that in 1,3,5−cyclohexatriene.

D The enthalpy change of atomisation of benzene is smaller than that of 1,3,5−cyclohexatriene.

9 Which of the following statements are correct for a system at dynamic equilibrium?

1 The rate of both forward and backward reaction is the same

2 The concentration of reactants is equal to the concentration of products

3 The rate constant of forward reaction is equal to the rate constant of the backward reaction

A 1 only **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

10 A pure sample of SO_3(l) is introduced into an evacuated vessel. The vessel, of constant volume, is heated to a constant temperature such that the equilibrium below is established.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The value of pressure is found to be 27% greater than if only SO_3(g) were present.

What is the mole fraction of oxygen in the equilibrium mixture?

A 0.119 **B** 0.213 **C** 0.425 **D** 0.787

11 Equal volumes of 1.35×10^{-5} mol dm^{-3} $Bi(NO_3)_3$ and 2.00×10^{-5} mol dm^{-3} NaOH were added to a conical flask. Equilibrium was achieved within a few minutes and the following observations were made.

Given that solubility of $Bi(OH)_3$ is 2.87×10^{-7} mol dm^{-3}, which option contains the correct descriptions?

	Precipitation of $Bi(OH)_3$	IP vs K_{sp} for the solution at equilibrium
A	Yes	IP > K_{sp}
B	Yes	IP = K_{sp}
C	No	IP = K_{sp}
D	No	IP < K_{sp}

12 Caesium-137 is a radioactive isotope with a half-life of 30.2 years. Following the Fukushima Daiichi nuclear disaster in 2011, it was reported that about 8.4 kg of Caesium-137 was released into the sea.

What is the mass of Caesium-137 left in the sea after 100 years?

A 0.801 kg

B 0.846 kg

C 1.05 kg

D 6.73 kg

13 For the reaction: $\mathbf{A}(g) + \mathbf{B}(g) \rightarrow \mathbf{C}(g) + \mathbf{D}(g)$, the following experimental data was obtained.

Expt No.	[**A**] /mol dm^{-3}	[**B**] /mol dm^{-3}	Initial rate of reaction /mol dm^{-3} s^{-1}
1	0.20	0.20	3.00×10^{-4}
2	0.60	0.20	9.00×10^{-4}
3	0.80	0.40	4.80×10^{-3}

Which of the following conclusions can be drawn for the reaction?

1 The unit for rate constant is mol^{-2} dm^{6} s^{-1}.

2 The overall equation is the rate determining step.

3 The initial rate of reaction can be calculated from the initial rate of formation of **C**(g).

A 1 only **B** 1 and 2 only **C** 1 and 3 only **D** 2 and 3 only

14 The following equilibrium are studied at a fixed temperature T °C.

Equilibrium 1: $H_2PO_4^- + SO_4^{2-} \ll HSO_4^- + HPO_4^{2-}$

Equilibrium 2: $HSO_4^- \ll SO_4^{2-} + H^+$ $K_c = K_2$

Equilibrium 3: $H_2PO_4^- \ll HPO_4^{2-} + H^+$ $K_c = K_3$

Given that $K_2 > K_3$, which of the following statements is correct?

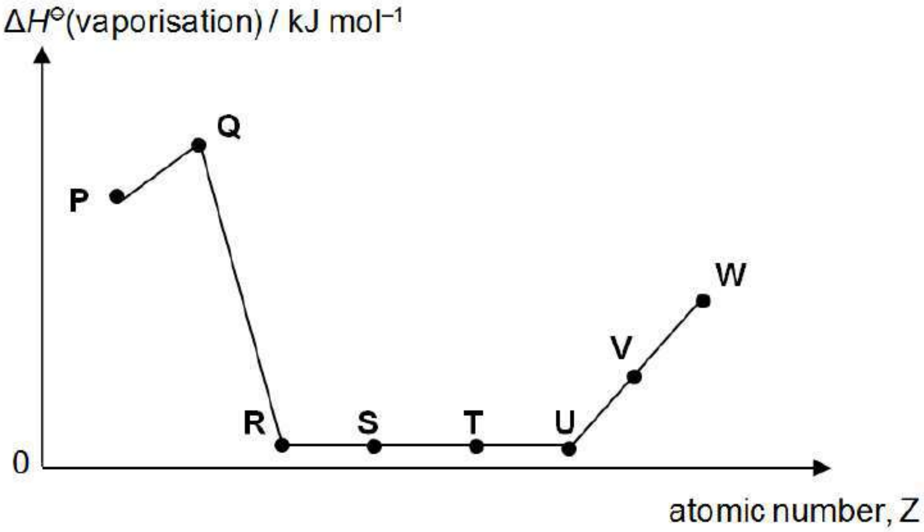
A HPO_4^{2-} is a stronger acid.

B $H_2PO_4^-$ is the conjugate base of HPO_4^{2-}.

C The position of Equilibrium 1 lies to the left.

D The rate of forward reaction for all three equilibrium decreases at (T+100) °C.

15 The graph below shows the variation in the standard enthalpy change of vaporisation, $\Delta H^{\ominus}$(vaporisation), for eight consecutive elements in the Periodic Table, all with atomic number, Z $\leq$ 20.



Which of the following statement is correct?

A Element **Q** forms an oxide which is amphoteric.

B Element **R** forms an oxide which is basic in aqueous solution.

C Element **V** forms a chloride which is neutral in aqueous solution.

D Element **W** forms a chloride which is basic in aqueous solution.

16 Element **E** is in the third period of the Periodic Table. The chloride of **E** has a simple molecular structure while the oxide of **E** has a giant ionic structure. Which of the following statements is **incorrect**?

A The atomic radius of **E** is larger than that of chlorine.

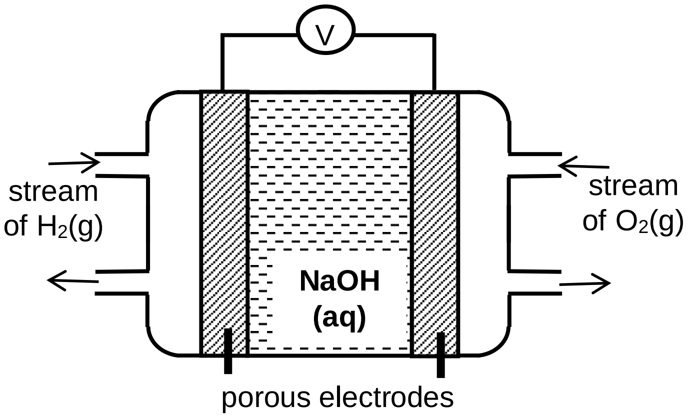
B The melting point of **E** is lower than its preceding element.

C The chloride of **E** dissolves in water to give an acidic solution.

D The oxide of **E** reacts with excess aqueous sodium hydroxide to form a colourless complex.

17 *Use of the Data Booklet is relevant in this question.*

A hydrogen-oxygen fuel cell is constructed using 1.00 mol dm^{-3} sodium hydroxide as the electrolyte. What is the change in pH of the solution around each electrode when the current is flowing?



	Cathode	Anode
A	increase	decrease
B	increase	increase
C	decrease	increase
D	decrease	decrease

18 *Use of the Data Booklet is relevant to this question.*

An antique car bumper is to be chrome plated. The bumper is dipped into a Cr^{3+} solution where it serves as an electrode of an electrolytic cell. Oxygen is formed on the other electrode.

Which of the following statements is correct?

A The bumper is the anode of the electrolytic cell.

B Reduction of water occurs at the cathode.

C For every 52 g of chromium plated, 3 mole of oxygen is evolved.

D It takes about 8 hours to plate 52 g of chromium, if the current used is 10 A.

19 When a dilute sulfate solution of a metal **J** is electrolysed, metal **J** and a diatomic gas **K** are produced at the cathode and the anode respectively in the molar ratio 2:1. In another experiment, the same quantity of electricity is used to electrolyse a saturated sodium chloride solution and a gas **L** is evolved at the anode.

What is the molar ratio of **J** : **K** : **L**?

A	2:1:1	**B**	2:1:2
C	4:2:1	**D**	4:2:3

20 Covalent bonds are formed when orbitals overlap. The shape of many organic molecules can be explained by the hybridisation of orbitals.

Which bond is **not** present in the molecule, HC˜CCHˆCH$_2$?

A A σ bond formed by 1s-2sp overlap

B A σ bond formed by 2sp-2sp^2 overlap

C A σ bond formed by 2sp-2sp^3 overlap

D A π bond formed by 2p-2p overlap

21 In the 1960s, a certain class of organic compounds was widely used in aerosol sprays, refrigerants and making foamed plastics. However, they were found to destroy the ozone layer in the upper atmosphere and viable replacements were sought to minimise ozone depletion.

Which of the following compounds can be used safely as a replacement?

A $CHBr_3$

B CF_3CBr_3

C $CHClFCClF_2$

D $CH_3CH_2CH_2CH_3$

22 For which property of the alkanes does the numerical value decrease down the homologous series?

A Density

B Enthalpy change of vapourisation

C Number of isomers

D Vapour pressure

23 Hydrogen bromide reacts with but-1-ene to form bromobutane.

Which statements are possible descriptions of the organic intermediate in this reaction?

1 It contains carbon, hydrogen and bromine.
2 It has a positive charge.
3 It reacts with a nucleophile.
4 It has a plane of symmetry.

A 1 and 3 only

B 2 and 3 only

C 2 and 4 only

D 3 and 4 only

24 Which salt will be the most acidic in aqueous solution?

A $CH_3CH_2CH_2NH_3Cl$

B $C_6H_5NH_3Cl$

C $MgCl_2$

D NH_4Cl

25 When propene is bubbled through iodine monochloride, ICl, dissolved in water, which products could be formed?

1 $CH_3CH(OH)CH_2Cl$

2 CH_3CHICH_2OH

3 $CH_3CHClCH_2I$

4 CH_3CHICH_2Cl

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 2, 3 and 4

26 Tetrapeptide, **P**, is formed by an unknown amino acid. **P** has a relative molecular mass of *M*.

What is the relative molecular mass of the amino acid?

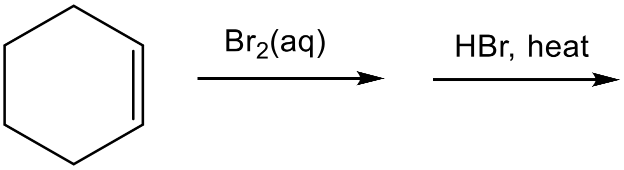
A $\frac{M}{4}$ **B** $\frac{M}{4}+18$ **C** $\frac{M+54}{4}$ **D** $\frac{M}{4}+54$

27 Which reaction yields a carbon compound incorporating deuterium, D? [D = ^2H]

	Reactant	Reagents and conditions
A	CH_3CH_2CN	NaOD, D_2O, heat
B	$(CH_3)_3COH$	conc H_2SO_4, heat
C	CH_3COCI_3	NaOD, D_2O, warm
D	$CD_2(OH)CO_2H$	acidified $KMnO_4$, heat

28 Which two-step synthesis process will not give a good yield of 1,2-dibromocyclohexane?

A



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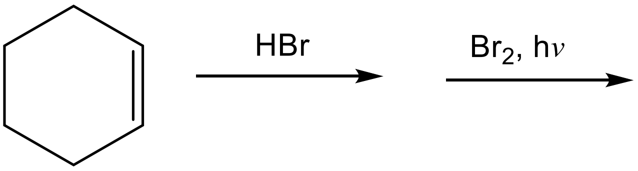
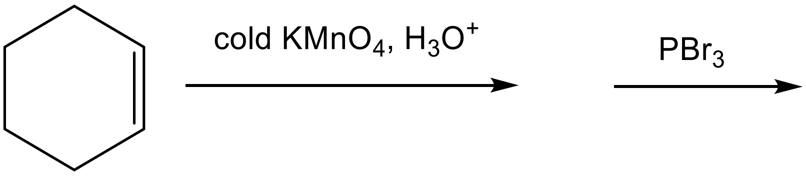


C



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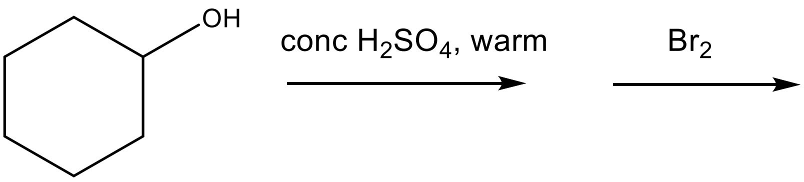
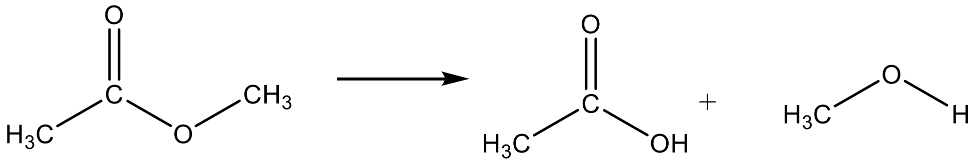


29 Which reaction will **not** take place in the presence of a suitable homogeneous catalyst?

A $CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3$

B



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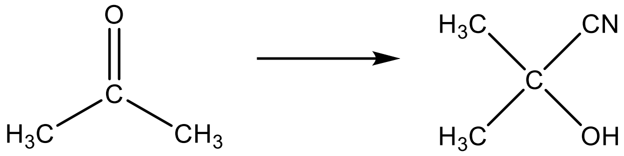

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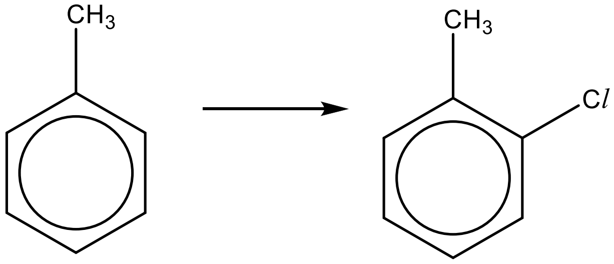
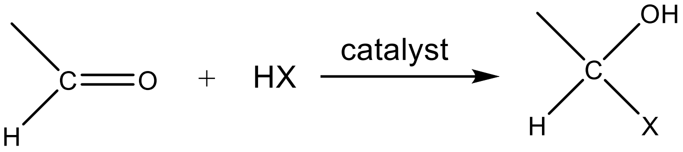
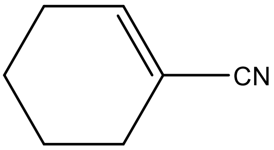


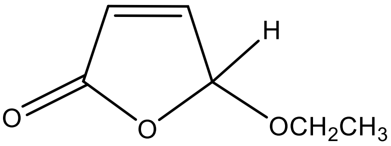
30 There is a range of reactions of the aldehyde group which have the pattern

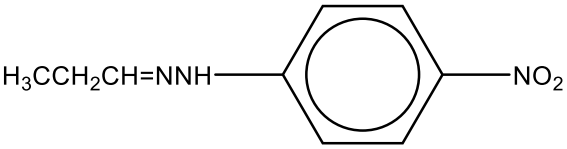


of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

1 

2 

3 

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3 only

END OF PAPER

RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME

CLASS 18J

CENTRE NUMBER S

INDEX NUMBER

H2 CHEMISTRY 9729/02

Paper 2 Structured Questions

18 September 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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.

Answer **all** questions in the space provided.
A Data Booklet is provided. Do NOT write anything on it.

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

Question Number	1	2	3	4	5	6	7	Total (Paper 2)	sf	Units
Marks	9	9	10	12	12	10	13	75		
Paper 1	30		**Paper 3**		80		**Total**	185		

This document consists of **21** printed pages and **3** blank pages.

1 Group 2 metals are also known as alkaline earth metals. The elements have similar properties and appearance. The metals are silvery-white and are reactive at room temperature and pressure.

(a) Ionisation energy of Group 2 varies down the group.

Explain how the 1st ionisation energy of beryllium and barium differs.

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[3]

(b) The nitrates, carbonates and hydroxides of Group 2 elements can undergo thermal decomposition.

(i) In the thermal decomposition of Group 2 nitrates, oxygen and a brown gas are also produced.

Write a balanced equation, with state symbols, for the decomposition of calcium nitrate.

……………………………………………………………………………… **[1]**

(ii) The nitrates of lead and zinc can undergo thermal decomposition similar to calcium nitrate. The decomposition temperatures of the three nitrates are given in the following table

Table 1.1

Compound	**Decomposition temperature /°C**
Lead(II) nitrate, $Pb(NO_3)_2$	290
Calcium nitrate, $Ca(NO_3)_2$	132
Zinc nitrate, $Zn(NO_3)_2$	105

Explain, with reference to the *Data Booklet,* the trend in the decomposition temperatures of the metal nitrates in the Table 1.1.

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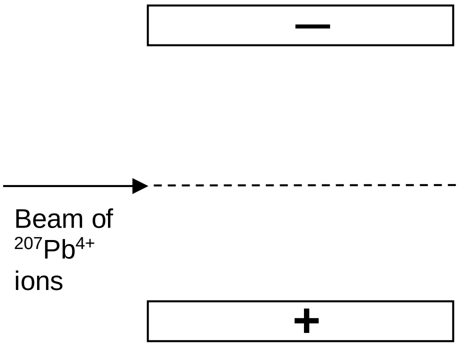
…………………………………………………………………………………………
[3]

(c) Lead can exhibit variable oxidation states and its cation can exist either as $^{207}Pb^{2+}$ or $^{207}Pb^{4+}$. **[2]**

Given that the angle of deflection for $^{207}Pb^{2+}$ is 8°, calculate the angle of deflection for $^{207}Pb^{4+}$ and draw a labelled line to the figure below to represent the path of a beam of $^{207}Pb^{4+}$ ions, at high temperature, in an electric field.



[Total: 9]

2 Citric acid ($H_3C_6H_5O_7$) is a naturally occuring weak organic tribasic acid. It is found in a variety of vegetables and fruits. In a typical sample of lemon, the concentration of citric acid is about 0.300 mol dm^{-3}.

Table 2.1

	K_{a1}	K_{a2}	K_{a3}
$H_3C_6H_5O_7$	1.43×10^{-3}	1.74×10^{-5}	3.98×10^{-7}

(a) Calculate the pH of a typical sample of lemon. You may ignore K_{a2} and K_{a3} for this calculation.

[1]

(b) Calculated the pH of solution containing 46.0 g dm^{-3} of $Na_3C_6H_5O_7$.

[3]

(c) **(i)** A buffer solution can resist changes in pH when small amounts of acid or base is added to it. Suggest two conditions necessary to make a good buffer solution.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… **[2]**

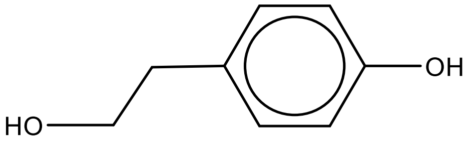
(ii) Calculate the mass of NaOH(s) required to be added to 50 cm^3 of 0.300 mol dm^{-3} citric acid for the preparation of buffer at pH = 6.40.

Clearly identify the acid and salt species in the buffer.

[3]

[Total: 9]

3 Olives are commonly used in foods and production of edible oils. In their natural state, olives contain organic compounds like tyrosol that make them unpalatable to people.



tyrosol

In order for olives to be made edible, their natural bitterness has to be removed in a process known as debittering. This is done by soaking olives in brine, followed by sodium hydroxide solution, which will react with tyrosol and extracted.

(a) **(i)** Write an equation for the reaction between tyrosol and sodium hydroxide.

.... **[1]**

(ii) State the different types of interaction that the product in **(a)(i)** will have with water molecules.

....

.... **[2]**

(iii) After treatment, tyrosol can be converted back to its original form. Outline a simple chemical test that could be carried out to check for the presence of tyrosol.

....

.... **[2]**

(iv) For this debittering process to be effective, the sodium hydroxide solution has to be changed frequently.

Suggest, using ideas behind Le Chatelier's principle, why the sodium hydroxide solution has to changed in order to remove tyrosol.

You may find it useful to use the equation $[T]_{olive} \rightleftharpoons [T]_{NaOH}$ where [T] refers to the concentration of tyrosol.

....

....

....

.... **[2]**

(b) **(i)** When tyrosol is heated with ethanoic acid with concentrated H_2SO_4, compound **D** is formed.

When bromine water is added to tyrosol, a brominated tyrosol, **E**, is formed.

Suggest a structure for compound **D** and **E**.

D	**E**

[2]

(ii) Explain how the acidity of brominated tyrosol might differ from that of tyrosol.

....

....

....

.... **[1]**

[Total: 10]

4 $SOCl_2$ and S_2Cl_2 are chlorine and sulfur containing compounds.

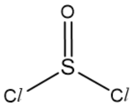
(a) Draw the dot-and-cross diagram of S_2Cl_2 and state its bond angle.

[2]

(b) The dipole moments and boiling points for $SOCl_2$ and S_2Cl_2 are shown in the table below.

The larger the dipole moment in Debye (*D*), the greater the difference in electrical charge in a species.

Table 4.1

Compound	M_r	Boiling point / °C	Net dipole moment / *D*
	119	74.6	1.44
S_2Cl_2	135.2	137.1	1.60

With reference to their structures and bonding and the information above, account for the large difference in their boiling points.

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………………………………………………………………………………….. **[3]**

(c) $SOCl_2$ is used in organic synthesis.

The following Synthetic Route A shows how a carboxylic acid can be converted into an amine.

Synthetic Route A

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{\text{Step 2}} CH_3CONH_2 \xrightarrow{\text{Step 3}} CH_3CH_2NH_2$$

(i) State the reagents and conditions for Steps 2 and 3.

Step 2 ……………………………………..

Step 3 …………………………………….. **[2]**

(ii) 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**, $C_5H_{10}O_2$.
- **T** undergoes the above Synthetic Route A to form the amine **U**, $C_5H_{13}N$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** can exhibit stereoisomerism.

Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**
U	

[3]

(iii) State the types of stereoisomerism shown by angelic acid and **T**.

angelic acid ……………………………………………..

T …………………………………………….. **[2]**

[Total: 12]

5 *Use of the Data Booklet and the information about the various oxidation states of vanadium from Table 5.1 are relevant to this question.*

Table 5.1

Example of Species	Oxidation State of Vanadium	Solution Colour	Wavelength / nm
V^{2+}	+2	violet	400
V^{3+}	+3	green	515
VO^{2+}	+4	blue	460
VO_2^+	+5	yellow	580

(a) In a solution containing V^{2+}(aq), water molecules act as ligands that bind to the vanadium cation in an octahedral arrangement and cause the 3d subshell in V^{2+} to split into two different energies. As a result, a solution of V^{2+}(aq) appears violet.

(i) Explain why a solution of V^{2+}(aq) is coloured.

……………………………………………………………………………...

……………………………………………………………………………...

……………………………………………………………………………...

……………………………………………………………………………... **[2]**

(ii) Given that the energy of light is inversely proportional to its wavelength, deduce which of the two solutions, V^{2+}(aq) or V^{3+}(aq), has a larger 3d-subshell splitting.

……………………………………………………………………………...

……………………………………………………………………………...

……………………………………………………………………………...

……………………………………………………………………………... **[2]**

(b) Frost-Ebsworth diagrams are the most common graphical method of representing redox relationships for species of a given element in different oxidation states.

In a Frost-Ebsworth diagram, values of $-\Delta G$ /F for the formation of M(N) from M(0), where N is the oxidation state, are plotted with increasing oxidation states.

From the relationship:

$$\Delta G = -\text{n}FE$$

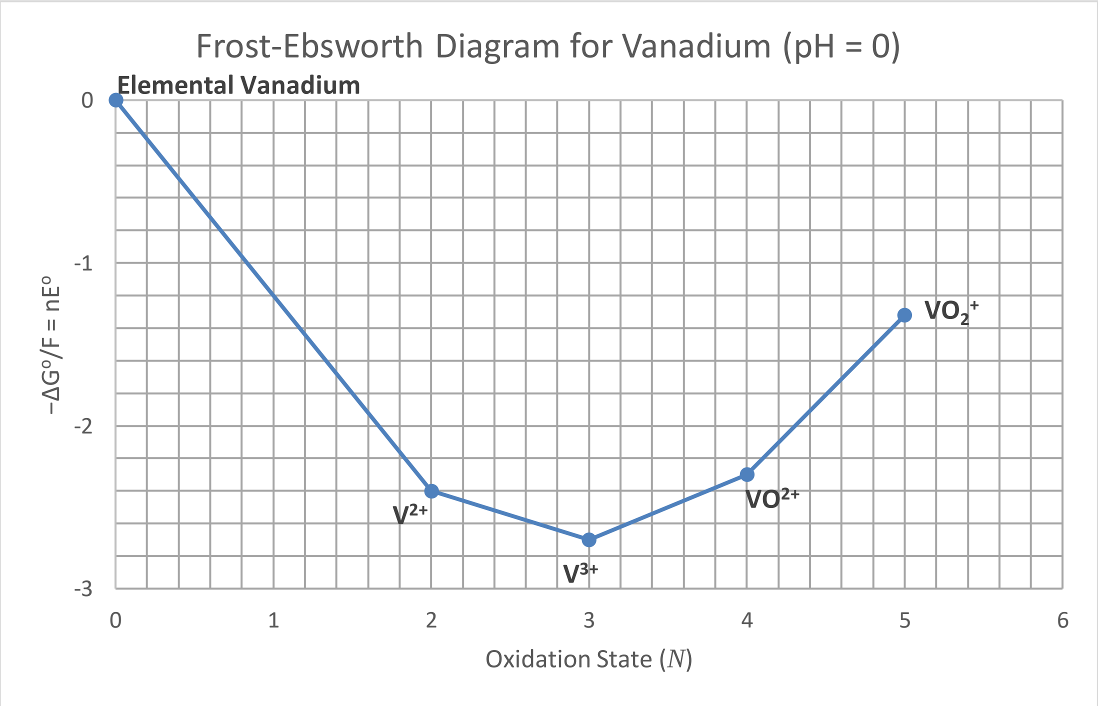
where n is the number of moles of electrons transferred during the redox reaction, it follows that $-\Delta G$ /F = nE , hence a Frost-Ebsworth diagram is essentially a plot of nE against oxidation states.

The ΔG for elements in their standard states is taken as zero.

The gradient of the line drawn between any two points on the plot corresponds to the E of the corresponding redox couple.

A Frost-Ebsworth diagram for vanadium in aqueous solution of pH 0 (i.e. $[H^+] = 1$ mol dm^{-3}) is shown below.

Fig. 5.1



(i) Fill in the blanks below the y-coordinates of the plotted points for V^{3+} and VO^{2+} to 1 decimal place.

V^{3+} : (3 , ……………)

VO^{2+}: (4 , ……………) **[1]**

(ii) For the V^{2+}/V redox couple, the coordinates for V^{2+} is (2, −2.40).

For the VO_2^+/VO^{2+} redox couple, the coordinates for VO_2^+ is (5, −1.32).

Calculate the *E* value for the VO_2^+/V^{2+} redox couple.

[1]

(iii) Suggest the significance of V^{3+} being the lowest point on the Frost-Ebsworth diagram.

……………………………………………………………………………...........

……………………………………………………………………………........... **[1]**

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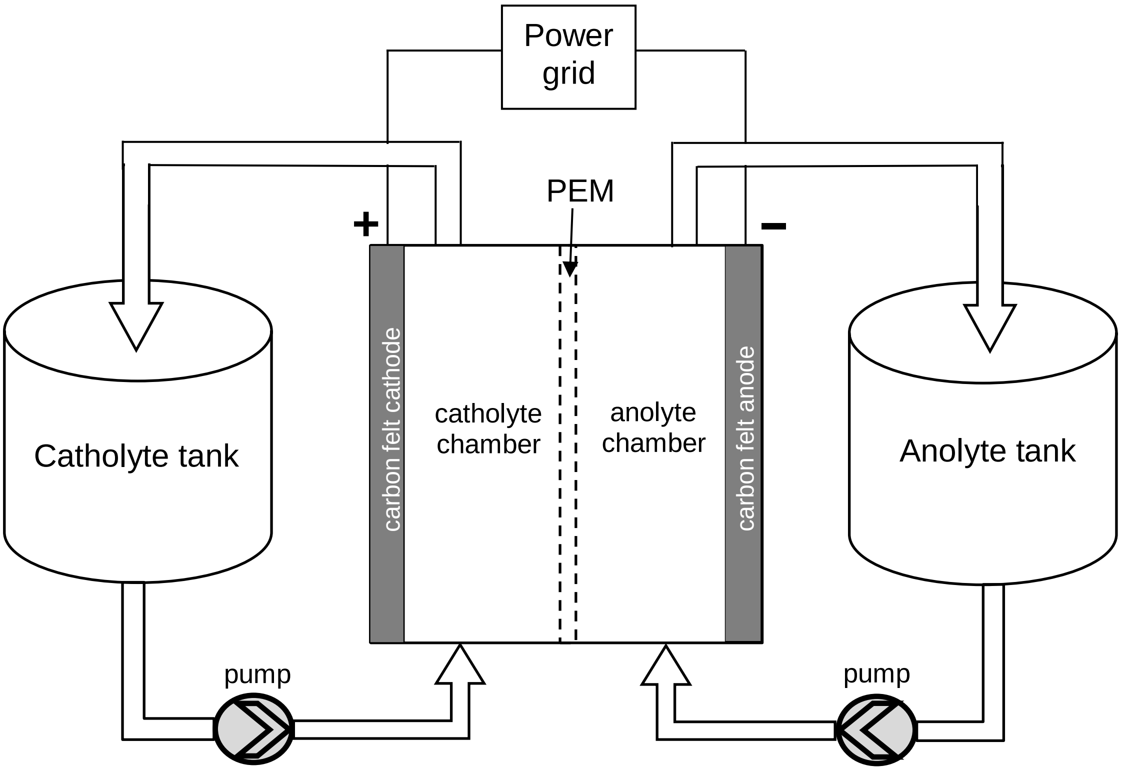
A recent exciting development in the energy storage industry is the vanadium redox flow battery (VRFB), a rechargeable electrochemical cell that employs aqueous vanadium ions in various oxidation states to store chemical potential energy. A 20-year-long cycle life and high energy efficiency are its key advantages, giving rise to its potential to power up cities in the near future.

A schematic diagram of a VRFB, during the discharge phase, is shown below, with the flow of the electrolytes in the connecting pipes shown in block arrows.

Fig. 5.2



Key Characteristics of the VRFB

1. The battery comprises of 2 electrolytes, a catholyte and an anolyte, that flow through the respective half-cells from separate storage tanks. Each electrolyte contains a redox couple, i.e. 2 vanadium species, dissolved in sulfuric acid.
2. The species in each redox couple differs from each other by **one oxidation state**.
3. These electrolytes are separated by a proton exchange membrane (PEM) whereby protons can migrate across to maintain electrical neutrality in the cell.
4. The predominant colours of the electrolytes flowing through the four connecting tubes are **all different**, based on the colours given in Table 5.1.

(c) **(i)** The e.m.f. of a single VRFB is 1.26 V.

With reference to the given information above and the *Data Booklet*, write down the relevant vanadium redox couples present in the catholyte and anolyte chambers in the schematic diagram above.

Catholyte chamber: ………………………….

Anolyte chamber: …………………………. **[2]**

(ii) Hence or otherwise, construct the overall equation of the redox process in the VRFB.

……………………………………………………………………………. **[1]**

(iii) Once a discharge cycle is completed, the VRFB will be connected to an external power supply to "charge up".

State the direction of proton transfer during the charging cycle.

……………………………………………………………………………. **[1]**

(iv) Suggest a suitable modification to the VRFB to increase the e.m.f without changing the species in the catholyte and anolyte chambers.

……………………………………………………………………………. **[1]**

[Total: 12]

6 When Group 1 metals are heated in an excess of air, alkali metal oxides, peroxides and superoxides are produced. The principal product obtained depends on the metal.

For potassium, its superoxide, KO_2, is formed predominantly.

(a) **(i)** The enthalpy change of formation of the oxides increases drastically as shown in Table 6.1. Suggest a reason for each of the following:

- $\Delta H_f(O_2^{2-})$ is more endothermic than $\Delta H_f(O_2^{-})$
- $\Delta H_f(O^{2-})$ is more endothermic than that of the other two anions

Table 6.1

	O_2^{-}	O_2^{2-}	O^{2-}
ΔH_f/ kJ mol^{-1}	–43.0	553	903

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………...

…………………………………………………………………………... **[2]**

…………………………………………………………………………...

(ii) Define the term *lattice energy*.

…………………………………………………………………………....

…………………………………………………………………………....

………………………………………………………………………….... **[1]**

(iii) Explain how the magnitude of lattice energy changes from KO_2 to K_2O_2 to K_2O.

…………………………………………………………………………....

…………………………………………………………………………....

…………………………………………………………………………....

…………………………………………………………………………....

………………………………………………………………………….... **[2]**

(b) Potassium superoxide, KO_2, is a rare yet stable salt of superoxide anion. It is used in rebreathers as it reacts with carbon dioxide exhaled to generate oxygen and potassium carbonate.

Potassium superoxide is stable as long as it is kept dry. Upon contact with water, it hydrolyses extremely quickly to give potassium hydroxide.

Interestingly, the alkaline products from both reactions aforementioned also absorb the exhaled CO_2.

The following table lists the ΔH values of the reactions.

Table 6.2

reaction	ΔH / kJ mol^{-1}
$2KO_2(s) + CO_2(g) \rightarrow K_2CO_3(aq) + \frac{3}{2}O_2(g)$	–219
$2KO_2(s) + H_2O(l) \rightarrow 2KOH(aq) + \frac{3}{2}O_2(g)$	–113
$CO_2(g) + K_2CO_3(aq) + H_2O(l) \rightarrow 2KHCO_3(aq)$	–100
$KOH(aq) + CO_2(g) \rightarrow KHCO_3(aq)$	ΔH_r

Using the data given in Table 6.2, construct a fully labelled energy cycle to determine ΔH_r.

$$2KO_2(s) + H_2O(l) \longrightarrow 2KOH(aq) + \frac{3}{2}O_2(g)$$

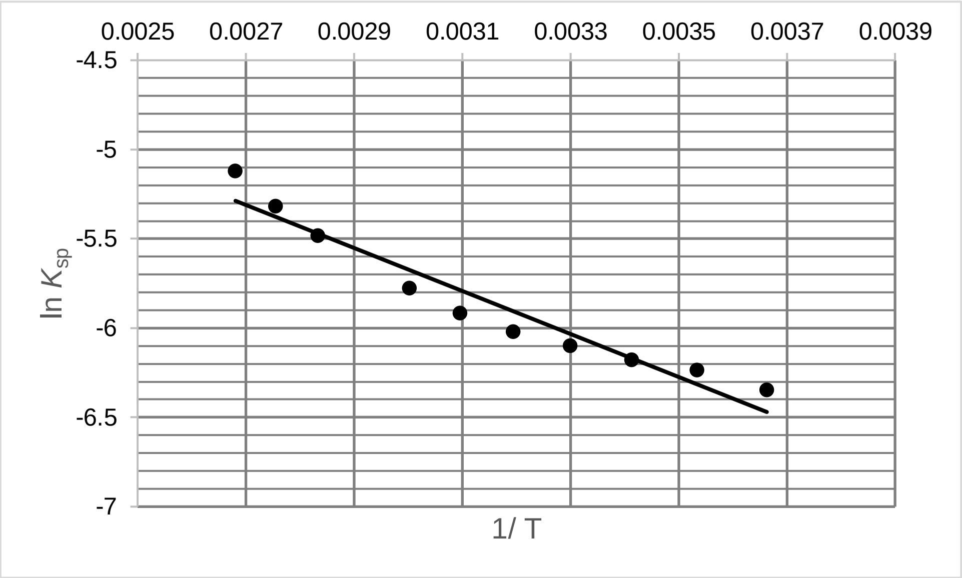
[3]

(c) The relationship between the thermodynamic functions, ΔG_{ppt}, ΔH_{ppt} and ΔS_{ppt} of a reaction and its equilibrium constant is given as follows.

$$\Delta G_{ppt} = \Delta H_{ppt} - T\Delta S_{ppt} = - RT \ln(K_{sp}).$$

An experiment was conducted to determine the entropy change of precipitation of potassium carbonate. The solubility product of potassium carbonate at various specific temperatures were determined and Figure 6.1 shows a plot of ln K_{sp} against 1/T which can be used to obtain ΔS_{ppt}.

Fig. 6.1



(i) Using the graph, determine ΔS_{ppt}.

[1]

(ii) Explain the significance of the sign of ΔS_{ppt} of K_2CO_3.

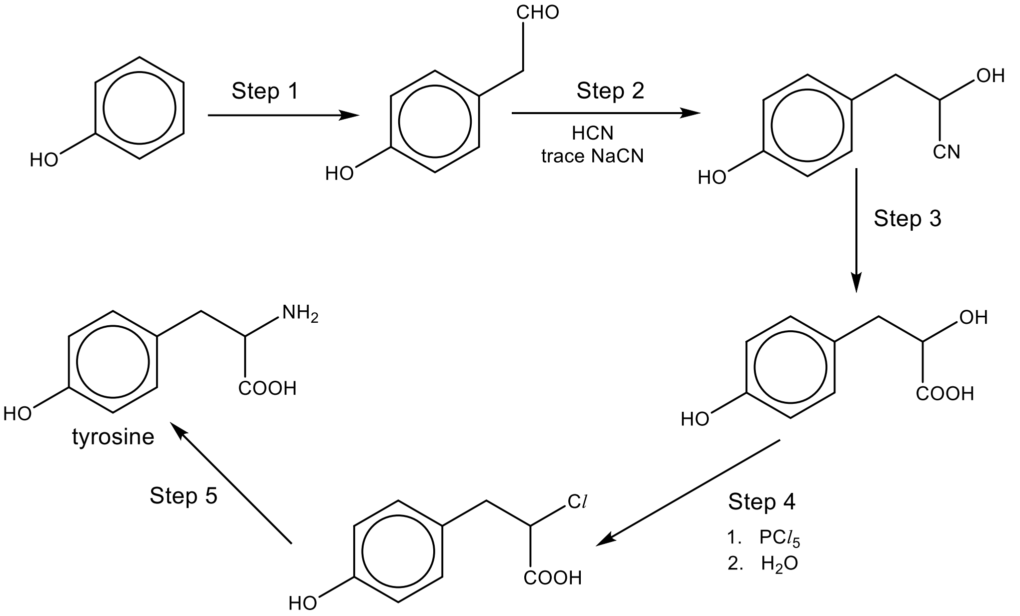
…………………………………………………………………………….... **[1]**

……………………………………………………………………………....

[Total: 10]

7 **(a)** Tyrosine is a naturally occurring amino acid.

The amino acid tyrosine can be synthesised from phenol by the route shown.



(i) Describe the mechanism in Step 2.

[3]

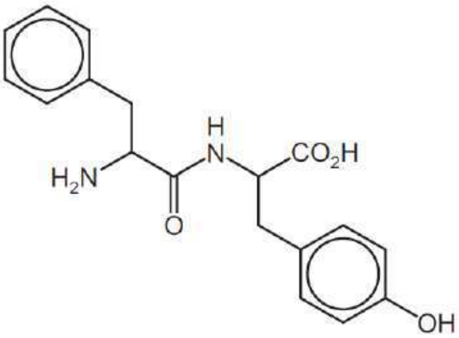
(ii) State the reagents and conditions for Steps 1, 3 and 5.

Step 1 ……………………………………………………

Step 3 ……………………………………………………

Step 5 …………………………………………………… **[3]**

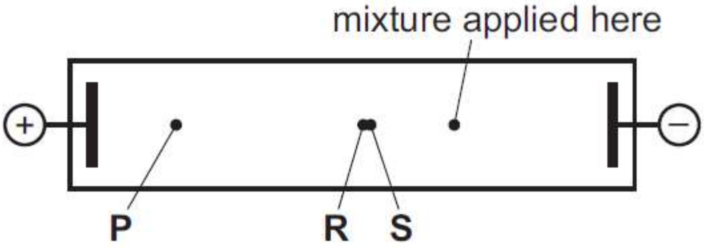
(b) The dipeptide phe-tyr has the following structure.



A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12.

Electrophoresis is a technique commonly used in the lab to separate species like amino acids. The speed of migration of the amino acids depends on their charge and size.

At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



(i) Draw the structure of the species responsible for spot **P**.

[1]

(ii) Suggest a simple modification to the electrophoresis setup to increase the separation for spots **R** and **S.**

………………………………………………………………………………..

……………………………………………………………………………….. **[1]**

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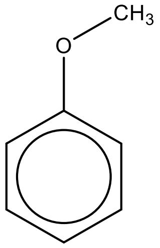
(c) Anisole, or methoxybenzene, is an organic compound with the formula $CH_3OC_6H_5$. It is a colorless liquid with a smell reminiscent of anise seed, and in fact many of its derivatives are found in natural and artificial fragrances. It is an ether and contain the C–O–C functional group.



anisole

Ether can be synthesised via Williamson ether synthesis which involves an alkoxide ion, $R'O^-$, reacting with an alkyl halide, RX.

$$R'O^- + RX \longrightarrow R'OR + X^-$$

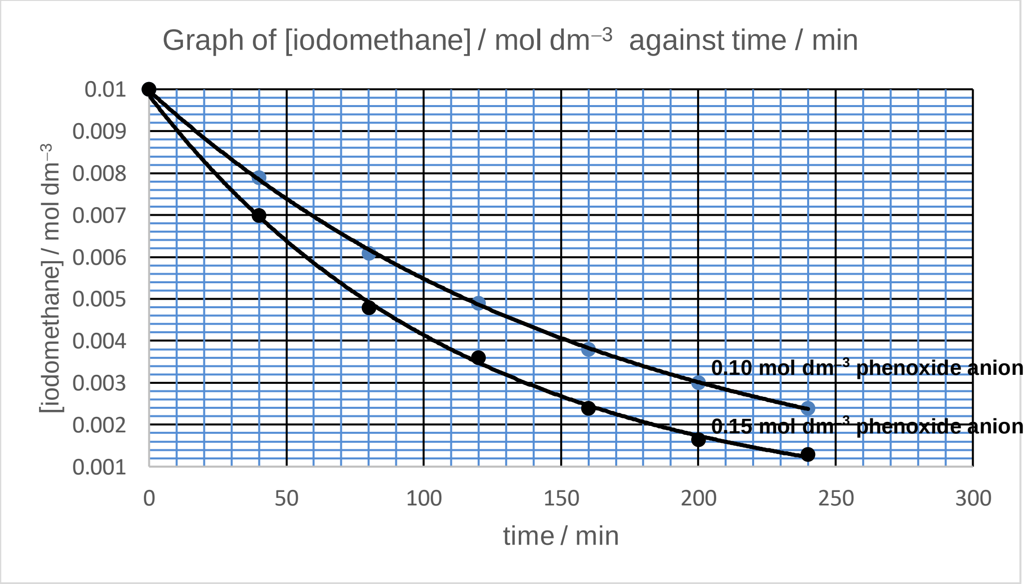
(i) To produce anisole, phenol is first reacted with sodium hydride, NaH, via an acid–base reaction to produce phenoxide ion.

Construct a balanced chemical equation for the reaction between phenol and NaH.

……………………………………………………………………………... **[1]**

(ii) The following graph shows the experimental findings of a Chemistry undergraduate student when iodomethane is reacted with 2 different concentrations of phenoxide ion.

Fig. 7.1



Using the graph, determine the order of reaction with respect to

- iodomethane
- phenoxide ion

Justify your answer in each case. **[4]**

Order of reaction with respect to iodomethane: ……………………………………………

Justification: ……………………………………………

……………………………………………

……………………………………………

……………………………………………

……………………………………………

Order of reaction with respect to phenoxide ion: ……………………………………………

Justification: ……………………………………………

……………………………………………

……………………………………………

……………………………………………

……………………………………………

[Total: 13]

~END OF PAPER~

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RIVER VALLEY HIGH SCHOOL
JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME								
CLASS	18J							
CENTRE NUMBER	S					INDEX NUMBER		

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **24 September 2019**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Booklet
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 page.
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.

This document consists of **15** printed pages and 1 blank page.

Section A

Answer **all** the questions from this section.

1 **(a)** **(i)** Hydrogen halide, HX, is soluble in both polar and nonpolar solvents. Describe the interactions formed when HX dissolves in polar solvents such as water. **[1]**

(ii) The boiling points of the first four hydrogen halides down Group 17 are listed in the following table.

Table 1.1

Hydrogen Halide	Boiling Point / °C
HF	20
HC*l*	−85
HBr	−67
HI	−35

Describe and explain the trend. **[2]**

(iii) Four gas jars containing a hydrogen halide from Table 1.1 were prepared. When a red-hot steel needle is introduced to the gas jars respectively, two of them showed intense colour changes while the other two showed no visible change.

With reference to the *Data Booklet*, describe and explain the observations. **[3]**

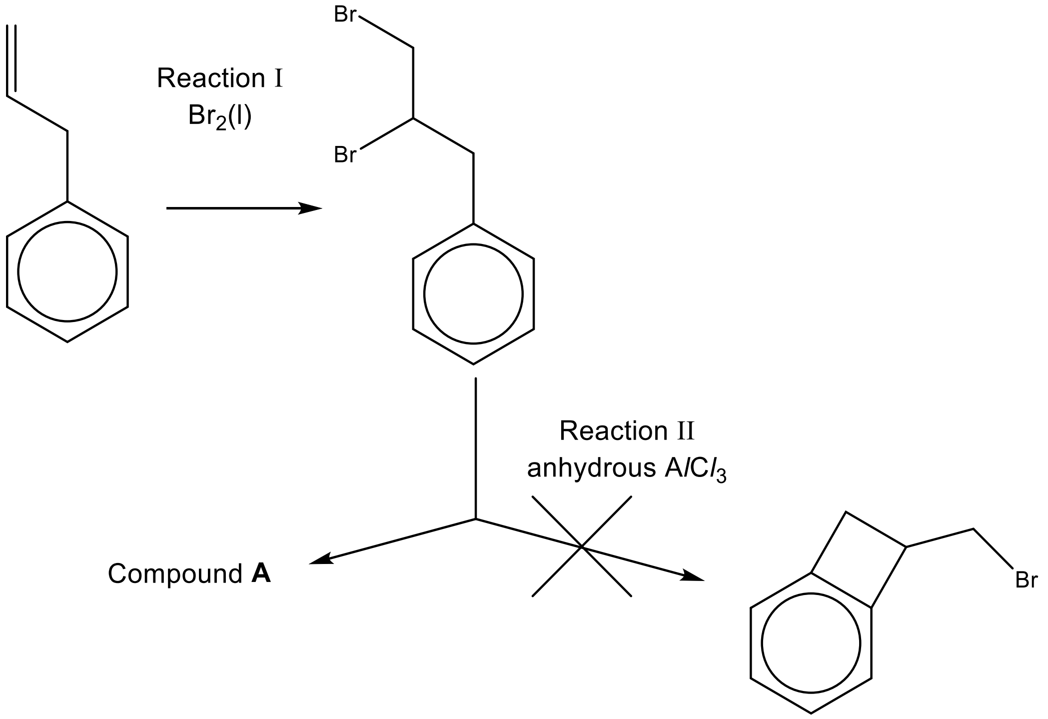
(b) **(i)** In an experiment, an excess of 5.00 g AgC*l*(s) was added to 1 dm^3 solution of 0.00100 mol dm^{-3} NaC*l* and allowed to reach equilibrium at 298 K. The mixture was then filtered and the residue was dried thoroughly. 100 cm^3 of the filtrate required the addition of 4.00×10^{-12} mol of NaBr for the first trace of AgBr to appear.

Given that solubility of AgBr in water is 0.140 mg L^{-1}, calculate the concentration of Ag^+ ions in the 100 cm^3 filtrate. **[2]**

(ii) Calculate the solubility of AgC*l* in mol dm^{-3}. **[2]**

(iii) Calculate the mass of residue collected from the filtration. **[1]**

(c)



Compound **A**

Compound **B**

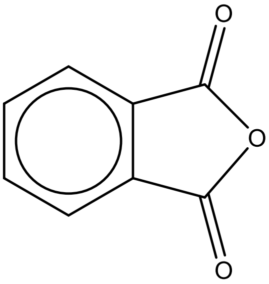
(i) There are two possible intermediates for Reaction I. Draw the structure of the more stable intermediate and explain its stability. **[2]**

(ii) Describe the mechanism of Reaction II to form Compound **A**. In your answer, use curly arrows to indicate the movement of electrons. **[2]**

(iii) With reference to the hybridisation of carbon atoms, explain why compound **B** is not a product from Reaction II. **[2]**

[Total: 17]

2 **(a)** Phthalic anhydride is the acid anhydride of phthalic acid. It is an important industrial chemical for the synthesis of phthalic esters, which are used as plasticisers to soften plastics

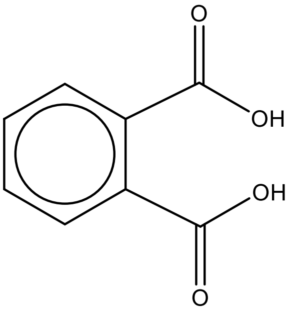


Phthalic anhydride

(i) Given that phthalic anhydride reacts with an alcohol to form a monoester as the only product, write an equation for the reaction of phthalic anhydride with propan-1-ol. **[1]**

(ii) The esterification of the monoester is more difficult to carry out and requires the removal of an inorganic by-product. Suggest the identity of the by-product. **[1]**

(b) Hydrolysis of phthalic anhydride produces phthalic acid, which is an aromatic dicarboxylic acid that can ionise in stages. Some information on phthalic acid and another aromatic acid are given below.



Phthalic acid

Table 2.1

	pK_1	pK_2
Phthalic acid	2.89	5.51
Benzoic acid	4.20	-

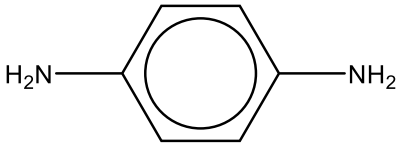
(i) Suggest a reason why the pK_2 of phthalic acid is higher than its pK_1. **[1]**

(ii) Calculate the pH of a solution that is obtained after 50 cm^3 of 0.1 mol dm$^{`3}$ of NaOH is added to 10 cm$^3$ of 0.2 mol dm$^{`3}$ phthalic acid. **[2]**

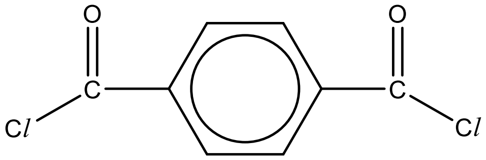
(iii) Sketch the pH-volume added curve you would expect to obtain when 50 cm^3 of 0.1 mol dm$^{`3}$ of NaOH is added to 10 cm$^3$ of 0.2 mol dm$^{`3}$ phthalic acid. Include relevant details from **(ii)** on your graph. **[3]**

(iv) Predict the structure of the ionic compound that will be formed when sodium benzoate is added to phthalic acid. **[1]**

(c) Kevlar is a heat resistant and strong synthetic polymer that is used in bullet-proof vests. Kevlar is synthesised in solution from the monomers of 1,4-phenylene-diamine and terephthaloyl chloride.



1,4-phenylene-diamine

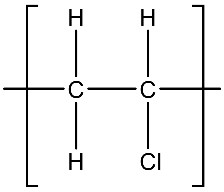


terephthaloyl chloride

(i) State the type of reaction that occurs between 1,4-phenylene-diamine and terephthaloyl chloride that will result in the formation of a polymer. **[1]**

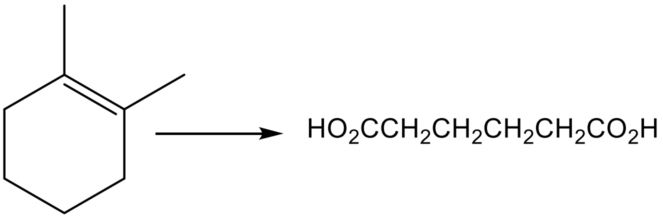
(ii) A repeating unit is a part of a polymer whose repetition would produce the complete polymer chain (except the end groups) by linking the repeating units together successively along the chain.

For example, the repeating unit of polyvinyl chloride is shown below.



Draw the structure of the repeating unit of Kevlar. **[1]**

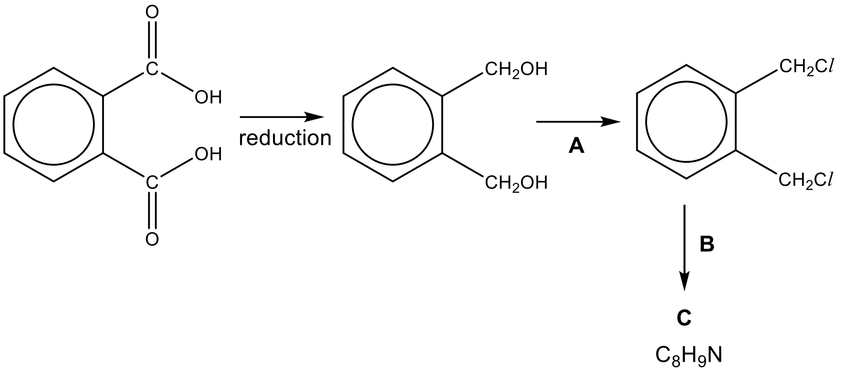
(d) Polyprotic organic acids are usual precursors in synthesis. Suggest how the polyprotic organic acid below can be synthesised. Indicate reagents and conditions you would use in each step, including the structure of the intermediate(s), if any.



$\longrightarrow HO_2CCH_2CH_2CH_2CH_2CO_2H$

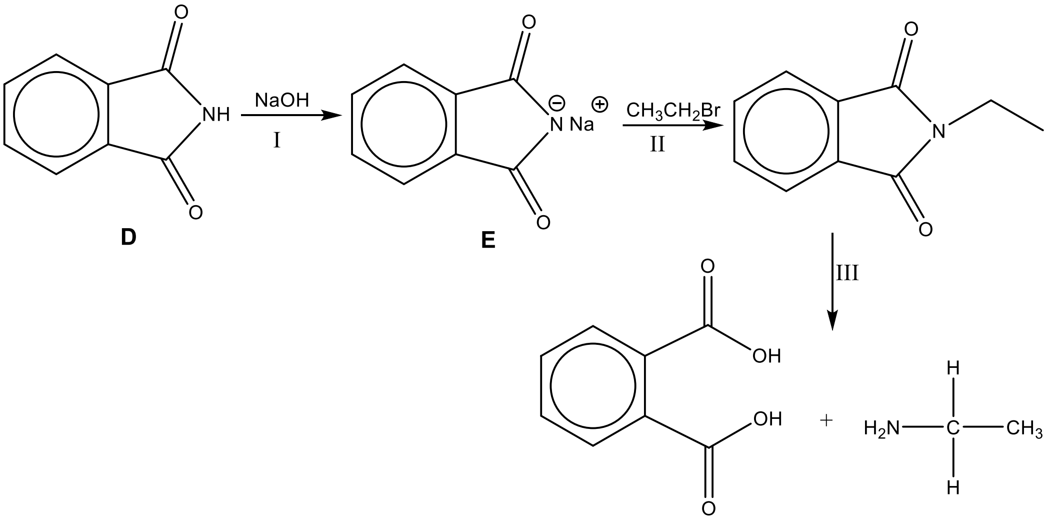
[2]

(e) Phthalic acid undergoes the reaction scheme below.



Suggest the reagents and conditions for Reactions **A** and **B** as well as the structure for Compound **C**. **[3]**

(f) Compound **D** is a useful intermediate for making primary amines from bromoalkanes, by the following method.



(i) State the types of reaction in Steps I, II and III. **[3]**

(ii) Suggest reagents and conditions for Step III. **[1]**

(iii) Draw a simple diagram to show how a water molecule can be attached to the anion in **E**. Label your diagram to show the dominant type of interaction involved. **[1]**

(iv) When **D** undergoes combustion, a student, Eugene, predicted that one of the likely products is either NO or N_2 gas. He carried out a simple experiment to determine the combustion equation for **D**.

First, he burnt 0.5 g of **D** in air. After combustion, he passed the gaseous mixture through potassium hydroxide and measured the volume of gas remaining at 30 ^oC and 1 atm. Eugene determined that the gaseous volume was 42.26 cm^3.

Using the information above, determine the identity of the gas and write an equation for the combustion reaction of **D**. **[3]**

[Total: 24]

3 Iron is the second most abundant metal in the earth's crust and is abundantly used in building materials such as steel. The two most common oxidation states of iron in its compounds are +2 and +3.

(a) When 5 cm^3 of 0.2 mol dm^{-3} iron(III) chloride solution was added to 10 cm^3 of 0.6 mol dm^{-3} sodium cyanide solution, the solution turned red.

When the resultant solution undergoes a redox reaction, the solution turned yellow and the complex **Y** formed has a M_r of 211.8.

Deduce, with the help of calculations and the *Data Booklet*, the formulae of the complexes formed when the solution turned red and yellow respectively. Write equations when appropriate. **[2]**

(b) Explain the following observations regarding iron and its compounds. Support your answers with data from the *Data Booklet* where appropriate.

(i) The electrical conductivity of iron is higher than that of calcium. **[1]**

(ii) The pH of a solution of iron(III) chloride is lower than the pH of a solution of iron(II) chloride of the same concentration. **[2]**

(c) Iron(III) ions catalyse the reaction between aqueous potassium peroxodisulfate, $K_2S_2O_8$, and aqueous potassium iodide.

(i) Explain, with the help of the *Data Booklet*, the role of Fe^{3+} in the reaction. **[2]**

(ii) Draw a fully-labelled energy profile diagram to show the above reaction, which is exothermic. **[3]**

(d) Compound **V**, with the molecular formula $C_8H_9NO_2$, is found to be able to relief pain and reduce fever. At room temperature, **V** is insoluble in water and dilute acids but soluble in aqueous sodium hydroxide. **V** reacts with aqueous bromine to form **W**, $C_8H_7NO_2Br_2$.

On heating **V** with dilute hydrochloric acid, compounds **X** and **Y** are formed. **X**, with the molecular formula C_6H_8NOCl, is soluble in water.

Y, on reduction with lithium aluminium hydride, forms **Z**. **Z** reacts with alkaline aqueous iodine to form a yellow precipitate.

Identify compounds **V** to **Z** and briefly explain the reactions described. **[9]**

[Total: 19]

Section B

Answer **one** question from this section.

4. Volatile organic compounds (VOCs) are carbon-containing chemical vapours that can come from both man-made and natural sources. VOCs generally have high vapour pressures at ordinary room temperatures.

The table below shows a list of the common VOCs found around us.

Table 4.1

VOC	Formula	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J mol^{-1} K^{-1}
Benzene	C_6H_6	+33.9	+113.6
Ethanol	C_2H_5OH	+38.6	+109.7
Methylbenzene	$C_6H_5CH_3$	+38.1	+87.3
Propanone	CH_3COCH_3	+31.3	+95.0

(a) **(i)** Using the Gibbs Equation,

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap},$$

explain whether the process of vaporisation is an enthalpy-driven or entropy-driven reaction. **[2]**

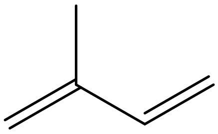
(ii) From Table 4.1, state the most volatile VOC at 330 K and calculate the corresponding ΔG_{vap}. **[1]**

(b) Dichloromethane, another common VOC of formula CH_2Cl_2, is synthesised industrially from methane via free radical chlorination.

(i) State the reagent and condition required to synthesise dichloromethane from methane. **[1]**

(ii) Describe the mechanism involved in this synthesis, showing the steps that produce dichloromethane. **[3]**

(c) Isoprene, C_5H_8, is one of the biologically generated VOCs by plants and algae. It is used to manufacture synthetic rubbers and elastomer plastics. It appears as a colourless, volatile liquid and is known to cause respiratory irritation from overexposure to its vapour.



(i) State the IUPAC nomenclature of isoprene. **[1]**

(ii) Yet, isoprene is the most abundant hydrocarbon measurable in human breath.

The estimated production rate of isoprene in the human body is 0.15 μmol kg^{-1} h^{-1}.

Calculate the mass, in mg, of isoprene estimated to be produced by a 65 kg person in a day.

[1 μmol = 10^{-6} mol] **[1]**

A gaseous mixture, made up of isoprene (C_5H_8) and carbon disulfide (CS_2), is prepared in a corresponding volume ratio of 1 : n.

The mixture is completely combusted with an excess of oxygen at 25 ^{o}C and 1 atm. After combustion, there was an overall volume contraction of 70 cm^3.

The resultant product mixture contains three gases, two of which are acidic, and water. Upon passing this mixture through aqueous sodium hydroxide, a further contraction of 170 cm^3 took place.

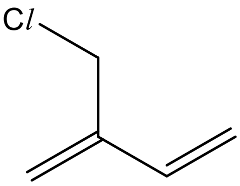
(iii) Given that complete combustion of carbon disulfide produces carbon dioxide and sulfur dioxide, write balanced equations for the complete combustion of isoprene and of carbon disulfide separately. **[2]**

(iv) Assuming that the volume of isoprene is x cm^3 in the gaseous mixture, find n using the balanced equations in **(c)(iii)**.

You may find proving the following expressions useful:

- $(n + 3)x = 70$ from the 1st contraction
- $(3n + 5)x = 170$ from the 2nd contraction **[3]**

(d) Compound **M**, a chlorinated form of isoprene of molecular formula C_5H_7Cl, is a liquid at room temperature.



Compound **M**

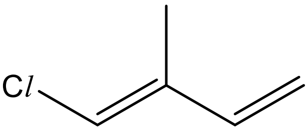
(i)

Enthalpy change of atomisation of carbon / kJ mol^{-1}	+715
Enthalpy change of vaporisation of compound **M /** kJ mol^{-1}	+30

Using the given data above and relevant data from the *Data Booklet*, construct a fully-labelled energy level diagram to calculate the enthalpy change of formation of compound **M**. **[4]**

(ii) Compound **N** is an isomer of compound **M**.

It is a liquid at room temperature and its enthalpy change of vaporisation is +30 kJ mol^{-1} as well.



Compound **N**

State the isomeric relationship between compounds **M** and **N**. **[1]**

(iii) It is found that the magnitude of its enthalpy change of formation is smaller than that of compound **M**. Suggest a possible reason for this. **[1]**

[Total: 20]

5 This question is about the chemistry of Period 3 elements.

(a) Describe the action of water on the oxides of magnesium, silicon and phosphorus.

Write equations for any reactions that occur, and suggest the pH for each of the resulting solutions.

[5]

(b) All wines contain sulfur dioxide for its anti-oxidant and anti-bacterial properties. However, if too much sulfur dioxide and sulfites are present, they would induce an unpleasant taste. Sulfur dioxide also contributes significantly to hangover.

The World Health Organisation recommends a maximum daily intake of 0.7 mg of SO_2 per kilogram of bodyweight.

Wineries use the Ripper titration to determine the concentration of SO_2 in mg L^{-1} in their wines. In a Ripper titration, 2 cm^3 of starch solution is added to 50 cm^3 of the wine in a conical flask. The wine is then titrated against a standard iodine solution.

17.70 cm^3 of 0.0100 mol dm^{-3} aqueous iodine is added until a dark colour appears and persists for at least 15 seconds.

(i) Write the balanced equation for the reaction between SO_2 and iodine. **[1]**

(ii) Determine the concentration of sulfur dioxide in the wine and state if it is advisable for a person of 70 kg to consume 400 mL of this bottle of wine. **[2]**

(c) Organometallic compounds, which contain a carbon-metal bond, are key intermediates in organic reactions to form a C–C bond. In general, when organometallic compounds are used on carbonyl compounds, alcohols are produced as shown in Fig 5.1.

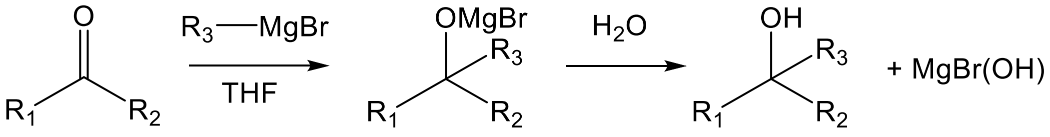


Fig 5.1

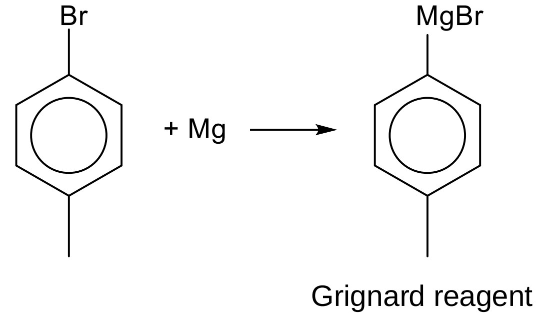
Common organometallic compounds are organolithium (contain carbon-lithium bond) and Grignard reagents (contain carbon-magnesium bond).

(i) In organolithium and Grignard reagents, carbon is a powerful nucleophile, which allows the formation of a C–C bond.

Explain how the nucleophilicity of carbon arises. **[1]**

An experiment was conducted to synthesise 4-toluic acid from 4-bromotoluene using a Grignard reagent. The Grignard reagent is first synthesised by a reaction between 4-bromotoluene and magnesium. The Grignard reagent is then used on dry ice to form 4-toluic acid in tetrahydrofuran (THF) solvent.

Synthesis of Grignard reagent:



Reaction:

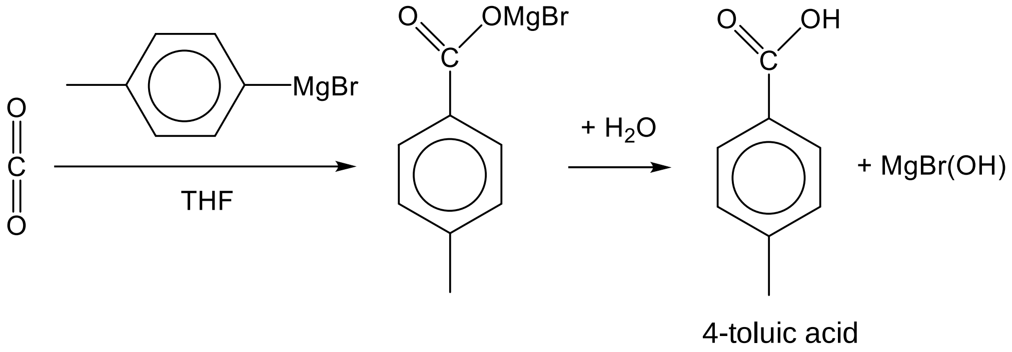


Fig 5.2 shows the reflux set-up of a Grignard reaction.

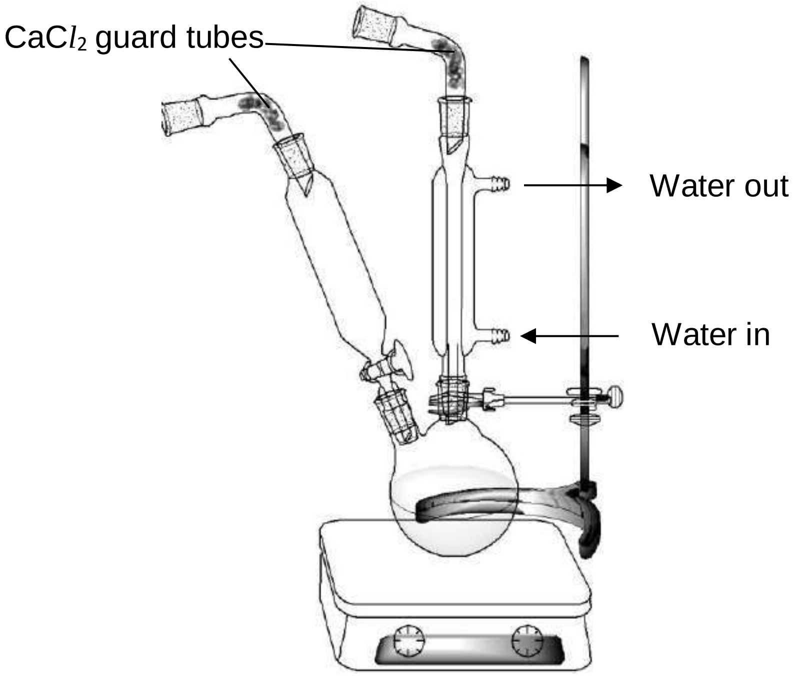


Fig 5.2

(ii) State the purpose of the calcium chloride guard tubes. **[1]**

(iii) Grignard reagents are destroyed readily upon the exposure to a small amount of moisture.

State the name of the reaction and draw the mechanism for this reaction using the Grignard reagent in Fig 5.2. **[2]**

A basic solvent extraction is used to purify the crude 4-toluic acid product. The crude product was dissolved in 20 cm^3 of dichloromethane (CH_2Cl_2) with 20 cm^3 of 10% NaOH.

The aqueous layer was extracted and combined before immersing in an ice-water bath. Concentrated hydrochloric acid was then added from a dispenser to the aqueous layer.

(iv) Explain the need for an ice-water bath in this step. **[1]**

In organic experiments, Thin Layer Chromatography (TLC) is often used to monitor the progress of a reaction and assess if the reaction is complete.

Fig. 5.3 shows a typical chromatography paper made up of silica (SiO_2) with the presence of hydroxyl groups on their surface.

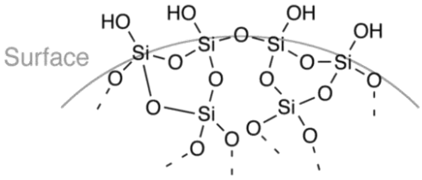


Fig. 5.3

When the reaction has proceeded for 60 minutes, a small portion of the reaction mixture, containing 4-bromotoluene and 4-toluic acid, was loaded on the TLC plate as shown in Fig. 5.4.

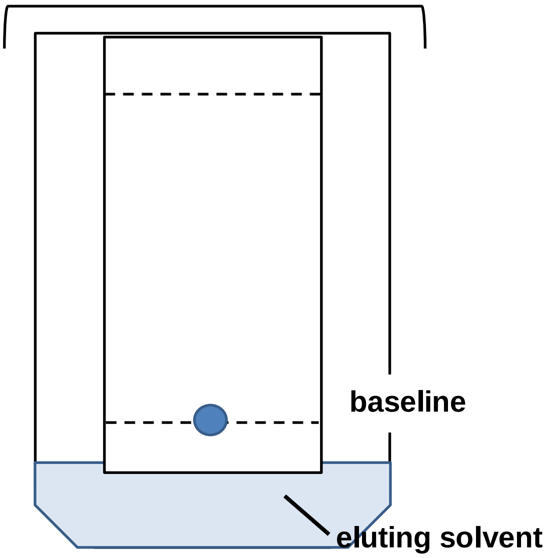


Fig. 5.4 TLC plate placed in TLC developing chamber

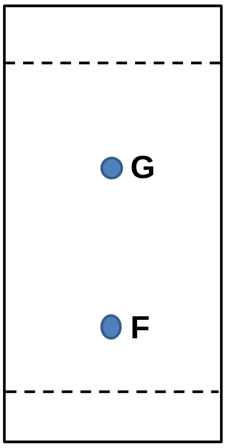


Fig. 5.5 TLC plate developed

The TLC plate was placed in a TLC developing chamber which contains an eluting solvent made up of ethyl acetate and hexane in a 1:2 volume ratio. As the eluting solvent passed through the spots on the baseline, depending on the interactions with the chromatogram and eluting solvent, the solute molecules travelled at different rates up the chromatogram. Each compound has a different retention factor, R_f, in the eluting solvent.

(v) The TLC plate is developed and the result is shown in Fig. 5.5.

Determine the R_f value of **F** in this TLC, given that the R_f is calculated as:

$$R_f = \frac{distance\ moved\ by\ solute}{migration\ distance\ moved\ by\ solvent}$$

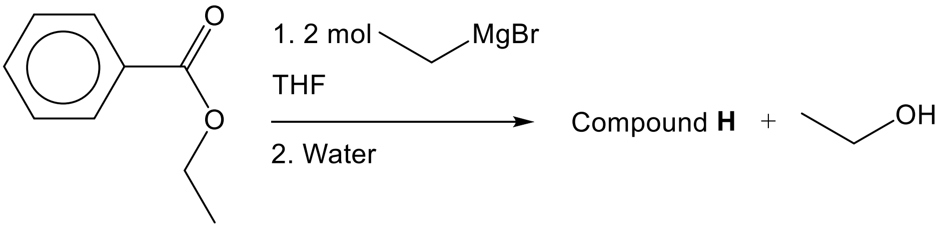
[1]

(vi) Consider the interactions between silica and 4-toluic acid, and between silica and 4-bromotoluene, identify **F** and **G**. Hence, explain the difference in the migration distance between 4-toluic acid and 4-bromotoluene.

[2]

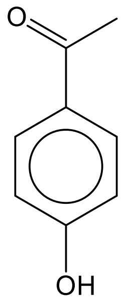
(vii) Suggest how the R_f value of 4-toluic acid will change when the eluting solvent is changed to ethyl acetate : hexane in a 2:1 volume ratio. **[1]**

(viii)

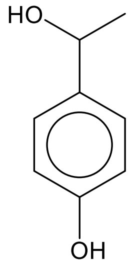


Suggest the structure for compound **H**. **[1]**

(ix) Compounds **J** and **K** are isomers of 4-toluic acid. Describe a simple chemical test to distinguish between compounds **J** and **K**.



Compound **J**



Compound **K**

[2]

[Total: 20]

– **End of Paper –**

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RIVER VALLEY HIGH SCHOOL

JC 2 PRELIM PRACTICAL EXAMINATION

H2 CHEMISTRY 9729

26 AUGUST 2019

2 HOURS 30 MINUTES

NAME ______________________________

CLASS 18J (   )

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

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

1 An experiment to investigate the behaviour of acids and bases in aqueous solution

FA 1 is 1.00 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$

FA 2 is sodium hydroxide, NaOH, between 1.5 to 2.5 mol dm^{-3}

FA 3 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

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.
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ $\qquad \Delta H_{neutralisation} = –57.1$ kJ mol^{-1}

The reaction between $H^+(aq)$ and $OH^-(aq)$ involves bond formation and is exothermic. It is possible to make use of this fact to perform a thermometric titration. This task involves two different acid-base reactions.

The first reaction is between sodium hydrogencarbonate, **FA 1**, and sodium hydroxide, **FA 2**.

Reaction 1:
$NaHCO_3(aq) + NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$ $\qquad \Delta H_{reaction\ 1}$

The molar enthalpy change for **Reaction 1**, $\Delta H_{reaction\ 1}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

Instead of using an indicator to determine the endpoint, you will perform a thermometric titration to determine the equivalence point of the reaction. The equivalence point is that point where $H^+(aq)$ from the acid and $OH^-(aq)$ from the base are present in equal molar amounts.

The second reaction is between sodium hydrogencarbonate, **FA 1**, and sulfuric acid, **FA 3**.

Reaction 2:
$NaHCO_3(aq) + \frac{1}{2}H_2SO_4(aq) \longrightarrow \frac{1}{2}Na_2SO_4(aq) + H_2O(l) + CO_2(g)$
$\Delta H_{reaction\ 2}$

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.

In your first experiment, you will perform a thermometric titration by adding portions of **FA 2** progressively to a known volume of **FA 1**. You will continue adding **FA 2** until the equivalence point is reached and passed. Throughout the experiment, you will note and record the temperature of the mixture after each addition.

You will then analyse your results graphically in order to determine the
- titration volume at the equivalence point, $V_{\text{equivalence}}$,
- maximum temperature change, $\Delta T_{\text{maximum 1}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 1}}$, for **Reaction 1**.

In your second experiment, you will mix together a given volume of **FA 1** with a suitable volume of **FA 3**.

You will then determine the
- maximum temperature change, $\Delta T_{\text{maximum 2}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 2}}$, for **Reaction 2**.

Reaction between FA 1 and FA 2

(a) **(i)** In this task you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 2** have been added. It is important that the volume of **FA 2** recorded is the total volume you have added up to that point when the temperature reading was made.

Note:
If you overshoot on an addition, record the **actual** total volume of **FA 2** added up to that point.

In an appropriate format in the space provided, record all values of temperature, *T,* to 0.1 °C, and each total volume of **FA 2** added to 0.05 cm^3.

1. Fill a burette with **FA 2**.
2. Place a Styrofoam cup inside a second Styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** to the first Styrofoam cup.
4. Stir the **FA 1** solution in the cup with the thermometer. Read and record its temperature.
5. From the burette, add 2.00 cm^3 of **FA 2** to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture, *T,* and the volume of **FA 2** added.
7. Repeat points 5 and 6 until a total of 30.00 cm^3 of **FA 2** has been added. After each addition of **FA 2**, record the maximum temperature of the mixture and the total volume of **FA 2** added up to that point.

Results

For Examiner's Use

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For Examiner's Use

(a) (ii) On the grid below, plot a graph of temperature, T against volume of **FA 2** added.

3	
4	
5	

(iii) Draw **two** smooth lines of best fit. Extrapolate these lines until they cross. Extrapolate these lines until they cross.

6	
7	
8	

(iv) Determine from your graph,

- the maximum temperature reached, T_{maximum},
- the maximum temperature change, $\Delta T_{\text{maximum 1}}$,
- the volume, $V_{\text{equivalence}}$, of **FA 2** needed to completely react with 25.0 cm^3 of **FA 1**.

Show on your graph how you obtained these values.

Record these values in the spaces provided below.

Maximum temperature reached, T_{maximum} = ...

Volume of **FA 2** used, $V_{\text{equivalence}}$ = ...

Supervisor
Student
Difference

Hence, calculate the maximum temperature change, $\Delta T_{\text{maximum 1}}$

= ....

Supervisor
Student
Difference

Reaction between FA 1 and FA 3

For Examiner's Use

(b) The molar enthalpy change for **Reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

In this task you will calculate a value for the molar enthalpy change, $\Delta H_{\text{reaction 2}}$. To do this you will need to determine the maximum temperature change produced when measured volumes of **FA 1** and **FA 3** are mixed. After considering the concentrations of **FA 1** and **FA 3**, you will select a suitable volume of **FA 3** to add to 40 cm^3 of **FA 1**.

(i) Choose a suitable volume of **FA 3**, $V_{\textbf{FA 3}}$, to be added to 40 cm^3 of **FA 1**. Explain your answer.

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(ii) Identify the apparatus you intend to use to measure the volume of **FA 1**.

Explain your choice.

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………………………………………………………………………………… **11**

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(iii) In an appropriate format in the space provided below, record all values of measured temperature for this experiment.

1. Label one Styrofoam cup, **A**. Label a second Styrofoam cup, **B**.
2. Place cup **A** inside a Styrofoam cup which is held in a glass beaker to prevent it from tipping over.
3. Transfer 40 cm^3 of **FA 1** into cup **A**.
4. Stir the **FA 1** solution in cup with the thermometer. Read and record its temperature, $T_{\textbf{FA 1}}$. This is the initial temperature of **FA 1**.
5. Wash and dry the thermometer.
6. Transfer your chosen volume of **FA 3** into cup **B**. Stir the **FA 3** solution with the thermometer. Read and record its temperature, $T_{\textbf{FA 3}}$. This is the initial temperature of **FA 3**.
7. Carefully add the contents of cup **B** to cup **A** in **small** portions to avoid too much frothing.
8. Place the lid on the cup and insert the thermometer through the lid. Stir the mixture.
9. Continue to stir the mixture. Measure and record the temperature, T_{mixture} that shows the maximum change from the initial temperature.

Results

For Examiner's Use

12	
13	

Calculations

(c) For the purposes of these calculations, you should 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}.

(i) Calculate the concentration of sodium hydroxide, [NaOH], in **FA 2**.

14	

[NaOH] in **FA 2** = ...

(ii) Calculate the heat change, *q*, for the reaction occurring in **(a)(i)**, and hence determine a value for the molar enthalpy change for **Reaction 1**, $\Delta H_{\text{reaction 1}}$.

15	
16	

q =.............................

$\Delta H_{\text{reaction 1}}$= ………………………………

(d) Use your results from **(b)(iii)** to calculate a value for the molar enthalpy change for **Reaction 2**, $\Delta H_{\text{reaction 2}}$. For the experiment in **(b)(iii)**, the weighted average initial temperature, T_{average}, of **FA 1** and **FA 3** may be calculated using the formula given below.

For Examiner's Use

$$T_{average} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA3} \times T_{FA3})}{(V_{FA1} + V_{FA3})}$$

17	
18	
19	

T_{average} = ...

q =.............................

$\Delta H_{\text{reaction 2}}$ = ...

(e) Ionic equations for neutralisation, **Reaction 1**, and **Reaction 2** are shown below.

$HCO_3^{-}\,(aq) + OH^{-}\,(aq) \longrightarrow CO_3^{2-}\,(aq) + H_2O\,(l) \qquad \Delta H_{\text{reaction 1}}$
$HCO_3^{-}(aq) + H^{+}\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g) \qquad \Delta H_{\text{reaction 2}}$

Use your answers in **(c)(ii)** and **(d)**, draw an energy cycle to determine a value for the molar enthalpy change, $\Delta H_{\text{reaction 3}}$, for **Reaction 3**.

Reaction 3:
$H_2O(l) + CO_2(g) + OH^{-}(aq) \longrightarrow CO_3^{2-}(g) + H_2O(l) + H^{+}(aq) \quad \Delta H_{\text{reaction 3}}$

20	
21	

(f) An alternative definition of acid-base behaviour was proposed by Brønsted and Lowry. **Reaction 1** and **Reaction 2** are both acid-base reactions involving hydrogencarbonate ions, HCO_3^{-}.

In terms of the *Brønsted-Lowry* theory of acids and bases, suggest the role of hydrogencarbonate ions, HCO_3^{-}, in **Reaction 1**.

Explain your answer.

Reaction 1

Role of HCO_3^{-} : ....

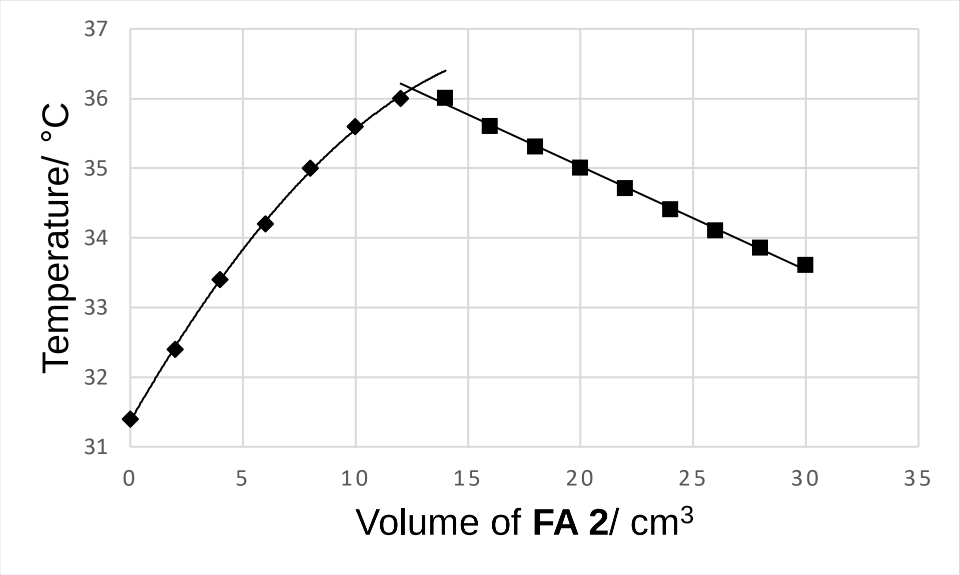
22	

Explanation : ....

....

....

(g) A student conducted the same experiment using a digital thermometer and obtained the graph as shown below.



Explain the shape of the graph.

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For Examiner's Use

(h) In the calculation of **(d)**, explain why the weighted average initial temperature was used.

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(h) With reference to the reaction between **FA 1** and **FA 2**, if the volume of NaOH is doubled, explain how it will affect the maximum temperature change?

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[Total: 27]

2 To determine the proticity of an unknown acid

For Examiner's Use

Acid base titration is commonly used to determine the concentration of an acid or base. In this experiment, the concentration of the acid is given and the aim of this investigation is to determine its proticity.

Acids are defined as substances that can donate hydrogen ions, H^+, to bases. Monoprotic acids contain one H^+ that can be donated per molecule. Diprotic acids contain two H^+ that can be donated per molecule.

You will determine using a titration method whether acid **Z** is monoprotic or diprotic.

- **FA 4** is a solution containing 11.55 g dm^{-3} of acid **Z**.
- **FA 5** is 0.105 mol dm^{-3} aqueous sodium hydroxide, NaOH.
- Thymol blue indicator

(a) Method

1. Pipette 25.0 cm^3 of solution **FA 4** into a conical flask.
2. Fill a burette with **FA 5**.
3. Add 3 drops of thymol blue indicator to the conical flask.
4. The colour change at the endpoint is yellow to blue.
5. Carry out as many accurate titrations as you think necessary to obtain consistent results.
6. Record, in a suitable form below, all of your burette readings and the volume of **FA 5** added in each accurate titration.

Results

28	
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For Examiner's Use

(b) From your titration results, obtain a suitable value for the volume of **FA 5** to be used in your calculations. Show clearly how you obtained this value.

32	

Volume of **FA 5** =............................

(c) Calculations

(i) Calculate the amount of H^+ present in 25.0 cm^3 of **FA 4**.

33	

Amount of H^+ in 25.0 cm^3 of **FA 4** = ...

(ii) Calculate the amount of H^+ present in 1 dm^3 of **FA 4**.

34	

Amount of H^+ in 1 dm^3 of **FA 4** = ...

(iii) **FA 4** contains 11.55 g dm^{-3} of acid **Z**. The relative molecular mass of **Z** is 126. Calculate amount of **Z** in 1 dm^3 of **FA 4**.

35	

Amount of **Z** in 1 dm^3 of **FA 4** = ...

(iv) Use your answers to **(ii)** and **(iii)** to determine whether **Z** is a monoprotic or a diprotic acid. Explain your answer.

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(v) Student **A** conducted this experiment on the day when the chemicals were freshly prepared. His average titre value was found to be *h* cm^3.

Three days later, he conducted the same experiment using the same chemicals but he found that the bottle of NaOH(aq) was left uncovered.

Suggest how his new titre value would compare to *h* cm^3 and explain your answer.

37	

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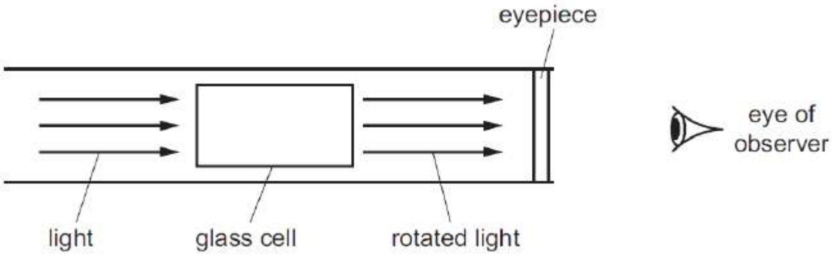
(d) Planning

For Examiner's Use

Sucrose, $C_{12}H_{22}O_{11}$, is a sugar. The concentration of a solution of sucrose can be measured by the optical rotation, α, of a sucrose solution instead of acid–base titration. The more concentrated the solution, the greater the optical rotation of the solution.

A polarimeter is used to measure optical rotation. Plane–polarised light is passed through a sample of the sucrose solution in a glass cell, and the observed angle of rotation, α_{obs}, is measured.

A simplified diagram of a polarimeter is shown.



If a glass cell of length 1 cm is filled with a solution of sucrose of concentration 1 g cm^{-3}, the measured angle of rotation is known as the specific rotation, [α].

The observed angle of rotation, α_{obs}, measured by the polarimeter is related mathematically to the concentration of the sucrose solution by the equation shown.

$$\alpha_{obs} = [\alpha]lc$$

α_{obs} is the observed angle of rotation.

[α] is a constant and is known as the specific rotation of sucrose solution.

l is path length which is 1 cm in the above description.

c is the concentration of sucrose, in g cm^{-3}

(i) Explain why a sucrose solution is able to rotate plane–polarised light.

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38	

(ii) Using the information given above, you are required to write a plan to determine the concentration of sucrose in a solution **X**.

You may assume that you are provided with:

- solid sucrose, $C_{12}H_{22}O_{11}$;
- solution **X**, of an unknown sucrose concentration less than 0.0800 g cm^{-3};
- access to a polarimeter and instructions for use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.
- glass cell of length 10 cm.

Your plan should include details of:

- the preparation of 250 cm^3 0.0800 g cm^{-3} sucrose solution using solid sucrose provided;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- a sketch of the calibration curve you would expect to obtain;
- how the calibration line would be used to determine the concentration of sucrose in solution **X**.

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For Examiner's Use

(iv) The glass cell of 10 cm length is expensive, so one cell is used for all the solutions that are placed in the polarimeter.

Suggest how you would ensure that the concentration of solution in the cell is accurate each time the cell is used for the different sucrose solutions.

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(v) Concentration of sucrose is the independent variable in this polarimeter experiment.

The glass cell of 10 cm length is replaced by a glass cell of 20 cm length. The 20 cm glass cell is filled with 0.0750 g cm^{-3} sucrose solution.

Given that α_{obs} of 0.0750 g cm^{-3} sucrose solution is $+6.11^{o}$, predict the value for the observed angle of rotation, α_{obs}, for the sucrose solution of concentration 0.0750 g cm^{-3} when the 20 cm cell is used.

47	

Predicted angle = …………………………..

[Total: 20]

3 Inorganic qualitative analysis

For Examiner's Use

(a) **FA 6** and **FA 7** each contain one anion and one cation.

Carry out the following tests and record your observations. For each test you should use a small spatula measure of **FA 6** or **FA 7**

	observations	
test	**FA 6**	**FA 7**
Add a small spatula measure to a 1 cm depth of deionised water in a test-tube and shake. Add 2 drops of universal indicator. Record the pH of the mixture.		
Heat a small spatula measure in a dry boiling tube until no further change is observed.		
Add a small spatula measure in a 2 cm depth of dilute hydrochloric acid in a boiling tube. Decant 1 cm depth of this solution into two test-tubes.	☒	☒

48	
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51	

To one test-tube, add aqueous sodium hydroxide.		
To the second test-tube, add aqueous ammonia.		

For Examiner's Use

(b) Mix a spatula measure of **FA 6** with a spatula measure of **FA 7**. Heat the mixture in a boiling tube. Record your observations.

State the type of reaction that has occurred.

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

……………………………………………………………………………………

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Type of reaction: ……………………………………………………………

52	
53	

(c) From your observations in **(a)** and **(b)**, identify the possible ions present in **FA 6** and **FA 7**.

If you are unable to identify an ion, write 'unknown'.

	cation	anion
FA 6		
FA 7		

54	
55	

[Total: 8]

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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

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RIVER VALLEY HIGH SCHOOL
JC2 PRELIM EXAMINATION

CANDIDATE NAME					
CLASS	18J				
CENTRE NUMBER	S	3	0	4	4

INDEX NUMBER				

H2 CHEMISTRY 9729/01

Paper 1 Multiple Choice

26 Sep 2019
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 **16** 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 50.00 cm^3 of a solution of 0.300 mol dm^{-3} MoO_x^{2-} was reduced to Mo^{3+} using Zn powder. The filtrate required 45.00 cm^3 of 0.200 mol dm^{-3} acidified $KMnO_4$ to revert back to its original form of MoO_x^{2-}.

What is the value of x?

A	1	**B**	2	**C**	3	**D**	4

2 10 cm^3 of an unknown hydrocarbon was combusted in excess oxygen gas. The gaseous mixture contracted by 30 cm^3. The gaseous mixture further contracted by 40 cm^3 when it was passed through aqueous sodium hydroxide. All volumes of gases were measured at room temperature and pressure.

1	cyclopropane
2	butane
3	cyclobutane
4	but-2-ene

What is the hydrocarbon?

A	1 and 2 only
B	2 and 3 only
C	3 and 4 only
D	2, 3 and 4

3 The successive ionisation energies, in kJ mol^{-1}, of elements **X** and **Y** are given below.

X	575	1820	2740	11600	14800	18400	23400
Y	1320	3390	5320	7470	11000	13330	71330

1 The element preceding **X** in the Periodic Table has a higher first ionisation energy.

2 Element **Y** has a lower first ionisation energy than the element preceding it in the Periodic Table.

3 **X** and **Y** forms a compound with the formula $\mathbf{X}_3\mathbf{Y}_2$.

4 Oxide of **X** dissolves in water to give an acidic solution.

Which statements about **X** and **Y** are true?

A	1 and 2 only
B	1 and 3 only
C	2 and 3 only
D	2 and 4 only

4 *Use of Data Booklet is relevant to this question.*

Some isotopes are unstable and undergo beta decay (β-decay).

β-decay is a process where a neutron transforms into a proton by the emission of an electron. The proton is retained in the nucleus.

Which of the following change describes a β-decay?

A $^{40}\text{K} \rightarrow {}^{40}\text{Ca}$

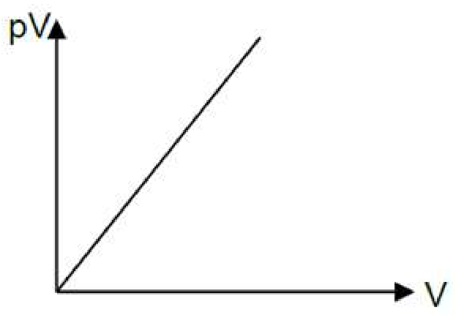
B $^{32}\text{P} \rightarrow {}^{31}\text{P}$

C $^{11}\text{C} \rightarrow {}^{12}\text{C}$

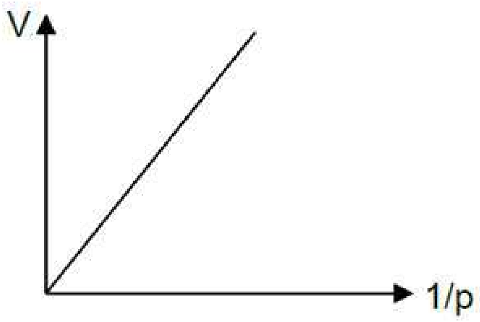
D $^{23}\text{Na} \rightarrow {}^{22}\text{Ne}$

5 Which graph does **not** describe the behaviour of a fixed mass of ideal gas at constant temperature?

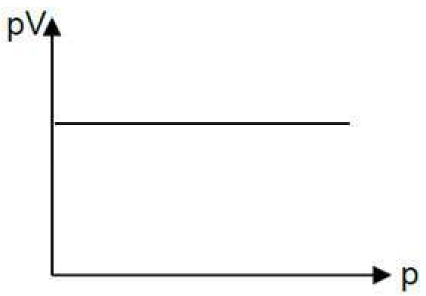
A



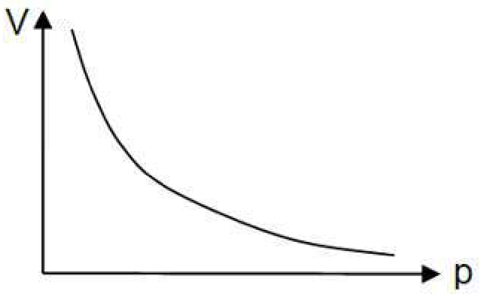
B



C



D



6 Which of the following statements are correct?

1 Covalent compounds can act as electrolytes in water.

2 Ionic bonds and covalent bonds can occur in the same compound.

3 An ionic compound will have the greatest degree of covalent character if both the cation and anion are large.

4 Ionic compounds can conduct electricity in both solid and liquid states.

A	1 and 2 only
B	1 and 4 only
C	3 and 4 only
D	2 and 4 only

7 Which of the following shows a decrease in bond angle from left to right?

A	$SiCl_4$	H_2O	NF_3
B	$AlCl_3$	NH_3	PH_3
C	PCl_3	PF_3	PBr_3
D	CCl_4	SF_6	XeF_4

8 The table below gives the standard enthalpy change of hydrogenation of three compounds to form cyclohexane:

Compound	$\Delta H_{\text{hydrogenation}}$ /kJ mol^{-1}
benzene	−206
1,3,5−cyclohexatriene	−360
cyclohexene	−120

Which of the following statements is correct?

A 1,3,5−cyclohexatriene is more stable than benzene.

B Benzene has a lower energy content than 1,3,5−cyclohexatriene.

C The C=C bond energy in cyclohexene is weaker than that in 1,3,5−cyclohexatriene.

D The enthalpy change of atomisation of benzene is smaller than that of 1,3,5−cyclohexatriene.

9 Which of the following statements are correct for a system at dynamic equilibrium?

1 The rate of both forward and backward reaction is the same

2 The concentration of reactants is equal to the concentration of products

3 The rate constant of forward reaction is equal to the rate constant of the backward reaction

A	1 only	**B**	1 and 2 only	**C**	1 and 3 only	**D**	2 and 3 only

10 A pure sample of $SO_3(l)$ is introduced into an evacuated vessel. The vessel, of constant volume, is heated to a constant temperature such that the equilibrium below is established.

$$2SO_2(g) \quad + \quad O_2(g) \quad \rightleftharpoons \quad 2SO_3(g)$$

The value of pressure is found to be 27% greater than if only $SO_3(g)$ were present.

What is the mole fraction of oxygen in the equilibrium mixture?

A	0.119	**B**	0.213	**C**	0.425	**D**	0.787

11 Equal volumes of 1.35 × 10^{-5} mol dm^{-3} $Bi(NO_3)_3$ and 2.00 × 10^{-5} mol dm^{-3} NaOH were added to a conical flask. Equilibrium was achieved within a few minutes and the following observations were made.

Given that solubility of $Bi(OH)_3$ is 2.87 × 10^{-7} mol dm^{-3}, which option contains the correct descriptions?

	Precipitation of $Bi(OH)_3$	IP vs K_{sp} for the solution at equilibrium
A	Yes	IP > K_{sp}
B	Yes	IP = K_{sp}
C	No	IP = K_{sp}
D	No	IP < K_{sp}

12 Caesium-137 is a radioactive isotope with a half-life of 30.2 years. Following the Fukushima Daiichi nuclear disaster in 2011, it was reported that about 8.4 kg of Caesium-137 was released into the sea.

What is the mass of Caesium-137 left in the sea after 100 years?

A	0.801 kg
B	0.846 kg
C	1.05 kg
D	6.73 kg

13 For the reaction: **A**(g) + **B**(g) → **C**(g) + **D**(g), the following experimental data was obtained.

Expt No.	[**A**] /mol dm^{-3}	[**B**] /mol dm^{-3}	Initial rate of reaction /mol dm^{-3} s^{-1}
1	0.20	0.20	3.00×10^{-4}
2	0.60	0.20	9.00×10^{-4}
3	0.80	0.40	4.80×10^{-3}

Which of the following conclusions can be drawn for the reaction?

1 The unit for rate constant is mol^{-2} dm^{6} s^{-1}.

2 The overall equation is the rate determining step.

3 The initial rate of reaction can be calculated from the initial rate of formation of **C**(g).

A	1 only	**B**	1 and 2 only	**C**	1 and 3 only	**D**	2 and 3 only

14 The following equilibrium are studied at a fixed temperature T °C.

Equilibrium 1: $H_2PO_4^- + SO_4^{2-} \ll HSO_4^- + HPO_4^{2-}$

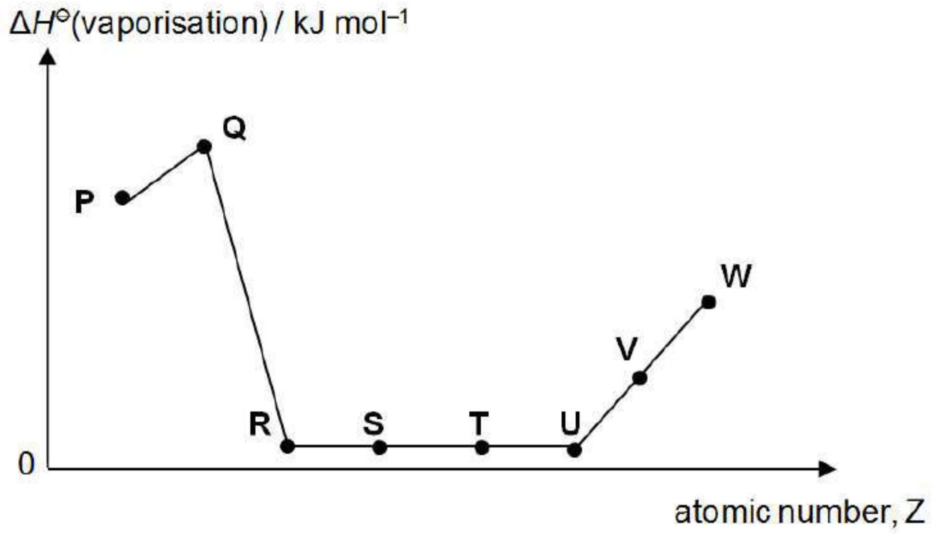
Equilibrium 2: $HSO_4^- \ll SO_4^{2-} + H^+$ $K_c = K_2$

Equilibrium 3: $H_2PO_4^- \ll HPO_4^{2-} + H^+$ $K_c = K_3$

Given that $K_2 > K_3$, which of the following statements is correct?

A	HPO_4^{2-} is a stronger acid.
B	$H_2PO_4^-$ is the conjugate base of HPO_4^{2-}.
C	The position of Equilibrium 1 lies to the left.
D	The rate of forward reaction for all three equilibrium decreases at (T+100) °C.

15 The graph below shows the variation in the standard enthalpy change of vaporisation, $\Delta H^{\ominus}$(vaporisation), for eight consecutive elements in the Periodic Table, all with atomic number, Z $\leq$ 20.

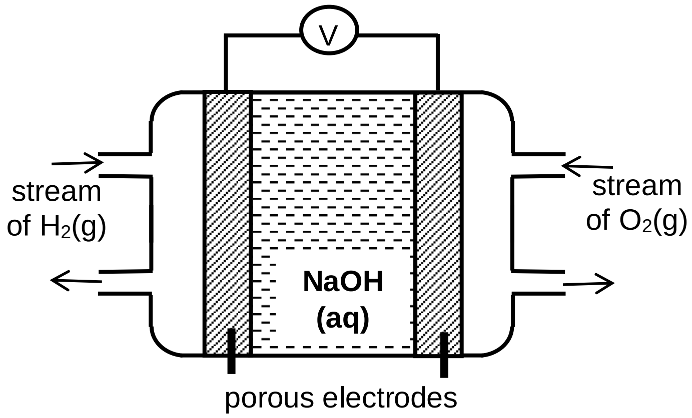


Which of the following statement is correct?

A	Element **Q** forms an oxide which is amphoteric.
B	Element **R** forms an oxide which is basic in aqueous solution.
C	Element **V** forms a chloride which is neutral in aqueous solution.
D	Element **W** forms a chloride which is basic in aqueous solution.

16 Element **E** is in the third period of the Periodic Table. The chloride of **E** has a simple molecular structure while the oxide of **E** has a giant ionic structure. Which of the following statements is **incorrect**?

A	The atomic radius of **E** is larger than that of chlorine.
B	The melting point of **E** is lower than its preceding element.
C	The chloride of **E** dissolves in water to give an acidic solution.
D	The oxide of **E** reacts with excess aqueous sodium hydroxide to form a colourless complex.

17	*Use of the Data Booklet is relevant in this question.* A hydrogen-oxygen fuel cell is constructed using 1.00 mol dm^{-3} sodium hydroxide as the electrolyte. What is the change in pH of the solution around each electrode when the current is flowing? 		
		Cathode	**Anode**
	A	increase	decrease
	B	increase	increase
	C	decrease	increase
	D	decrease	decrease

18	*Use of the Data Booklet is relevant to this question.* An antique car bumper is to be chrome plated. The bumper is dipped into a Cr^{3+} solution where it serves as an electrode of an electrolytic cell. Oxygen is formed on the other electrode. Which of the following statements is correct?	
	A	The bumper is the anode of the electrolytic cell.
	B	Reduction of water occurs at the cathode.
	C	For every 52 g of chromium plated, 3 mole of oxygen is evolved.
	D	It takes about 8 hours to plate 52 g of chromium, if the current used is 10 A.

19 When a dilute sulfate solution of a metal **J** is electrolysed, metal **J** and a diatomic gas **K** are produced at the cathode and the anode respectively in the molar ratio 2:1. In another experiment, the same quantity of electricity is used to electrolyse a saturated sodium chloride solution and a gas **L** is evolved at the anode.

What is the molar ratio of **J** : **K** : **L**?

A	2:1:1	**B**	2:1:2
C	4:2:1	**D**	4:2:3

20 Covalent bonds are formed when orbitals overlap. The shape of many organic molecules can be explained by the hybridisation of orbitals.

Which bond is **not** present in the molecule, HC˜CCHˆCH$_2$?

A	A σ bond formed by 1s-2sp overlap
B	A σ bond formed by 2sp-2sp^2 overlap
C	A σ bond formed by 2sp-2sp^3 overlap
D	A π bond formed by 2p-2p overlap

21 In the 1960s, a certain class of organic compounds was widely used in aerosol sprays, refrigerants and making foamed plastics. However, they were found to destroy the ozone layer in the upper atmosphere and viable replacements were sought to minimise ozone depletion.

Which of the following compounds can be used safely as a replacement?

A	$CHBr_3$
B	CF_3CBr_3
C	$CHClFCClF_2$
D	$CH_3CH_2CH_2CH_3$

22	For which property of the alkanes does the numerical value decrease down the homologous series?	
	A	Density
	B	Enthalpy change of vapourisation
	C	Number of isomers
	D	Vapour pressure

23	Hydrogen bromide reacts with but-1-ene to form bromobutane. Which statements are possible descriptions of the organic intermediate in this reaction? 1 It contains carbon, hydrogen and bromine. 2 It has a positive charge. 3 It reacts with a nucleophile. 4 It has a plane of symmetry.	
	A	1 and 3 only
	B	2 and 3 only
	C	2 and 4 only
	D	3 and 4 only

24	Which salt will be the most acidic in aqueous solution?	
	A	$CH_3CH_2CH_2NH_3Cl$
	B	$C_6H_5NH_3Cl$
	C	$MgCl_2$
	D	NH_4Cl

25 When propene is bubbled through iodine monochloride, ICl, dissolved in water, which products could be formed?

1 $CH_3CH(OH)CH_2Cl$

2 CH_3CHICH_2OH

3 $CH_3CHClCH_2I$

4 CH_3CHICH_2Cl

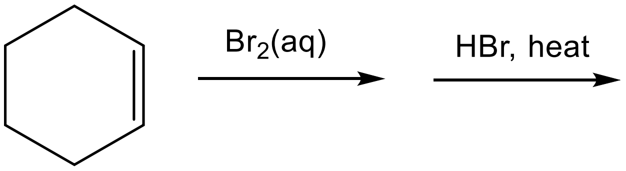
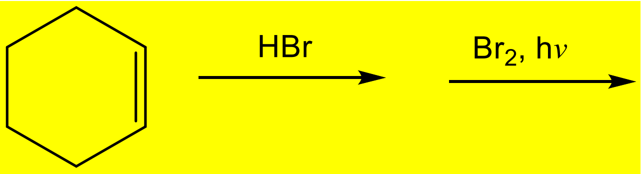
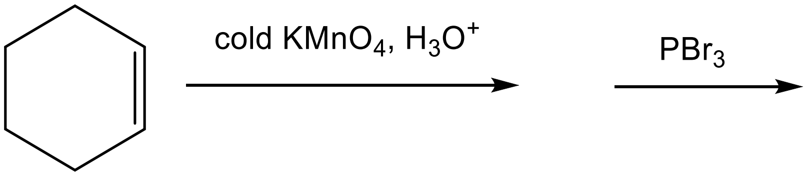
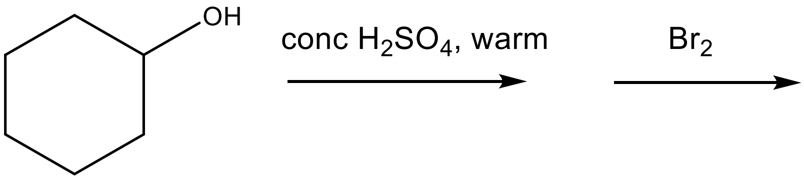
A	1 and 2 only
B	2 and 3 only
C	3 and 4 only
D	2, 3 and 4

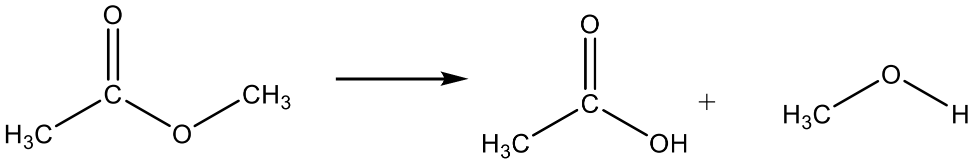
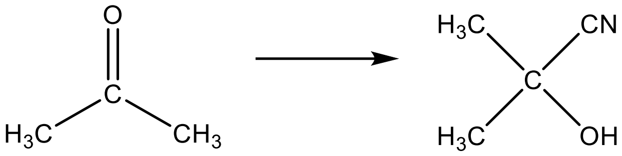
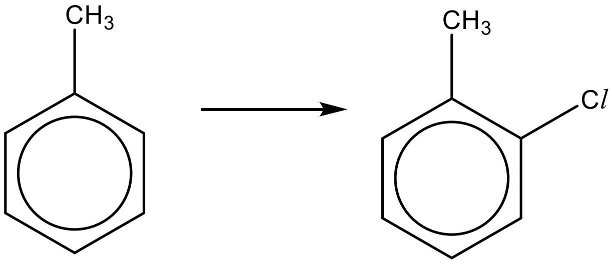
26 Tetrapeptide, **P**, is formed by an unknown amino acid. **P** has a relative molecular mass of *M*.

What is the relative molecular mass of the amino acid?

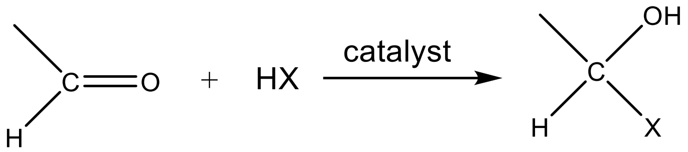
A	$\frac{M}{4}$	**B**	$\frac{M}{4} + 18$	**C**	$\frac{M + 54}{4}$	**D**	$\frac{M}{4} + 54$

27	Which reaction yields a carbon compound incorporating deuterium, D? [D = ^2H]			
		Reactant	Reagents and conditions	
	A	CH_3CH_2CN	NaOD, D_2O, heat	
	B	$(CH_3)_3COH$	conc H_2SO_4, heat	
	C	CH_3COCI_3	NaOD, D_2O, warm	
	D	$CD_2(OH)CO_2H$	acidified $KMnO_4$, heat	

28	Which two-step synthesis process will not give a good yield of 1,2-dibromocyclohexane?	
	A	
	B	
	C	
	D	

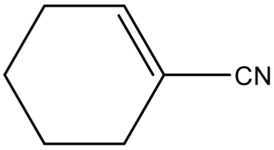
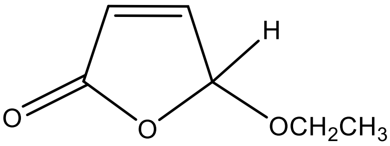
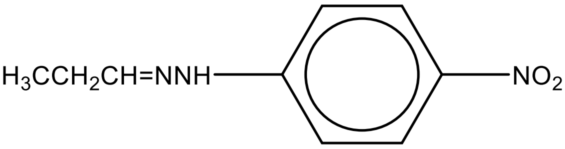
29	Which reaction will **not** take place in the presence of a suitable homogeneous catalyst?	
	A	$CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3$
	B	
	C	
	D	

30 There is a range of reactions of the aldehyde group which have the pattern



of which the formation of a cyanohydrin (where X = CN) is one.

Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

1	
2	
3	

A	1 and 2 only
B	1 and 3 only
C	2 and 3 only
D	1, 2 and 3 only

END OF PAPER

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

Suggested Answers for 9729 H2 CM 2019 JC 2 Prelim

Paper 2

1 **(a)** Barium has a larger nuclear charge and larger shielding effect than beryllium. Although there is an increase in nuclear charge in barium, it is cancelled out by the simultaneous increase in shielding effect by inner shells of electrons. Barium has a bigger atomic radius than beryllium. **[3]**

Hence the valence electrons become increasingly less attracted by the positive nucleus and less energy is required to remove the valence electrons. Therefore 1st IE of Ba is lower than the 1st IE of beryllium.

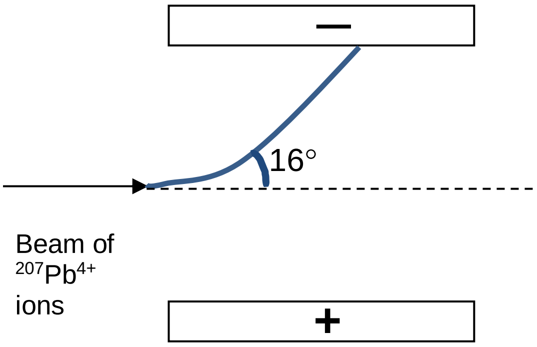
(b) **(i)** $Ca(NO_3)_2\ (s) \rightarrow CaO\ (s) + 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$ **[1]**

(ii) **[3]**

cations	**Ionic radius/nm**
Pb^{2+}	0.120
Zn^{2+}	0.074
Ca^{2+}	0.099

The ionic radius of the metal cation increases from Zn^{2+} to Ca^{2+} to Pb^{2+} and its charge density decreases. As a result, the ability of M^{2+} to polarise the electron cloud of the large NO_3^- anion decreases and the N–O bonds are weakened to a smaller extent. Hence $Zn(NO_3)_2$ decomposes at the lowest temperature followed by $Ca(NO_3)_2$ and lastly $Pb(NO_3)_2$.

(c) **[2]**



$\frac{charge}{mass}$ for $Pb^{2+} = \frac{+2}{207.2} = 0.00965$

$\frac{charge}{mass}$ for $Pb^{4+} = \frac{+4}{207.2} = 0.01930$

Angle of deflection= $\frac{0.01930}{0.00965} \times 8 = 16°C$

[Total: 9]

2 **(a)** $K_{a1} = X^2/ (0.300 - X)$; assuming x is very small and $0.300 - X = 0.300$

$X = 0.0207 \text{mol dm}^{-3}$

$pH = -lg\ 0.0207 = 1.68$ **[1]**

(b) $[Na_3C_6H_5O_7] = 46/ (23.0 \times 3 + 12.0 \times 6 + 16.0 \times 7 + 1.0 \times 5)$

$= 0.178 \text{ mol dm}^{-3}$

$K_b = K_w / K_a = 10^{-14} / (3.98 \times 10^{-7}) = 2.51 \times 10^{-8} \text{ mol dm}^{-3}$

$K_b = [OH^-]^2 / 0.178 = 2.51 \times 10^{-8}$

$[OH^-] = 6.69 \times 10^{-5} \text{ mol dm}^{-3}$

$pH = 14 - pOH$

$pH = 9.82$ **[3]**

(c) **(i)** [salt] = [acid] / Amount of acid = Amount of salt / Larger volume of buffer

Amounts of salt and acid are relatively higher than the amount of acid or alkali added. **[2]**

(ii) $pH = 6.40 = pK_{a3}$

buffer consist of $HC_6H_5O_7^{2-}$ and $C_6H_5O_7^{3-}$

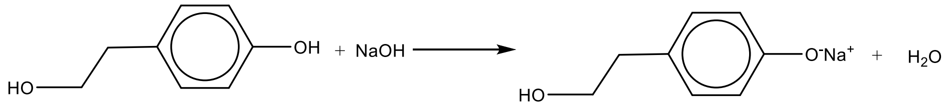
Amt of of citric acid = $0.300 \times 0.05 = 0.0150$ mol

Amt of NaOH needed = $0.0150 \times 2.5 = 0.0375$ mol

mass = $0.0375 \times (23.0 + 16.0 + 1.0) = 1.50$ g **[3]**

[Total: 9]

3 **(a)** **(i)**



[1]

(ii) Ion-dipole interactions **[2]**

Hydrogen bonding

Instantaneous dipole-induced dipole forces

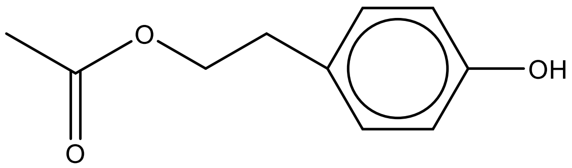
(iii) Neutral $FeCl_3$. Violet colouration will be observed if tyrosol is present. There will be no violet colouration if tyrosol is not present. **[2]**

(iv) When the NaOH solution is changed, $[T]_{NaOH}$=0/ lowered. **[2]**

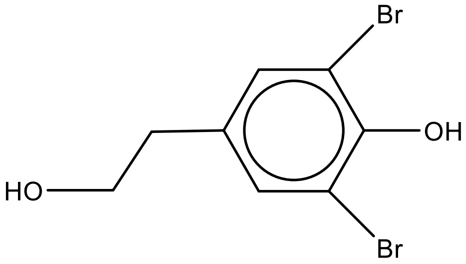
Equilibirum position shifts right to dissolve more tyrosol and counteract the change.

More tyrosol will be removed from the olives.

(b) **(i)** **[2]**



D:

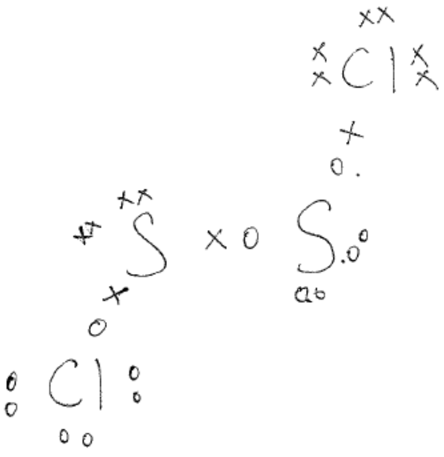


E:

(ii) The brominated tyrosol is a stronger acid than tyrosol. In the brominated phenoxide ion, the electron-withdrawing bromine atoms increase the delocalisation of the negative charge into the benzene ring, making the brominated phenoxide ion more stable than the phenoxide ion in tyrosol. **[1]**

[Total: 10]

4 **(a)**



Bond angle is 104.5^0 **[2]**

(b) All two compounds have simple covalent structures/ are simple covalent molecules.

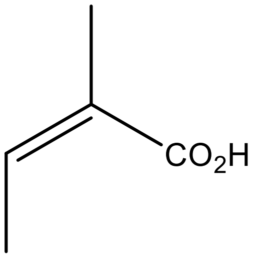
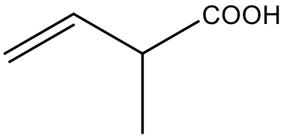
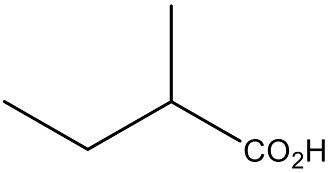
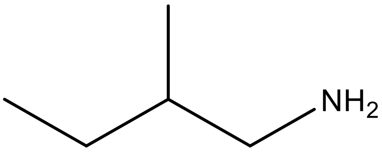
For $SOCl_2$ and S_2Cl_2, there exists permanent dipole-permanent dipole interactions and instantaneous dipole-induced dipole interactions between molecules. **[3]**

As S_2Cl_2 has a larger number of electrons/electron cloud and is more polar, more energy is required to overcome the stronger instantaneous dipole-induced dipole interactions and stronger permanent dipole-permanent dipole interactions between S_2Cl_2 molecules than $SOCl_2$ molecules. Therefore, S_2Cl_2 has a higher boiling point than $SOCl_2$.

(c) **(i)** Step 2: NH_3, rtp **[2]**

Step 3: $LiAlH_4$ in dry ether..

(ii)

 	
angelic acid	**T**
	
U	

[3]

(iii)

angelic acid	cis – trans isomerism / enantiomerism
T	enantiomerism

[2]

[Total: 12]

5 **(a)** **(i)** The difference in energies (ΔE) between these 2 sets of 3d orbitals is small and radiation from the visible region of the electromagnetic spectrum is absorbed when an electron is promoted from a lower energy d orbital to another unfilled/partially-filled d orbital of higher energy.

The colour observed (violet) corresponds to the complement of the absorbed colours (yellow). **[2]**

(ii) Vanadium(II) / V^{2+}(aq). Because V^{2+}(aq) is violet and V^{3+}(aq) is green, which means that for V^{2+} and V^{3+}, the complement colours, yellow and red respectively, are absorbed.

Since the energy of light is inversely proportional to its wavelength, the energy gap between the 2 sets of d orbitals in V^{2+} will be larger as the wavelength of yellow light is shorter than that of red light. **[2]**

(b) **(i)** V^{3+} : (3 , −2.7)

VO^{2+}: (4 , −2.3) **[1]**

(ii) E (VO_2^+/V^{2+}) = gradient of line joining VO_2^+ and V^{2+} points

$$= \frac{-2.40-(-1.32)}{2-5} = \mathbf{+0.36\ V}$$ **[1]**

(iii) $-\Delta G$ /F is the most negative here, hence ΔG for V^{3+} is the most positive. Thus V^{3+} is the most (thermodynamically) stable species of vanadium / +3 is the most stable oxidation state of vanadium.

Or V^{3+} will not undergo redox (i.e. oxidation (to VO^{2+}) and reduction (to V^{2+})) easily **[1]**

(c) **(i)** Catholyte chamber: VO_2^+ / VO^{2+}

Anolyte chamber: V^{3+} / V^{2+} **[2]**

(ii) $V^{2+} + VO_2^+ + 2H^+ \rightarrow VO^{2+} + V^{3+} + H_2O$ **[1]**

(iii) From anolyte chamber towards catholyte chamber / Right to left **[1]**

(iv) Increase the concentration of VO_2^+ in the VO_2^+/VO^{2+} redox couple (i.e. catholyte) and/or increase the concentration of V^{2+} in the V^{3+}/V^{2+} redox couple (i.e. anolyte)

or

Attach a number of VRFB cells in series **[1]**

[Total: 12]

6 **(a)** **(i)** Energy is needed to overcome the repulsion to add an electron to a negatively charged O_2^-, hence the $\Delta H_f(O_2^{2-})$ is more positive than $\Delta H_f(O_2^-)$. **[2]**

ΔH_f (O^{2-}) is highly endothermic/ requires a lot of energy as it involves the breaking of a double bond and the addition of 2 electrons to a single atom/ single $^-O–O^-$ bond requires the addition of an electron to a negatively charged O^-.

(ii) *Enthalpy change* when **1 mole of the solid ionic compound** is formed **from** its **constituent gaseous ions** under standard conditions. **[1]**

(iil) $LE \propto \left|\frac{q_1.q_2}{r_1+r_2}\right|$. As the charges of O^{2-} and O_2^{2-} are higher than O_2^-, the ionic size of O_2^{2-} is larger than that of O^{2-}**,** the magnitudes of LE of decreases in the order $K_2O > K_2O_2 > KO_2$. **[2]**

(b) **[3]**

$$\begin{tikzcd}
2KO_2(s) + H_2O(l) \arrow[rr] \arrow[d, "\begin{array}{c}+CO_2(g)\\ -219\end{array}"'] & & 2KOH(aq) + \frac{3}{2}O_2(g) \arrow[ddl, "\begin{array}{c}+2CO_2(g)\\ \mathbf{2(\Delta H_r)}\end{array}"] \\
K_2CO_3(aq) + \frac{3}{2}O_2(g) + H_2O(l) \arrow[dr, "\begin{array}{c}+CO_2(g)\\ -100\end{array}"'] & & \\
 & 2KHCO_3(aq) + \frac{3}{2}O_2(g) &
\end{tikzcd}$$

By Hess' Law, $2(\Delta H_r) = (-113) + (-219) + (-100)$

$\Delta H_r = -103$ kJ mol^{-1}

(c) **(i)** $\Delta H_{ppt} - T\Delta S_{ppt} = -RT\ln(K_{sp})$ **[1]**

$$\ln(K_{sp}) = \frac{\Delta H}{-RT} + \frac{\Delta S}{R}$$

From graph, gradient = $\frac{-5.3-(-6.3)}{0.0027-0.0035}$ =–1250 K

At (0.0027, –5.3), $-5.3 = -1250(0.0027) + \frac{\Delta S}{R}$

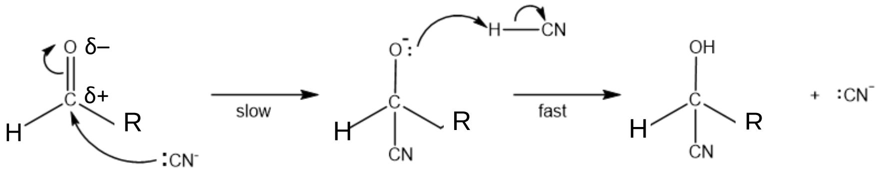
$$\frac{\Delta S}{R} = \frac{\Delta S}{8.31} = -1.925$$

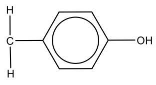
$\Delta S = -1.925 \times 8.31 = -16.0$ J mol^{-1} K^{-1}

(ii) Entropy/ Disorder decreases because there are less ways to distribute the energy/ arrange the ions/ particles as they have to take up fixed positions in the lattice structure. **[1]**

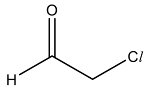
[Total: 10]

7 **(a)** **(i)** $NaCN \longrightarrow Na^+ + CN^-$ **[3]**



R is 

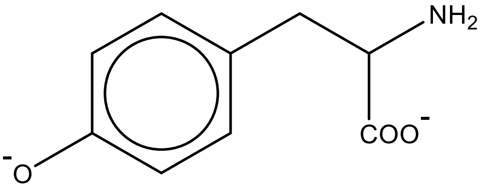
(ii) step 1

Anhydrous $AlCl_3$, 

step 3 H_2SO_4 (aq), heat (under reflux) **[3]**

step 5 (excess) alcoholic NH_3, heat in a sealed tube

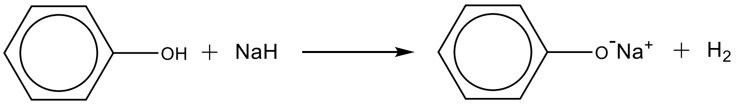
(b) **(i)**



[1]

(ii) Use a longer gel plate / Apply a higher voltage / Change the pH / Run for a longer time. **[2]**

(c) **(i)**



[1]

(ii)

Order of reaction with respect to iodomethane:	1
Justification:	[phenoxide] = 0.10 M, constant half life of 118.0 ± 5 min OR [phenoxide] = 0.15 M, constant half life of 80.0 ± 5 min
Order of reaction with respect to phenoxide:	1
Justification:	When concentration of phenoxide times 1.5, rate/ gradient times 1.5.

[4]

[Total: 15]

Suggested Answers for 9729 H2 CM 2019 JC 2 Prelim

Paper 3

1 **(a)** **(i)** When dissolved in a polar solvent such as water, they dissociate to form strong acids, releasing H$^+$ and X$^-$ ions forming ion-dipole interactions with water. **[1]**

(ii) HF has an exceptionally high boiling point compared to the other hydrogen halides as hydrogen bonds exist between HF molecules but not between the rest of the HX molecules. More energy is needed to overcome the stronger hydrogen bonds.

Boiling point of the hydrogen halides increases from HC*l* to HBr to HI.

The strength of instantaneous dipole-induced dipole interactions between the hydrogen halide molecules increases as the number of electrons in the molecules increases. More energy is needed to overcome the stronger id-id interactions. **[2]**

(iii) When a red-hot steel needle is introduced, HBr produces red brown bromine vapour. HI gives violet fumes of iodine. HF and HC*l* do not/show little tendency to decompose.

Bond	Bond Energies/ kJ mol^{-1}
H–F	+562
H–C*l*	+431
H–Br	+366
H–I	+299

Less energy is required to break the weaker H–X bond.

The thermal stability of hydrogen halides decreases down the Group due to decreasing H–X bond energy. **[3]**

(b) **(i)** Solubility of AgBr = $0.140 \times 10^{-3} / (107.9 + 79.9)$

$= 7.45 \times 10^{-7}$ mol dm^{-3}

$[Br^-] = 4.00\times 10^{-12} / 0.100 = 4.00\times 10^{-11}$ mol dm^{-3}

$[Ag^+]\,[Br^-] = K_{sp}$

$[Ag^+]\,(4.00\times 10^{-11}) = (7.45 \times 10^{-7})^2$

$[Ag^+] = 0.0139$ mol dm^{-3} **[2]**

(ii) In the saturated AgC*l*,

$[Ag^+]\,[Cl^-] = K_{sp}$

$(0.0139)(0.0139 + 0.001) = K_{sp}$

$K_{sp} = 0.000206$ mol^2 dm^{-6}

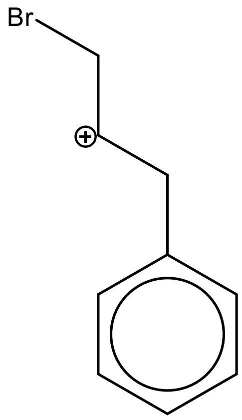
Solubility = $(0.00206)^{1/2} = 0.0144$ mol dm^{-3} **[2]**

(iii) Mass of AgC*l* dissolved in 1 dm^3 = (0.0139)(107.9 + 35.5)

= 1.99 g

Mass of residue = 5.00 – 1.99 = 3.01 g **[1]**

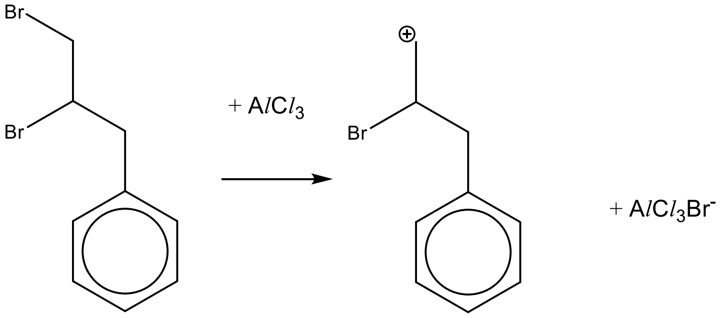
(c) (i)

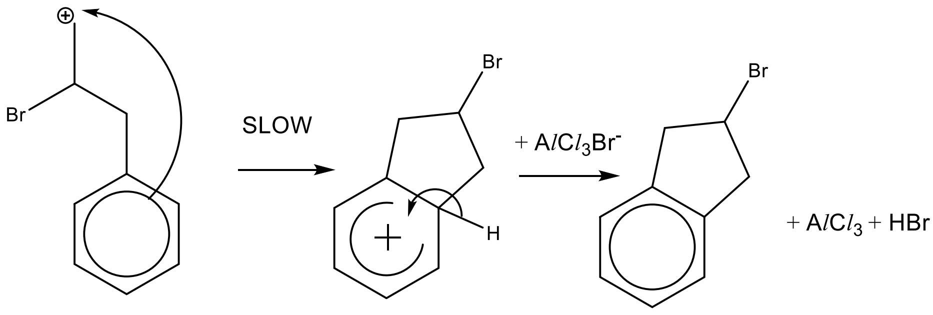


<u>The higher the number of electron donating groups attached to carbocation, the more stable the carbocation</u>.

As the 2 possible intermediate contains a primary carbocation and secondary carbocation respectively, intermediate with the secondary carbocation is more stable. **[2]**

(ii)





[2]

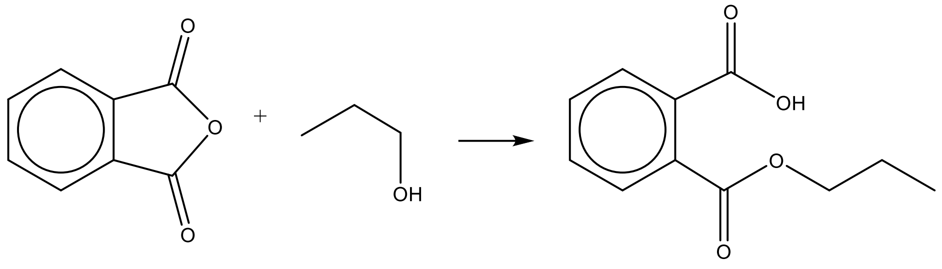
(iii) Compound **B** has a 4 membered ring form in place of the 5 membered ring presented in the reaction scheme.

The 4 membered ring consist of <u>2 carbon atoms with sp^2 hybridised orbitals 120° from each other and 2 carbon atoms with sp^3 hybridised orbitals at 109.5° from each other</u>.

To fit into 4 membered ring, <u>all 4 carbons are forced into 90° bond angle which exerts high angle strains</u> making the 4 membered ring formation unfavourable. **[2]**

[Total: 17]

2 **(a)** **(i)**



[1]

(ii) H_2O/Water **[1]**

(b) **(i)** For pK_1, the H^+ is removed from a neutral molecule. For pK_2, the <u>removal of a H^+ from the anion</u> that already carries a negative charge is electrostatically unfavourable.

OR <u>Favourable intramolecular hydrogen bonding</u> in the anion will be <u>disrupted</u> when it dissociates in pK_2. **[1]**

(ii) Phthalic acid is the limiting reagent/NaOH is in excess

Amount of excess NaOH = $\frac{50}{1000}\times 0.1-\left(\frac{10}{1000}\times 0.2\times 2\right)$

= $1.0\times10^{`3}$ mol

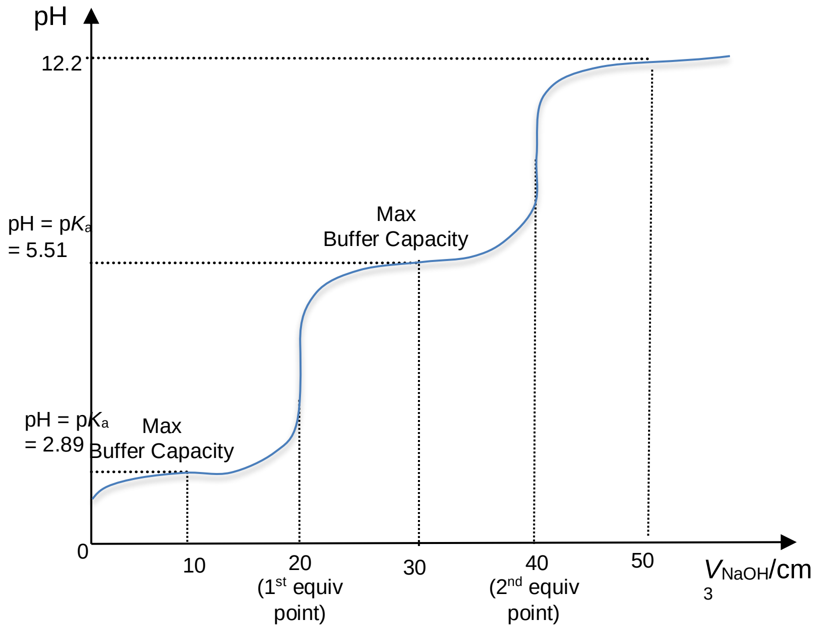
$[OH^{`}] = \frac{1.0\times10^{-3}}{\frac{60}{1000}} = 1.667\times10^{`2}$ mol dm$^{`3}$

pOH = `lg($1.667\times10^{`2}$) = 1.78

pH = 14`1.78 = 12.2

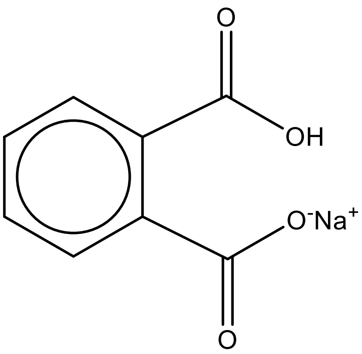
[2]

(iii)



[3]

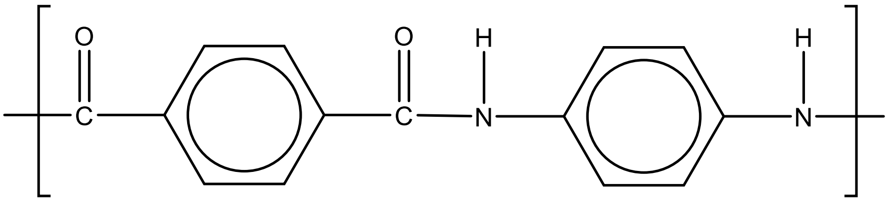
(iv)



[1]

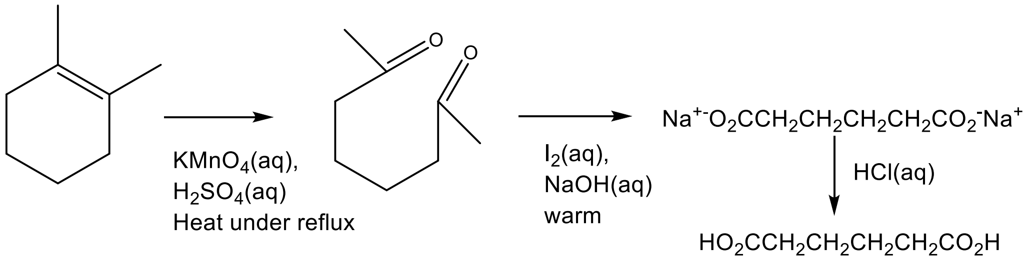
(c) **(i)** Condensation **[1]**

(ii)



[1]

(d)

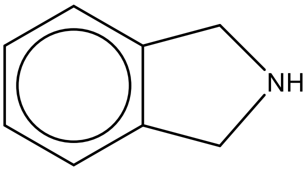


[2]

(e) Reaction **A**: PCl_5, room temperature

Reaction **B**: limited ethanolic NH_3, heat in a sealed tube

Structure of **C**:



[3]

(f) **(i)** I: acid-base reaction (alkaline hydrolysis is not accepted)

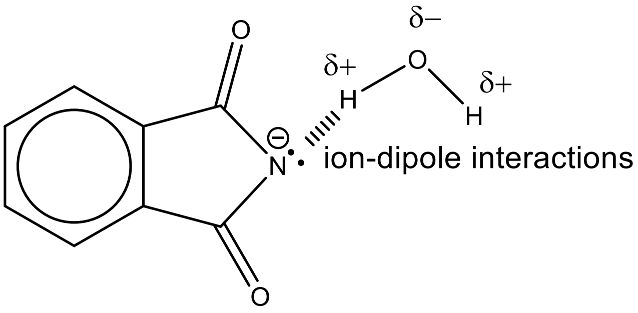
II: nucleophilic substitution

III: hydrolysis **[3]**

(ii) H_2SO_4(aq) and heat under reflux, followed by controlled amount of strong base.

Or NaOH(aq) and heat under reflux, followed by controlled amount of strong acid **[1]**

(iii)



[1]

(iv) Amt of **D** = $\frac{0.5}{147}$ = $3.401 \times 10^{`3}$ mol

Amt of gaseous product = $\frac{pV}{RT} = \frac{(101325)(42.26\times10^{-6})}{8.31\times303}$ = $1.701\times 10^{`3}$ mol

Since mole ratio of **D**: Gaseous Product = 2:1, gaseous product is N_2 gas.

$4C_8H_5O_2N + 33O_2 \rightarrow 32CO_2 + 10H_2O + 2N_2$ **[3]**

[Total: 24]

3 **(a)** Amt of Fe^{3+} = $\frac{5}{1000}\times0.2=0.00100$ mol

Amt of CN– = $\frac{6}{1000}\times0.6=0.00600$ mol

Since ratio of Fe^{3+} : CN^{-} = 1:6,

H_2O ligand is displaced.

Complex in red solution : $[Fe(CN)_6]^{3-}$

Formation of red solution : $[Fe(H_2O)_6]^{3+} + 6CN^{-} \rightarrow [Fe(CN)_6]^{3-} + 6H_2O$

Complex in yellow solution : $[Fe(CN)_6]^{4-}$ **[2]**

(b) **(i)** 3d and 4s electrons have similar energies. More valence electrons from Fe is contributed to the sea of delocalised (mobile) electrons then Ca, thus Fe has a higher electrical conductivity. **[1]**

(ii) Both aqueous Fe^{2+} and Fe^{3+} exist as aqua complexes with formulae $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ respectively.

Ionic radius of Fe^{2+} = 0.061 nm

ionic radius of Fe^{3+} is 0.055 nm

With a smaller radius and a higher charge, Fe^{3+} has a higher charge density**,** water molecules in $[Fe(H_2O)_6]^{3+}$ is polarised and the O–H bonds are weakened to a greater extent, $[H^+]$/$[H_3O^+]$ increases. Hence, the pH is lower.
$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$ **[2]**

(c) **(i)** Role of Fe^{3+} : Homogeneous catalyst

The reaction between peroxodisulfate ions $S_2O_8^{2-}$ and iodide ions I^- can be catalysed by either Fe^{2+} or Fe^{3+}.

$$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-} \quad E^\ominus = +2.01\text{ V}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\ominus = +0.77\text{ V}$$

$$I_2 + 2e^- \rightleftharpoons 2I^- \quad E^\ominus = +0.54\text{ V}$$

Reaction catalysed by Fe^{3+}(aq):

Step 1: Formation of an intermediate

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$$

$$E^\ominus_{cell} = +0.77 - (+0.54) = +0.23\text{ V}$$

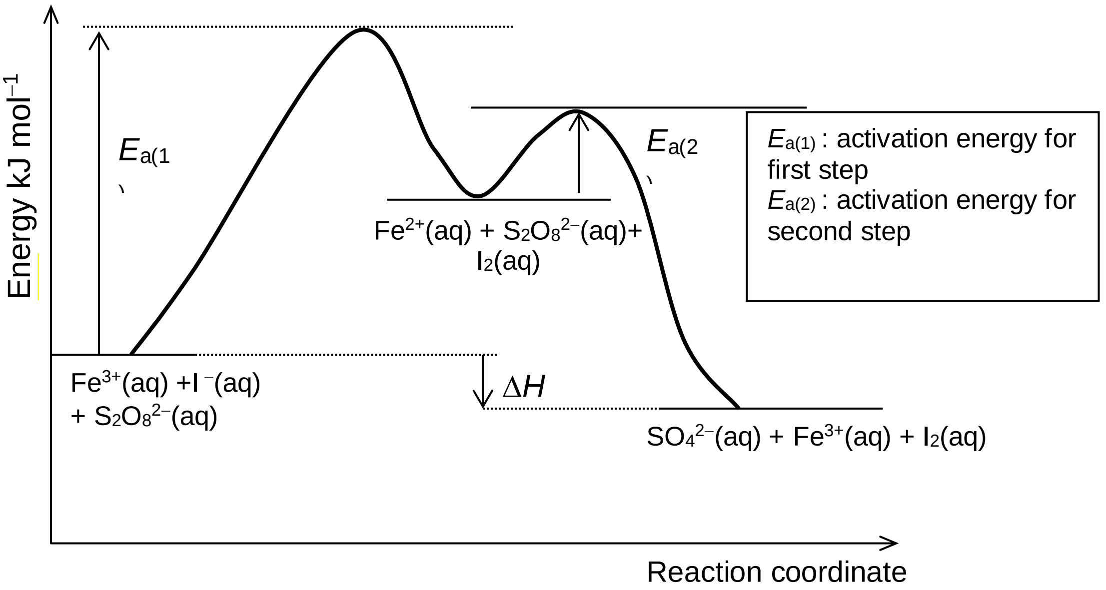
Step 2: Regeneration of catalyst

$$S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$$

$$E^\ominus_{cell} = +2.01 - (+0.77) = +1.24\text{ V}$$

[2]

(ii) **[3]**



(c) **V** has a molecular formula of $C_8H_9NO_2$.

The C:H ratio is ≈ 1:1.

⇒**V** contains a benzene ring

V is insoluble in water and acids

⇒**V** contains an amide

V undergoes acid-base reaction in NaOH

⇒**V** contains a phenol or carboxylic acid group

V undergoes electrophilic substitution with aq Br_2 to form **W**

⇒ **W** has a side chain in either position 2, 4 w.r.t. OH

V undergoes acidic hydrolysis to form compound **X** and **Y**

⇒ salt and carboxylic acid is formed.

X is soluble in water

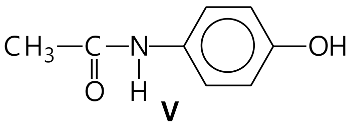
⇒ **X** is an ammonium salt

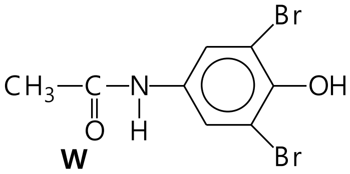
Y on reduction with $LiAlH_4$ forms **Z**

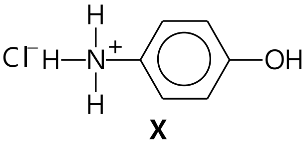
⇒ **Z** is an alcohol

Z undergoes positive iodoform test/oxidation to form a yellow precipitate.

⇒ **Z** is $–CH(CH_3)(OH)$ group


V


W


X

CH_3COOH
Y

CH_3CH_2OH
Z

[9]

[Total: 19]

4 **(a)** **(i)** ΔH_{vap} positive due to the energy required to overcome the intermolecular forces between molecules.

ΔS_{vap} positive due to the changing from liquid to gaseous state, hence $-T\Delta S_{vap}$ negative

For vaporisation to be spontaneous, $|-T\Delta S_{vap}| > |\Delta H_{vap}|$, hence it is an entropy-driven reaction. **[2]**

(ii) Benzene is the most volatile VOC.

$\Delta G_{vap} = 33.9 - 330(\frac{113.6}{1000}) = -3.59 \text{ kJ mol}^{-1}$

(For the others: ethanol +2.40 , methylbenzene +9.29 , propanone −0.05) **[1]**

(b) **(i)** Excess chlorine, uv light, (limited methane) **[1]**

(ii) Initiation

U

$Cl_2 \rightarrow 2Cl\bullet$ **[3]**

Propagation

$CH_4 + Cl\bullet \rightarrow \bullet CH_3 + HCl$

$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

$CH_3Cl + Cl\bullet \rightarrow \bullet CH_2Cl + HCl$

$\bullet CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$ (must show)

Termination

$\bullet CH_2Cl + Cl\bullet \rightarrow CH_2Cl_2$ (must show)

$2Cl\bullet \rightarrow Cl_2$

$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$

$\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$

$\bullet CH_2Cl + \bullet CH_2Cl \rightarrow ClCH_2CH_2Cl$ (Any 1 of these other 4)

(c) **(i)** 2-methyl-buta-1,3-diene or 2-methyl-1,3-butadiene **[1]**

(ii) Mass produced = $(0.15 \times 10^{-6} \times 68.0 \times 1000) \times 65 \times 24$

= 15.9 mg **[1]**

(iii) $C_5H_8 + 7O_2 \rightarrow 5CO_2 + 4H_2O$

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$ **[2]**

(iv)

Let x be the volume of C_5H_8 and nx be the volume of CS_2 initially.

Combining the eqns: $C_5H_8 + 7O_2 \rightarrow 5CO_2 + 4H_2O$ & $nCS_2 + 3nO_2 \rightarrow nCO_2 + 2nSO_2$

Combustion Process:

	C_5H_8 +	nCS_2 +	$(3n+7)O_2$ →	$(n+5)CO_2$ +	$2nSO_2$ +	$4H_2O$
Initial vol	x	nx	excess V_{O2}	-	-	-
Change	*–x*	*–nx*	*–(3n+7)x*	*+(n+5)x*	*+2nx*	-
After rxn	0	0	(excess V_{O2} – 3nx – 7x)	(n+5)x	2nx	-

Volume of gas before combustion = excess V_{O2} + x + nx

Volume of gas after combustion = excess V_{O2} – 3nx – 7x + nx + 5x + 2nx

= excess V_{O2} – 2x

(Volume before combustion) – (Volume after combustion) = 1st volume contraction (excess V_{O2} + x + nx) – (excess V_{O2} – 2x) = 1st volume contraction

$x + nx + 2x = 70$

$3x + nx = 70$

$\mathbf{(n + 3)x = 70}$ **------- (1)**

Volume of CO_2 and SO_2 in resultant mixture = 2nd volume contraction

$5x + nx + 2nx = 170$

$\mathbf{(3n + 5)x = 170}$ **------ (2)**

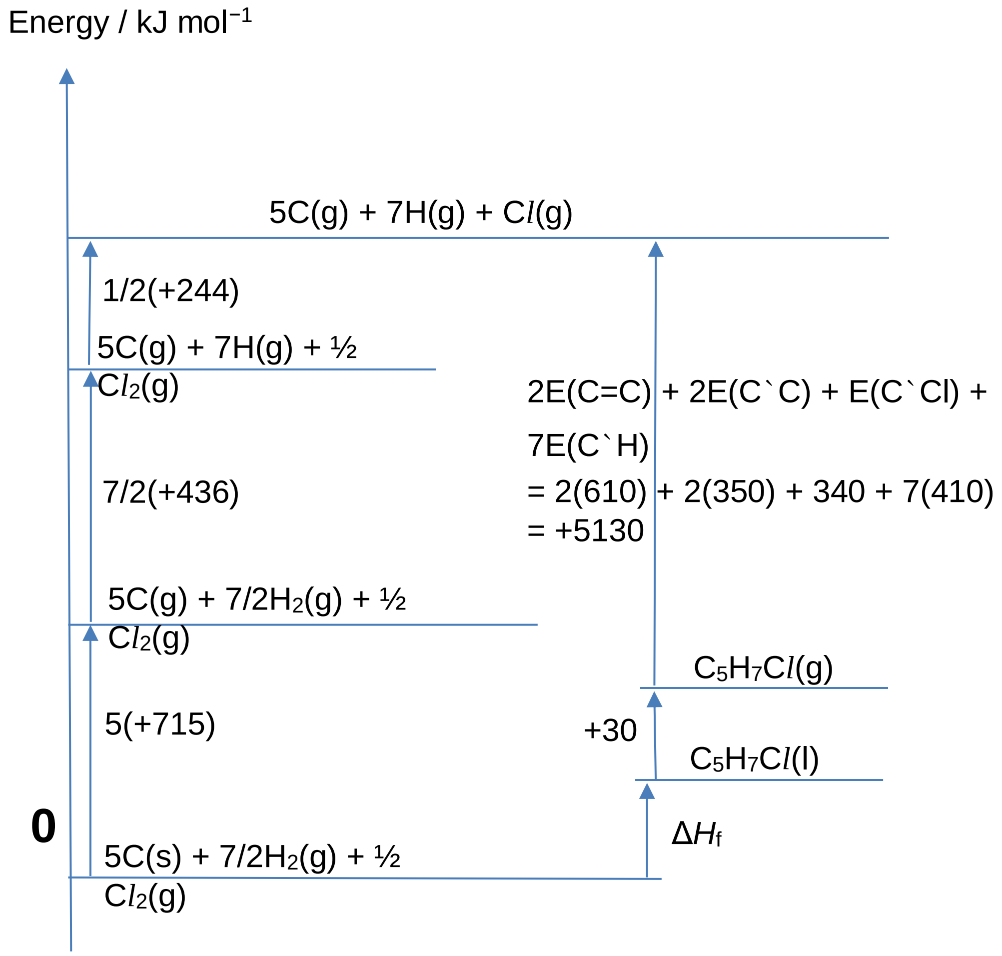
$$\frac{(1)}{(2)}: \qquad \frac{n+3}{3n+5} = \frac{70}{170}$$ **[3]**

$170n + 510 = 210n + 350$

$210n – 170n = 510 – 350$

$40n = 160$ ➔ $\mathbf{n = 4}$

(d) (i) **[4]**



$\Delta H_f = +(5223 – 5160) = \underline{+63}$ kJ mol^{-1}

(d) **(ii)** constitutional / structural / functional group isomerism. **[1]**

(iii) The C`C*l* bond in compound **N** has a partial double bond character due to the delocalisation of lone pair on C*l* into the neighbouring C^C π electron system.

Hence the C`C*l* bond energy will be larger than +340 kJ mol^{-1} and will in turn decrease the magnitude of compound **N**'s enthalpy change of formation. **[1]**

[Total: 20]

5 **(a)** MgO(s) reacts with water to form $Mg(OH)_2(s)$, which dissolves sparingly in water to give a weakly alkaline (pH = 8) solution. **[5]**

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

$SiO_2(s)$ is insoluble in water as a large amount of energy is required to break the many strong covalent bonds in the giant covalent structure. Since the oxide does not dissolve in water, it will not affect the pH (*i.e.* pH = 7).

$P_4O_{10}(s)$ react violently/vigorously with water to give an acidic solution (pH = 2).

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$
OR $P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$

(b) **(i)** $SO_2(aq) + 2H_2O(l) + I_2(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$ **[1]**

(ii) Amount of I_2 = $\frac{17.70}{1000} \times 0.0100 = 1.77 \times 10^{-4}$ mol **[2]**

Amount of SO_2 in 50 cm^3 = 1.77×10^{-4} mol

$[SO_2] = \frac{1.77 \times 10^{-4}}{50 \times 10^{-3}} = 3.54 \times 10^{-3}$

Concentration of SO_2 in mg L^{-1} = $3.54 \times 10^{-3} \times 64.1 = 227$ mg L^{-1}

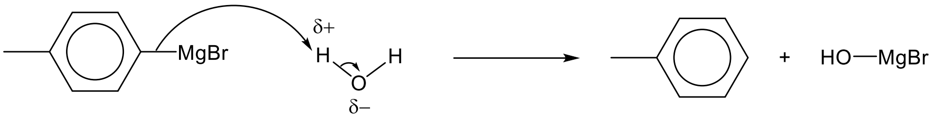
Amount of SO_2 per kg $= \frac{227 \times \frac{400}{1000}}{70} = 1.30 > 0.7$

Exceeded the maximum daily intake of SO_2 so it is not advisable.

(c) **(i)** Lithium and magnesium are highly electropositive, polarised the bond towards carbon. **[1]**

(ii) It is used to avoid prolonged exposure to the moisture in the air/ as a dehydrating agent. **[1]**

(iii) Hydrolysis/ nucleophilic substitution **[2]**



Accept OH^- $MgBr^+$

(iv) Acidification of benzoate/4-toluate ion is a highly exothermic process as O–H bonds are formed and no bonds are broken. **[1]**

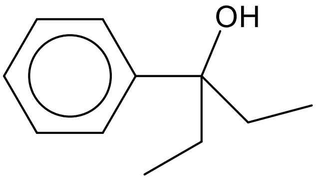
(v) $R_f = \frac{0.85}{4.35} = 0.195$ **[1]**

(vi) **F**: 4-toluic acid, **G**: 4-bromotoluene **[2]**

4-toluic acid forms stronger hydrogen bonding with the hydroxyl group of the silica surface, hence, 4-bromotoluene travels further than 4-toluic acid.

(vii) The R_f value will increase. **[1]**

(viii)



[1]

(ix) Test: Acidified $K_2Cr_2O_7$, heat **[2]**

Observation: Orange dichromate turned green for Compound **K** but not **J**.

Or

Test: 2,4-DNPH

Observation: Orange ppt is formed for Compound **J** but not **K**.

Or

Test: PCl_5 or PCl_3 or $SOCl_2$

Observation: White fumes of HCl evolved for Compound **K** but not **J**.

[Total: 20]

Suggested Solutions for 9729 2019 Prelim Practical Examinations

1 An experiment to investigate the behaviour of acids and bases in aqueous solution

FA 1 is 1.00 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$

FA 2 is sodium hydroxide, NaOH, between 1.5 to 2.5 mol dm^{-3}

FA 3 is 2.00 mol dm^{-3} sulfuric acid, H_2SO_4

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.
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H_{neutralisation} = -57.1 \text{ kJ mol}^{-1}$

The reaction between H^+(aq) and OH^-(aq) involves bond formation and so is exothermic. It is possible to make use of this fact to perform a thermometric titration. This task involves two different acid-base reactions.

The first reaction is between sodium hydrogencarbonate, **FA 1**, and sodium hydroxide, **FA 2**.

Reaction 1:
$NaHCO_3(aq) + NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l) \qquad ⊔\Delta H_{reaction\ 1}$

The molar enthalpy change for **Reaction 1**, $\Delta H_{reaction\ 1}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with NaOH.

Instead of using an indicator to determine the endpoint, you will perform a thermometric titration to determine the equivalence point of the reaction. The equivalence point is that point where H^+(aq) from the acid and OH^-(aq) from the base are present in equal molar amounts.

The second reaction is between sodium hydrogencarbonate, **FA 1**, and sulfuric acid, **FA 3**.

Reaction 2:
$NaHCO_3(aq) + ½H_2SO_4(aq) \longrightarrow ½Na_2SO_4(aq) + H_2O(l) + CO_2(g)$
$\Delta H_{reaction\ 2}$

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.

In your first experiment, you will perform a thermometric titration by adding portions of **FA 2** progressively to a known volume of **FA 1**. You will continue adding **FA 2** until the equivalence point is reached and passed. Throughout the experiment you will note and record the temperature of the mixture after each addition.

You will then analyse your results graphically in order to determine the
- titration volume at the equivalence point, $V_{\text{equivalence}}$,
- maximum temperature change, $\Delta T_{\text{maximum 1}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 1}}$, for **Reaction 1**.

In your second experiment, you will mix together a given volume of **FA 1** with a suitable volume of **FA 3**.

You will then determine the
- maximum temperature change, $\Delta T_{\text{maximum 2}}$,
- molar enthalpy change, $\Delta H_{\text{reaction 2}}$, for **Reaction 2**.

Reaction between FA 1 and FA 2

(a) **(i)** In this task you will need to record the maximum temperature of the reaction mixture when specified volumes of **FA 2** have been added. It is important that the volume of **FA 2** recorded is the total volume you have added up to that point when the temperature reading was made.

Note:
If you overshoot on an addition, record the **actual** total volume of **FA 2** added up to that point.

In an appropriate format in the space provided, record all values of temperature, *T,* to 0.1 °C, and each total volume of **FA 2** added to 0.05 cm^3.

1. Fill a burette with **FA 2**.
2. Place a Styrofoam cup inside a second Styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Using a pipette, transfer 25.0 cm^3 of **FA 1** to the first Styrofoam cup.
4. Stir the **FA 1** solution in the cup with the thermometer. Read and record its temperature.
5. From the burette, add 2.00 cm^3 of **FA 2** to the cup and stir the mixture thoroughly.
6. Read and record the maximum temperature of the mixture, *T,* and the volume of **FA 2** added.
7. Repeat points 5 and 6 until a total of 30.00 cm^3 of **FA 2** has been added. After each addition of **FA 2**, record the maximum temperature of the mixture and the total volume of **FA 2** added up to that point.

Results

For Examiner's Use

Volume of FA2 added/cm^3	***Maximum temperature/°C***
0.00	*31.8*
2.00	*33.0*
4.00	*34.0*
6.00	*34.8*
8.00	*35.4*
10.00	*36.0*
12.00	*36.4*
14.00	*36.6*
16.00	*36.4*
18.00	*36.2*
20.00	*35.8*
22.00	*35.3*
24.00	*35.0*
26.00	*34.8*
28.00	*34.6*
30.00	*34.4*

1	
2	

Note:

- *Correct headers and units (Final Temp not accepted as header);*
- *Proper tabulation of volumes and temperatures*
- *Thermometer readings to 1dp*
- *Total volume of FA2 to 2dp*

(a) **(ii)** On the grid below, plot a graph of temperature, T against volume of **FA 2** added.

For Examiner's Use

3	
4	
5	

(iii) Draw **two** smooth lines of best fit. Extrapolate these lines until they cross. Extrapolate these lines until they cross.

Note:

- *Axes correct way round **+** correct labels **+** units **+** scale.*
- *Awkward scales (e.g. 3:10) are not allowed.*
- *The plotted points must occupy at least half of the grid in both directions.*
- *All points must be correctly plotted within ±½ small square.*
- *Graph lines may be **curved/ straight** best-fit lines, drawn so as to best reflect the distribution of points **before** and **after** the equivalence point. These lines should be extrapolated until they **cross**.*

6	
7	
8	

Supervisor
Student
Difference

(iv) Determine from your graph,

- the maximum temperature reached, T_{maximum},
- the maximum temperature change, $\Delta T_{\text{maximum 1}}$,
- the volume, $V_{\text{equivalence}}$, of **FA 2** needed to completely react with 25.0 cm^3 of **FA 1**.

Show on your graph how you obtained these values.

Record these values in the spaces provided below.

Maximum temperature reached, T_{maximum} = ...

Volume of **FA 2** used, $V_{\text{equivalence}}$ = ...

Supervisor
Student
Difference

Hence, calculate the maximum temperature change, $\Delta T_{\text{maximum 1}}$

= ....

Note:

- *Correct reading, to ±½ small square, of Tmaximum; correct calculation of ΔTmaximum**;** correct reading, to ±½ small square, of Vequivalence.*
- *Accuracy based on difference between Supervisor's and Student's values*

Reaction between FA 1 and FA 3

For Examiner's Use

(b) The molar enthalpy change for **Reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of $NaHCO_3$ reacts completely with H_2SO_4.

In this task you will calculate a value for the molar enthalpy change, $\Delta H_{\text{reaction 2}}$. To do this you will need to determine the maximum temperature change produced when measured volumes of **FA 1** and **FA 3** are mixed. After considering the concentrations of **FA 1** and **FA 3**, you will select a suitable volume of **FA 3** to add to 40 cm^3 of **FA 1**.

(i) Choose a suitable volume of **FA 3**, $V_{\textbf{FA 3}}$, to be added to 40 cm^3 of **FA 1**. Explain your answer.

Volume should be between 10cm^3 ≤ V_{FA3} ≤ 20cm^3 to add sufficient **FA3** for complete reaction/provide an excess of acid for reaction. (Adding too much **FA3** will result in larger percentage uncertainty due to lower temperature rise)

9	
10	

(ii) Identify the apparatus you intend to use to measure the volume of **FA 1**.

Explain your choice.

Burette. Since **FA1** is the limiting reagent, exact measurement is required. So <u>precise/ accurate</u> measurement of ±0.05 cm^3 is required.

11	

(iii) In an appropriate format in the space provided below, record all values of measured temperature for this experiment.

1. Label one styrofoam cup, **A**. Label a second Styrofoam cup, **B**.
2. Place cup **A** inside a styrofoam cup which is held in a glass beaker to prevent it tipping over.
3. Transfer 40 cm^3 of **FA 1** into cup **A**.
4. Stir the **FA 1** solution in cup with the thermometer. Read and record its temperature, $T_{\textbf{FA 1}}$. This is the initial temperature of **FA 1**.
5. Wash and dry the thermometer.

6. Transfer your chosen volume of **FA 3** into cup **B**. Stir the **FA 3** solution with the thermometer. Read and record its temperature, $T_{\mathbf{FA\ 3}}$. This is the initial temperature of **FA 3**.
7. Carefully add the contents of cup **B** to cup **A** in **small** portions to avoid too much frothing.
8. Place the lid on the cup and insert the thermometer through the lid. Stir the mixture.
9. Continue to stir the mixture. Measure and record the temperature, T_{mixture} that shows the maximum change from the initial temperature.

12	
13	

Results

T_{FA1}/°C	T_{FA3}/°C	$T_{mixture}$/°C
31.6	*31.0*	*31.8*

For Examiner's Use

Note:

- *Correct headers and units*
- *Proper tabulation of temperature of FA1, FA3 and maximum temperature change in a table.*
- *Recording of thermometer readings to 1dp*

Calculations

(c) For the purposes of these calculations, you should 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}.

(i) Calculate the concentration of sodium hydroxide, [NaOH], in **FA 2**.

$$[\text{NaOH}] = \frac{25.0\ x\ 10^{-3}}{Vequivalence\ x\ 10^{-3}} = \text{XXX}$$

[NaOH] in **FA 2** = ...

14	

(ii) Calculate the heat change, *q*, for the reaction occurring in **(a)(i)**, and hence determine a value for the molar enthalpy change for **Reaction 1**, $\Delta H_{\text{reaction 1}}$.

$m = 25.0 + V_{\text{equivalence}}$

$q = \text{mc}\Delta T_{\text{maximum}}$

$n\text{NaHCO}_3 = 25.0 \times 10^{-3}$

$\Delta H\text{reaction 1} = -\frac{q}{25.0\ x\ 10^{-3}}$

15	
16	

Note: – sign must be present.

(d) Use your results from **(b)(iii)** to calculate a value for the molar enthalpy change for **Reaction 2**, $\Delta H_{\text{reaction 2}}$. For the experiment in **(b)(iii)**, the weighted average initial temperature, T_{average}, of **FA 1** and **FA 3** may be calculated using the formula given below.

For Examiner's Use

$$T_{average} = \frac{(V_{FA1} \times T_{FA1}) + (V_{FA3} \times T_{FA3})}{(V_{FA1} + V_{FA3})}$$

Calculation of T_{average} using formula given

$\Delta T_{\text{maximum 2}} = |T_{\text{mixture}} - T_{\text{average}}|$
$q = (V_{\text{FA 1}} + V_{\text{FA 3}}) \times 4.18 \times \text{temperature change}$

$\Delta H_{\text{reaction 2}} = -\frac{q}{40.0\ x\ 10^{-3}}$

17	
18	
19	

T_{average} = ...

q =..............................

$\Delta H_{\text{reaction 2}}$ = ...

For Examiner's Use

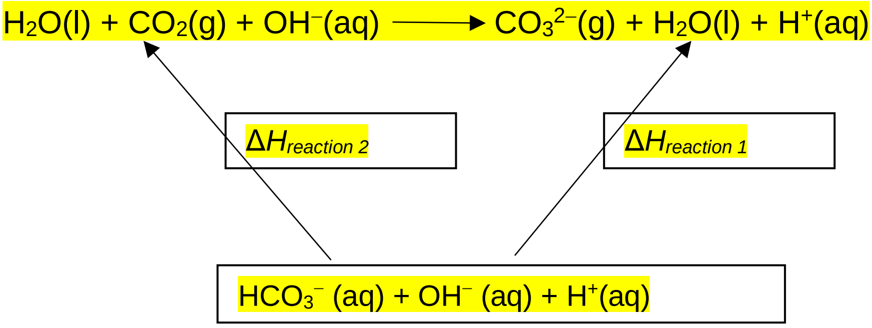
(e) Ionic equations for neutralisation, **Reaction 1**, and **Reaction 2** are shown below.

$HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$ $\Delta H_{\text{reaction 1}}$
$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$ $\Delta H_{\text{reaction 2}}$

An equation for this reaction is given below.

Reaction 3:
$H_2O(l) + CO_2(g) + OH^-(aq) \longrightarrow CO_3^{2-}(g) + H_2O(l) + H^+(aq)$ $\Delta H_{\text{reaction 3}}$

Use your answers in **(c)(ii)** and **(d)**, draw an energy cycle to determine a value for the molar enthalpy change for this reaction, $\Delta H_{\text{reaction 3}}$.



$\Delta H_{\text{reaction 3}} = \Delta H_{reaction\ 1} - \Delta H_{reaction2}$

20	
21	

(f) An alternative definition of acid-base behaviour was proposed by Brønsted and Lowry. **Reaction 1** and **Reaction 2** are both acid-base reactions involving hydrogencarbonate ions, HCO_3^-.

In terms of the *Brønsted-Lowry* theory of acids and bases, suggest the role of hydrogencarbonate ions, HCO_3^-, in **Reaction 1**.

Explain your answer in each case.

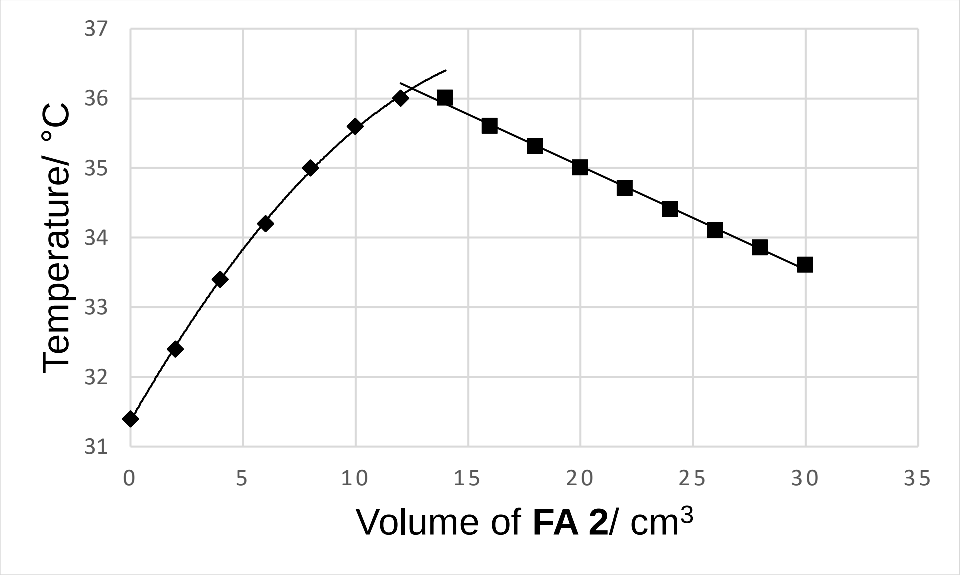
Reaction 1

Role : acid

Explanation : HCO_3^- loses an H^+ ion

22	

(g) A student conducted the same experiment using a digital thermometer and obtained the graph as shown below.



Explain the shape of the graph.

Before equivalence point, T rises/ gradient is positive with each addition of NaOH as reaction is exothermic.

Nearing equivalence point, T rise is smaller / gradient is less positive/ becoming gentler
as the same amount of heat is used to heat up a larger volume of reaction mixture / greater heat loss to surroudings due to steeper temperature gradient.

23	
24	
25	

After equivalence point, T decreases OR gradient is negative with each addition of NaOH. No heat is evolved/ Reaction is completed and addition of **FA 2** cools the solution. (**FA 2** is at a lower temperature than the reaction mixture)

(h) In the calculation of **(d)**, explain why the weighted average initial temperature was used.

The initial temperature and volume of sodium hydrogencarbonate and NaOH is different. Hence by considering the mass of the solution, the average initial temperature is calculated with respect to its mass and the average initial temperature will be more accurate.

26	

(h) With reference to the reaction between **FA 1** and **FA 2**, if the volume of NaOH is doubled, explain how it will affect the maximum temperature change?

No effect on the maximum temperature change. FA 1 is the limiting reagent OR the same amount of heat released at equivalence point is used to heat up the same total volume of solution.

27	

[Total: 27]

2 To determine the proticity of an unknown acid

For Examiner's Use

Acid base titration is commonly used to determine the concentration of an acid or base. In this experiment, the concentration of the acid is given and the aim of this investigation is to determine its proticity.

Acids are defined as substances that can donate hydrogen ions, H^+, to bases. Monoprotic acids contain one H^+ that can be donated per molecule. Diprotic acids contain two H^+ that can be donated per molecule.

You will determine using a titration method whether acid **Z** is monoprotic or diprotic.

- **FA 4** is a solution containing 11.55 g dm^{-3} of acid **Z**.
- **FA 5** is 0.105 mol dm^{-3} aqueous sodium hydroxide, NaOH.
- Thymol blue indicator

(a) Method

- Pipette 25.0 cm^3 of solution **FA 4** into a conical flask.
- Fill a burette with **FA 5**.
- Add 3 drops of thymol blue indicator to the conical flask.
- The colour change at the endpoint is yellow to blue.
- Carry out as many accurate titrations as you think necessary to obtain consistent results.
- Record, in a suitable form below, all of your burette readings and the volume of **FA 5** added in each accurate titration.

Results

Titration number	1	2	3	
Final burette reading /cm^3	24.50	49.00		
Initial burette reading /cm^3	0.00	24.50		
Volume of **FA 5**(used) /cm^3	24.50	24.50		

28	
29	
30	
31	

Note:

- *Correct headers and units*
- *Proper tabulation of burette readings*
- *Burette readings in the table recorded to the nearest 0.05 cm^3*
- *Check consistency of two uncorrected titres ≤ 0.10 cm^3*
- *Accuracy based on difference between Supervisor's and Student's values*

(b) From your titration results, obtain a suitable value for the volume of **FA 5** to be used in your calculations. Show clearly how you obtained this value.

Average of any two volume of **FA 1** to 2dp.

Volume of **FA 5** =............................

32	

(c) **Calculations**

(i) Calculate the amount of H^+ present in 25.0 cm^3 of **FA 4**.

Amt of H^+ = **(b)** × 0.105 / 1000

Amt of H^+

$= (24.50/1000) \times 0.105$

$= 2.573 \times 10^{-3}$

$= 2.57 \times 10^{-3}$ mol

33	

Amount of H^+ in 25.0 cm^3 of **FA 4** = ...

(ii) Calculate the amount of H^+ present in 1 dm^3 of **FA 4**.

Amt of H^+ = Amt of H^+ from **(c)(i)** × (1000 / 25)

Amt of H^+

$= 2.573 \times 10^{-3} \times (1000 / 25)$

$= 1.029 \times 10^{-1}$

$= 1.03 \times 10^{-1}$ mol

34	

Amount of H^+ in 1 dm^3 of **FA 4** = ...

(iii) **FA 4** contains 11.55 g dm^{-3} of acid **Z**. The relative molecular mass of **Z** is 126. Calculate amount of **Z** in 1 dm^3 of **FA 4**.

For Examiner's Use

Amt of Z = 11.15 / 126 = 9.17×10^{-2} mol

Amount of **Z** in 1 dm^3 of **FA 4** = ...

35	

(iv) Use your answers to **(ii)** and **(iii)** to determine whether **Z** is a monoprotic or a diprotic acid. Explain your answer.

Z is a monoprotic acid as the amount of H^+ in 1 dm^3 of **FA 4** is similar to the amount of **Z** in 1 dm^3 of **FA 4**.

36	

(v) Student **A** conducted this experiment on the day when the chemicals were freshly prepared. His average titre value was found to be *h* cm^3.

Three days later, he conducted the same experiment using the same chemicals but he found that the bottle of NaOH(aq) was left uncovered.

Suggest how his new titre value would compare to *h* cm^3 and explain your answer.

37	

New titre value is lower. Water evaporated from the NaOH (aq). Concentration of NaOH (aq) is higher.

OR

New titre value is higher. NaOH (aq) reacted with CO_2 in the air via acid-base reaction. Concentration of NaOH (aq) is lower.

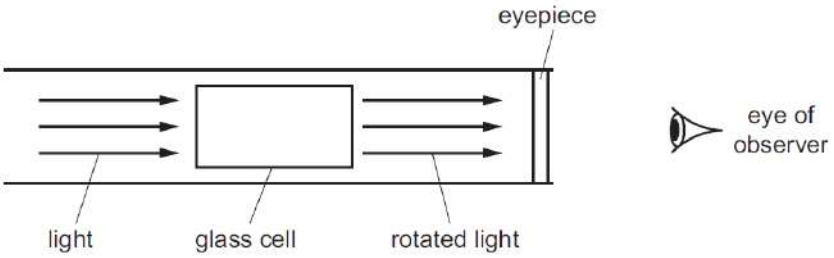
(d) Planning

For Examiner's Use

Sucrose, $C_{12}H_{22}O_{11}$, is a sugar. The concentration of a solution of sucrose can be measured by the optical rotation, α, of a sucrose solution instead of acid–base titration. The more concentrated the solution, the greater the optical rotation of the solution.

A polarimeter is used to measure optical rotation. Plane–polarised light is passed through a sample of the sucrose solution in a glass cell, and the observed angle of rotation, α_{obs}, is measured.

A simplified diagram of a polarimeter is shown.



If a glass cell of length 10 cm is filled with a solution of sucrose of concentration 1 g cm^{-3}, the measured angle of rotation is known as the specific rotation, [α].

The observed angle of rotation, α_{obs}, measured by the polarimeter is related mathematically to the concentration of the sucrose solution by the equation shown.

$$\alpha_{obs} = [\alpha]lc$$

α_{obs} is the observed angle of rotation.

[α] is a constant and is known as the specific rotation of sucrose solution.

l is path length which is 10 cm in the above description.

c is the concentration of sucrose, in g cm^{-3}

(i) Explain why a sucrose solution is able to rotate plane–polarised light.

Sucrose contains at least 1 chiral C/ Sucrose is optically active.

38	

(ii) Using the information given above, you are required to write a plan to determine the concentration of sucrose in a solution **X**.

You may assume that you are provided with:

- solution **X**, of unknown sucrose concentration less than 0.0800 g cm^{-3};
- access to a polarimeter and instructions for use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plans should include details of:

- the preparation of 250 cm^3 0.0800 g cm^{-3} sucrose solution using your answer in **(d)(ii);**
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- a sketch of the calibration curve you would expect to obtain;
- how the calibration line would be used to determine the concentration of sucrose in solution **X**.

Note:

- *Calculate mass of sucrose to use (20.0g)*
- *Proper weighing of sucrose (using electronic balance and reweighing vessel with residual solid)*
- *Procedure to prepare homogenous standard solution of 250 cm^3 0.0800 g cm^{-3} sucrose solution using volumetric flask.*
- *Description of procedure and apparatus (with stated volumes) to prepare diluted solutions.*
- *Concentrations chosen must be well spread out*
- *State the volumes of DI water and stock solution to be added to prepare diluted solutions (min. 3 sets)*
- *Note that total volume of stock solution used cannot exceed volume of stock solution prepared (i.e. 250cm^3)*
- *Scan/ Measure/ Record for each concentration.*
- *Sketch of α_{obs} against concentration. (straight line passing through origin)*
- *Measuring of α_{obs} of solution X and intrapolation to find accurate concentration.*

Example:

Weigh accurately a clean dry empty 100 cm^3 beaker using a weighing balance and record the mass.

Place about 20.00 g sucrose solid in the beaker and reweigh.

For Examiner's Use

Calculate the accurate mass of the sucrose by subtracting the mass of the empty beaker from the mass of beaker and sucrose.

Dissolve the sucrose in deionised water.

Transfer the sucrose solution and its rinsings to a 250.0 cm^3 volumetric flask.

Make-up to the mark with deionised water adding dropwise close to mark and shake the flask well to obtain a homogenous solution.

	100 cm^3 volumetric flask
Concentration of sucrose solution / g dm^{-3}	Volume of 0.0800 g dm^{-3} sucrose solution / cm^3
0.0800	NA
0.0400	50.00
0.0200	25.00
0.0100	12.50
0.0050	6.25

39	
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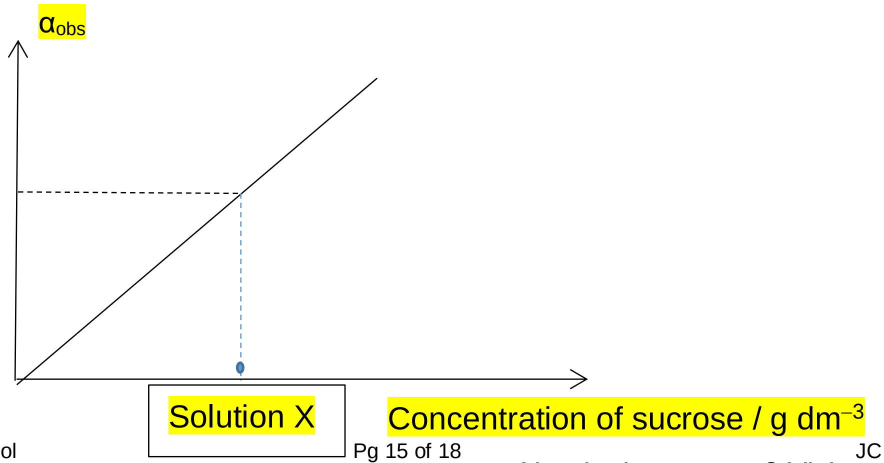
45	

To prepare the diluted sucrose solutions, the appropriate volume of 0.0800 g dm^{-3} sucrose(aq) as shown in the table above is transferred using a burette to a 100 / 250 cm^3 volumetric flask and topped up to the mark with deionised water.

The flask is then well shaken to produce a homogeneous solution.

Measure the rotation values for each sucrose concentration.

A graph of rotation against concentration of the sucrose(aq) used is plotted. A straight line passing through the origin should be obtained.



The rotation value given by the sucrose solution prepared from solution X is measured and the corresponding concentration read off from the calibration graph.

(iv) The glass cell of 10 cm length is expensive, so one cell is used for all the solutions that are placed in the polarimeter.

Suggest how you would ensure that the concentration of solution in the cell is accurate each time the cell is used for the different sucrose solutions.

46	

Rinse/ wash out with small volume of solution of concentration to be used.

(v) Concentration of sucrose is the independent variable in this polarimeter experiment.

The glass cell of 10 cm length is replaced by a glass cell of 20 cm length. The 20 cm glass cell is filled with 0.0750 g cm^{-3} sucrose solution.

Given that α_{obs} of 0.0750 g cm^{-3} sucrose solution is $+6.11^o$, predict the value for the observed angle of rotation, α_{obs}, for the sucrose solution of concentration 0.0750 g cm^{-3} when the 20 cm cell is used. Explain your answer.

Predicted angle = $+12.22^o$

47	

[Total: 20]

3 Inorganic qualitative analysis

For Examiner's Use

(a) **FA 6** and **FA 7** each contain one anion and one cation.

Carry out the following tests and record your observations. For each test you should use a small spatula measure of **FA 6 or FA 7**

	observations	
test	**FA 6**	**FA 7**
Add a small spatula measure to a 1 cm depth of deionised water in a test-tube and shake. Add 2 drops of universal indicator.	**FA 6** is a white solid (ppt not accepted) **FA 6** is sparingly soluble/ insoluble Green to Blue/Purple	**FA 7** is a white solid (ppt not accepted) **FA 7** dissolves to give a colourless solution.

Record the pH of the mixture.	pH 10–14	Green to Orange/ Red pH 1–3
Heat a small spatula measure in a dry boiling tube until no further change.	Water vapour /condensation / steam observed on cooler part of boiling tube.	White solid forms on cold part or top of tube / white fumes/ smoke. Moist red litmus paper turned blue* On strong heating, moist blue litmus paper turned to red. Water vapour/ condensation/ steam observed on cooler part of boiling tube.
Add a small spatula measure in a 2 cm depth of dilute hydrochloric acid in a boiling tube. Decant 1 cm depth of this solution into two test-tubes.		

48	
49	
50	
51	

To one test-tube, add aqueous sodium hydroxide.	White ppt formed; insoluble in excess NaOH	No (observable) reaction / no change / no ppt
To the second test-tube, add aqueous ammonia.	White ppt formed; insoluble in excess NH_3(aq)	No (observable) reaction / no change / no ppt

(b) Mix a spatula measure of **FA 6** with a spatula measure of **FA 7**. Heat the mixture in a boiling tube. Record your observations.

State the type of reaction that has occurred.

Observations:

Colourless, pungent gas evolved that turns **moist red litmus blue**. The gas is NH_3.

52	
53	

Type of reaction: Acid-base

(c) From your observations in **(a)** and **(b)**, identify the possible ions present in **FA 6** and **FA 7**.

If you are unable to identify an ion, write 'unknown'.

	cation	anion
FA 6	Mg^{2+}	OH^-/ strong conjugate base
FA 7	NH_4^+	Unknown

54	
55	

[Total: 8]

END OF PAPER

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examination

H2 Chemistry (9729) **19 Sep 2019**

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 (including this page).

1 Which statement about one mole of sodium metal is always true?

A It has the same mass as one mole of ^{12}C.

B It has the same number of atoms as 18 g of water.

C It has the same number of atoms as $\frac{1}{12}$ mole of ^{12}C.

D It has the same number of atoms as 12 dm^3 of fluorine gas at r.t.p.

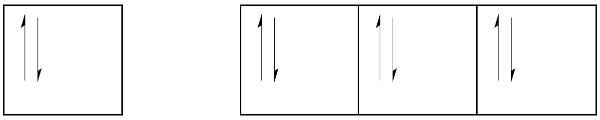
2 0.84 g of an oxide **M**O of a metal **M** was dissolved in excess sulfuric acid. 25.0 cm^3 of 0.12 mol dm^{-3} potassium manganate(VII) solution was required to oxidise $\mathbf{M^{2+}}$ to $\mathbf{M^{3+}}$.

What is the relative atomic mass of **M**?

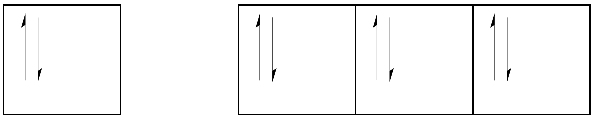
A 36.0 **B** 40.0 **C** 52.0 **D** 56.0

3 **X** and **Y** are elements found in the first three periods of the Periodic Table. The outermost shell electronic configurations of two species are given as follows:

$\mathbf{X}^{2-}$:



$\mathbf{Y}^{2+}$:



What can best be deduced from the above information?

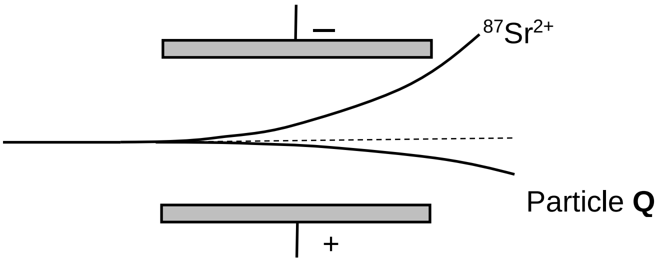
A **X** has a larger proton number than **Y**.

B **X** has more unpaired electrons than **Y** at the ground state.

C **X** exists as a gas while **Y** is a solid at standard condition.

D $\mathbf{X}^{2-}$ and $\mathbf{Y}^{2+}$ are isoelectronic.

4 In an experiment, a sample of gaseous $^{87}Sr^{2+}$ was passed through an electric field. The angle of deflection for $^{87}Sr^{2+}$ was observed to be 2°.



The experiment was repeated with gaseous sample of particle **Q**.

Which of following could be **Q**?

A $^{74}As^{3-}$ **B** $^{19}F^{-}$ **C** $^{79}Se^{2-}$ **D** $^{127}Te^{2-}$

5 $BeCl_2$ reacts with CH_3NH_2 to form compound **Z** (M_r = 142.0).

Which of the following statements are correct?

1 The hybridisation state of N in **Z** is sp^3.

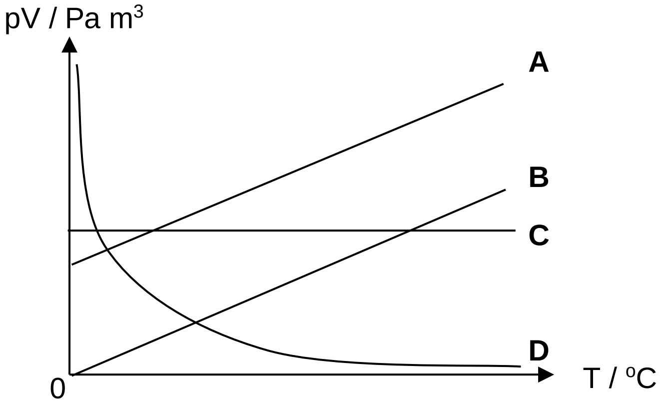
2 Hydrogen bonds exist between molecules of compound **Z**.

3 1 mol of compound **Z** is formed from 1 mol of $BeCl_2$ and 2 mol of CH_3NH_2.

A 1, 2 and 3 **B** 1 and 2 only

C 1 and 3 only **D** 3 only

6 Which of the following graphs correctly describes the variation of pV with temperature for a fixed amount of an ideal gas?



7 The conversion of graphite into diamond is an endothermic reaction.

$$C(graphite) \longrightarrow C(diamond)$$

Which of the following statements are correct?

1 The carbon-carbon bonds in graphite are stronger than that in diamond.
2 The activation energy of the conversion of graphite to diamond is larger than that of the reverse reaction.
3 The enthalpy change of atomisation of diamond is less endothermic than that of graphite.
4 The enthalpy change of combustion of diamond is less exothermic than that of graphite.

A 1 and 2 only **B** 1 and 3 only

C 1, 2 and 3 only **D** 1, 2 and 4 only

8 Given the following enthalpy changes:

	ΔH / kJ mol^{-1}
Enthalpy change of formation of $H_2S(g)$	–20.6
Enthalpy change of formation of $H_2O(l)$	–286.0
Enthalpy change of vaporisation of $H_2O(l)$	+40.7

What is the enthalpy change (in kJ mol^{-1}) of reaction for the following reaction?

$$H_2S(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s)$$

A –224.7 **B** –265.4 **C** –306.6 **D** -347.3

9 Which equation corresponds to the enthalpy change stated?

A $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ $\Delta H^{\theta}_{neutralisation}$

B $Na^+(s) + aq \rightarrow Na^+(aq)$ $\Delta H^{\theta}_{hydration}(Na^+)$

C $Al_2O_3(s) \rightarrow 2Al^{3+}(g) + 3O^{2-}(g)$ $\Delta H^{\theta}_{lattice\ energy}(Al_2O_3)$

D $O_2(g) \rightarrow 2O(g)$ $2\Delta H^{\theta}_{atomisation}(O_2)$

10 A chemical plant illegally dumped some radioactive waste in a landfill. This waste composed of two radioactive isotopes **X** and **Y**. The half-life of **X** is 4 days whereas that of **Y** is 2 days. The authorities found out about this illegal dumping only when the waste had been in the landfill for 8 days. They did an immediate analysis on a sample of the waste and found equal amounts of **X** and **Y**.

Considering that the decay of radioactive isotopes follows first-order kinetics, what is the initial molar ratio of **X** to **Y** if the waste had been in the landfill for 4 days?

	X	:	**Y**
A	1	:	2
B	1	:	4
C	2	:	1
D	4	:	1

11 Hydrogen reacts with nitrogen monoxide to form nitrogen and steam only. The rate equation for this reaction is rate = $k[NO]^2[H_2]$.

Which could be the mechanism for this reaction?

A

$NO + 2H_2 \xrightarrow{\text{slow}} NH_2 + H_2O$

$NH_2 + NO \rightarrow N_2 + H_2O$

B

$2NO \xrightarrow{\text{slow}} N_2 + O$

$2H_2 + O \rightarrow 2H_2O$

C

$2NO + H_2 \xrightarrow{\text{slow}} N_2 + H_2O_2$

$N_2 + 2H_2 \rightarrow N_2H_4$

D

$2NO + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$

$N_2O + H_2 \rightarrow N_2 + H_2O$

12 The table below shows the values of the ionic product of water, K_w, at two different temperatures.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
60	1.00×10^{-13}

Which of the following statements is correct for pure water?

A The ionic dissociation of water is an exothermic process.

B At 60 °C, the pH is less than 7.

C At 60 °C, the pH is more than the pOH.

D At 60 °C, the solution becomes more acidic.

13 The numerical value of the equilibrium constant, K_c, for the following reaction at 25°C is 1.2 x 10^5.

$$CO\,(g) + 2H_2(g) \rightleftharpoons CH_3OH\,(g) \qquad \Delta H^\ominus < 0$$

Which statements about the reaction is correct?

1 The units for K_c is mol^{-1}dm^3.

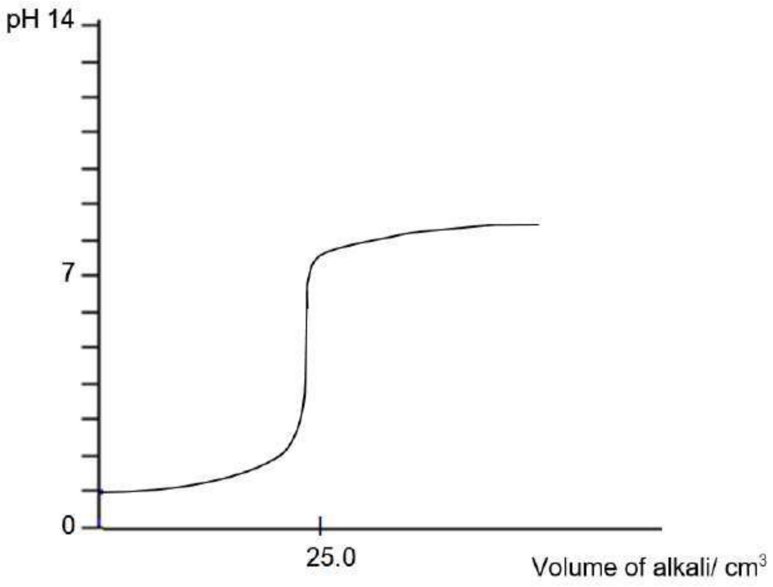
2 $\Delta G^\ominus$ is less than zero.

3 The equilibrium position shifts when an inert gas is added at constant volume.

A 1 and 3 only **B** 2 only

C 2 and 3 only **D** 1, 2 and 3

14 The graph shows the change in pH when an alkali is gradually added to 25 cm^3 of an acid.



Which of the following statements about the titration is correct?

A Acidic buffer is formed after the equivalence point.

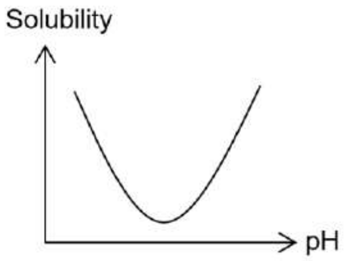
B Both phenolphthalein and methyl orange can be used as the indicator for this titration.

C This is a titration between 0.10 mol dm^{-3} of HCl(aq) and 0.10 mol dm^{-3} of NH_3(aq).

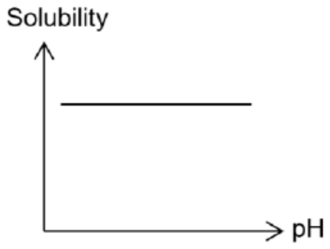
D The maximum buffer capacity occurs when 12.5 cm^3 of alkali is added.

15 CaF_2 is a sparingly soluble salt and is added to a weakly acidic solution of HF. The pH of the solution is adjusted by adding NaOH. Which diagram shows how the solubility of CaF_2 will vary with the pH of the solution at constant temperature?

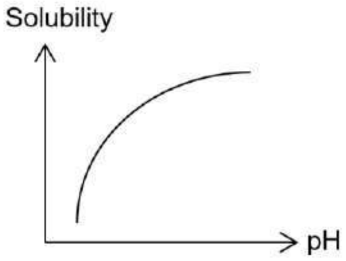
A



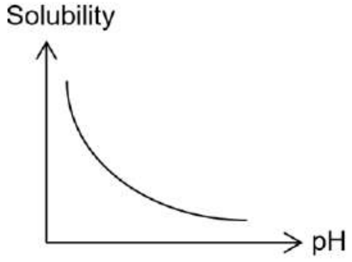
B



C



D



16 Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?

A Ammonium ethanoate is completely ionised in aqueous solution.

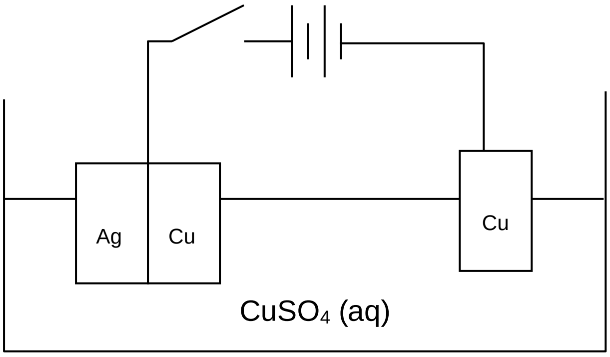
B Ammonium ethanoate is strongly acidic in aqueous solution.

C Ammonia is a stronger base than water.

D Liquid ammonia is more polar solvent than water.

17 Use of *Data Booklet* is relevant to this question.

The following circuit with a switch was set up as shown in the diagram:



Which electrode reactions will occur when the switch is closed?

	Anode reaction	Cathode reaction
A	Silver dissolves preferentially	Hydrogen is evolved
B	Copper dissolves preferentially	Copper is precipitated
C	Silver dissolves preferentially	Copper is precipitated
D	Silver and copper both dissolve together	Hydrogen is evolved

18 Some relevant redox half-equations are given below:

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

$S + 2H^+ + 2e^- \rightleftharpoons H_2S$ $E^\ominus = +0.14$ V

Which of the following statements are true when hydrogen sulfide is bubbled into acidified aqueous sodium dichromate(VI)?

1 The solution turns orange to green.

2 White precipitate is observed.

3 The reaction has a positive entropy change.

A 1 only **B** 1 and 2 only

C 1, 2 and 3 **D** None of the statements are true

19 Elements **X**, **Y** and **Z** are in Period 3 of the Periodic Table.

- The oxide of **X** gives an aqueous solution of pH less than pH 7.
- The oxide of **Y** reacts with both strong acids and strong alkalis.
- The oxide of **Z** gives an aqueous solution which is strongly alkaline.

What is the order of increasing atomic radius for these elements?

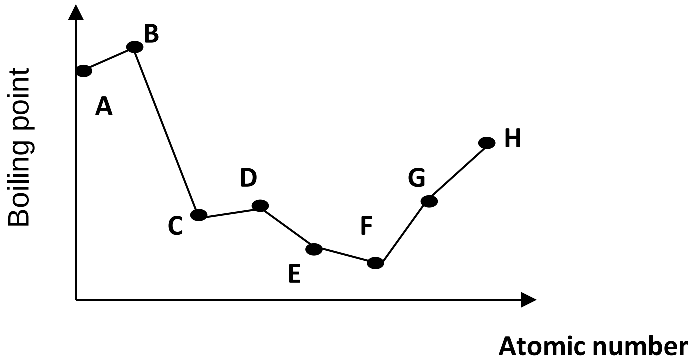
A **X** < **Y** < **Z**

B **X** < **Z** < **Y**

C **Y** < **Z** < **X**

D **Z** < **Y** < **X**

20 The graph below shows the variation in the boiling points for eight consecutive elements in the Periodic Table, all with atomic number between 10 and 20.



Which of the following statements is correct?

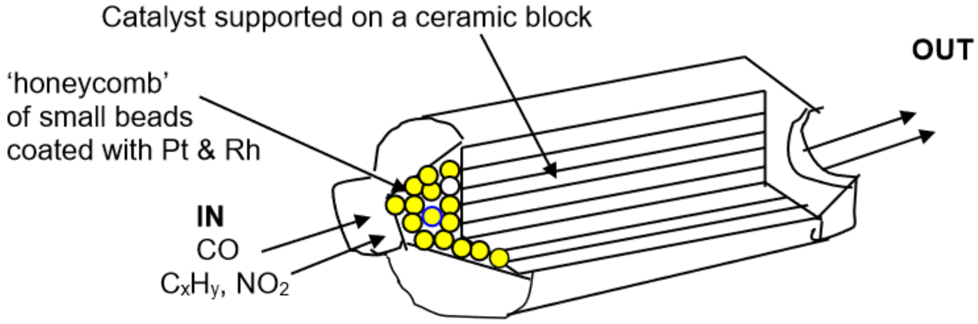
A Element **G** does not conduct electricity.

B Element **D** forms only one acidic oxide.

C Element **A** and beryllium are in the same group

D Element **C** forms a chloride which hydrolyses readily to give a strongly acidic solution.

21 A catalytic converter is part of the exhaust system in modern cars.



Which of the following statements are true concerning the reactions and processes in the catalytic converter?

1 $CO_2 + NO \rightarrow CO + NO_2$

2 $2CO + 2NO \rightarrow 2CO_2 + N_2$

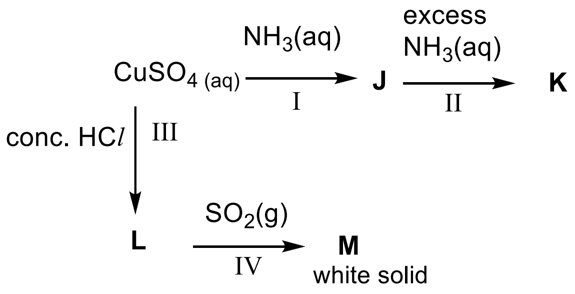
3 $C_xH_y + (2x + \frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x + \frac{y}{4})N_2$

4 Platinum and rhodium catalyse the reactions

A 1, 2, 3 and 4 **B** 1 and 2 only

C 2 and 3 only **D** 2, 3 and 4 only

22 Copper(II) sulfate solution reacted as shown in the scheme below.



Which of the following statements are correct?

1 NH_3 functions as a ligand in reaction I.

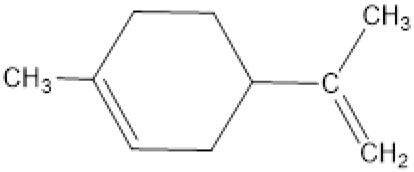
2 The coordination number of complex **L** is 4.

3 The oxidation number of the Cu in **M** is +1.

A 1, 2 and 3 **B** 1 and 2 only

C 1 and 3 **D** 2 and 3 only

23 Limonene is an oil formed in the peel of citrus fruits.

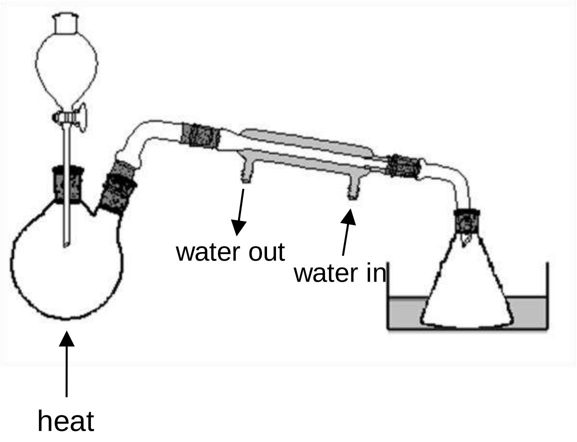


Limonene

When limonene reacts with excess bromine at room temperature in the dark, how many **more** chiral centers than limonene does the product molecule have?

A 2 **B** 3 **C** 4 **D** 5

24 The diagram below shows some laboratory apparatus.



Which preparations could this apparatus be used for?

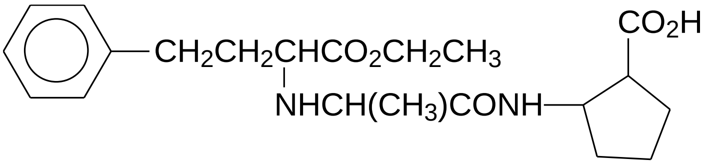
A 1,2-dibromoethane from ethene and bromine

B ethanal from ethanol, sodium dichromate(VI) and sulfuric acid

C propanone from propan-1-ol, sodium manganate(VII) and sulfuric acid

D butan-2-ol from butanone, lithium aluminum hydride in dry ether

25 A prodrug is a molecule that can be converted into its active form in the body. An example is *Enalapril*, as shown below. The active form of *Enalapril* can be formed when enzymes in the body hydrolyse the esters found on the molecule.



Enalapril

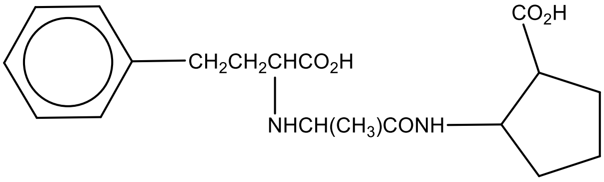
Which of the following is **not** true about *Enalapril*?

A *Enalapril* turns orange aqueous $K_2Cr_2O_7$ green when heated in an acidic medium.

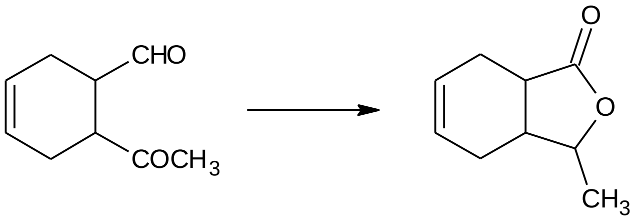
B *Enalapril* does not react with 2,4–dinitrophenylhydrazine.

C *Enalapril* reacts with two moles ethanoyl chloride.

D The active form of *Enalapril* has the structure



26 Compound **V** can be converted to compound **W** in three stages.



Compound **V** Compound **W**

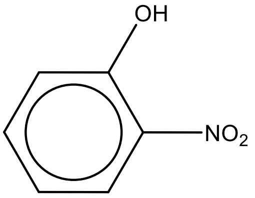
Which sequence of reagents and conditions can be used to carry out this conversion?

	Stage 1	**Stage 2**	**Stage 3**
A	hot acidified $KMnO_4$	H_2 with Pt catalyst	heat with dilute H_2SO_4
B	hot acidified $K_2Cr_2O_7$	$NaBH_4$ in ethanol	heat with dilute H_2SO_4
C	hot Fehling's reagent, followed by acidification	$NaBH_4$ in ethanol	heat with a few drops of conc. H_2SO_4
D	hot Tollens' reagent, followed by acidification	LiA/H_4 in dry ether	heat with a few drops of conc. H_2SO_4

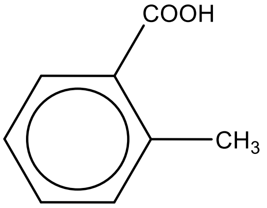
27 Phenol has a pK_a of 10.0.

Which one of the following has a higher pK_a value than phenol?

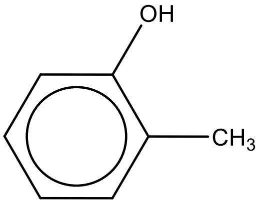
A



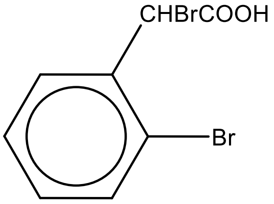
B



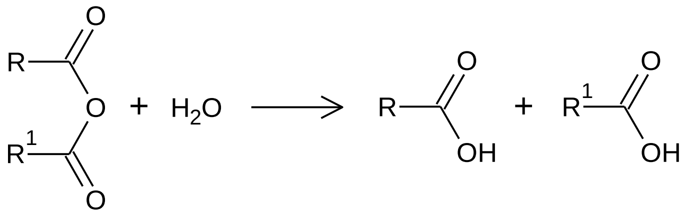
C



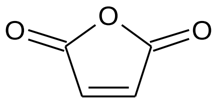
D



28 An acid anhydride is a carboxylic acid derivative that undergoes hydrolysis in water similar to acyl chlorides and esters. A mixture of carboxylic acids is produced in the case of the anhydride.



Based on the information above, which of the following can be deduced when maleic anhydride undergoes hydrolysis in the presence of water labelled with the ^{18}O isotope?



maleic anhydride

A The resulting product is non-planar.

B The product is labelled with the ^{18}O isotope.

C Two carboxylic acid molecules are produced for every molecule of maleic anhydride.

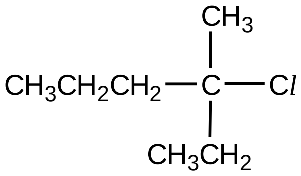
D The reaction is faster than when maleic anhydride undergoes hydrolysis in the presence of water labelled with the ^{16}O isotope.

29 Which of the following reactions will **not** form a racemic mixture of products?

A CH_3COCH_3 with HCN in trace amounts of NaOH

B $CH_3CH_2CH_2COCH_3$ with HCN in trace amounts of NaCN

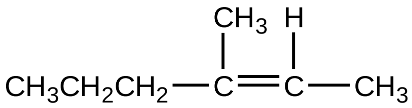
C



$$CH_3CH_2CH_2-\underset{\underset{CH_3CH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl$$

with KOH(aq), heat under reflux

D

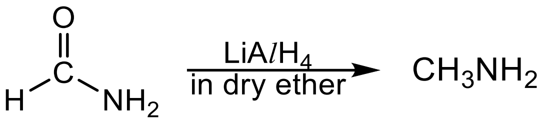


$$CH_3CH_2CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_3$$

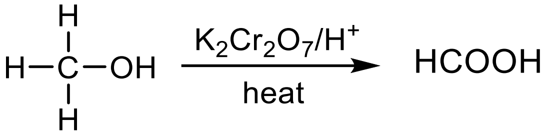
with HBr(g)

30 In which reaction will the oxidation number of carbon change by 4?

1

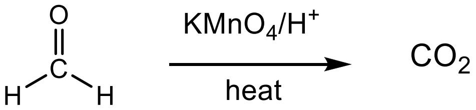


2



$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH \xrightarrow[\text{heat}]{K_2Cr_2O_7/H^+} HCOOH$$

3



A 1, 2 and 3 **B** 2 only

C 1 and 3 only **D** 1 only

End of Paper

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

Chemistry (9729) **30 August 2019**

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	**9**	**8**	**20**	**25**	**13**	**75**

This document consists of **20** printed pages (including this page).

1. **(a)** **P**, **Q**, **R and S** are consecutive elements in Period 4.

The table below shows the first four ionisation energies (in kJ mol^{-1}) of the elements.

Element	**1st I.E.**	**2nd I.E.**	**3rd I.E.**	**4th I.E.**	**5th I.E.**
P	908	1730	3828	5980	7970
Q	577	1980	2960	6190	8284
R	762	1540	3300	4390	9020
S	947	1798	2735	4837	6043

(i) Explain why the second ionisation energy of **Q** is higher than that of **R**. **[2]**

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(ii) Explain why **P** is not considered to be a transition metal like most of the d-block metals. **[1]**

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(b) The idea of covalent bonding was first described in 1916 by an American physical chemist Gilbert Newton Lewis. HCOC*l* is an example of a polar covalent molecule.

(i) Explain what is *covalent bonding*. **[1]**

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1. (b) (ii) State what is meant by the term *polar* when applied to a covalent bond. **[1]**

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(iii) State and explain with reference to the Valence Shell Electron Pair Repulsion theory, the shape of HCOC*l* molecule. **[2]**

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(iv) The molecule of HCOC*l* contains both σ (sigma) and π (pi) bonds. Draw labelled diagrams to show how orbitals overlap to form

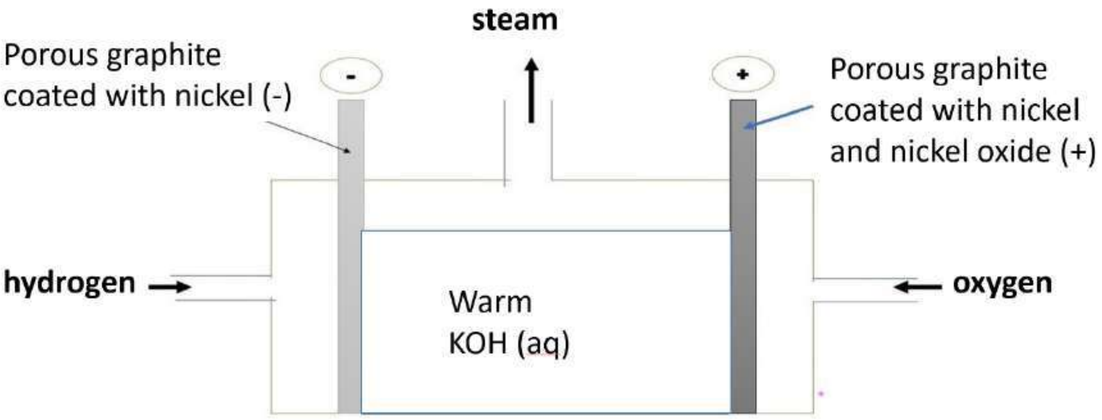
- a σ (sigma) bond

[2]

- a π (pi) bond

[Total:9]

2 Below is a labelled diagram of a hydrogen-oxygen fuel cell in an alkaline electrolyte.



(i) Write the half equations for both electrodes and hence the overall equation. **[2]**

Cathode ………………………………………………………………………

Anode …………………………………………………………………………

Overall ………………………………………………………………………..…

(ii) Calculate ∆$G^{\ominus}$ for the above reaction and state whether it is spontaneous. **[3]**

2. **(a)** **(iii)** The hydrogen-oxygen fuel cell produces 1.5 A of current. Hydrogen gas is contained in a 1 dm^3 tank at a pressure and temperature of 200 atm and 20 ^oC respectively. Determine the number of days the fuel cell can operate before the hydrogen gas runs out. Give your answer to the nearest whole number. You may assume there is an unlimited supply of O_2. **[3]**

[Total:8]

3. Spider silk is a protein fiber. Major amino acids in the silk proteins are alanine and glycine. Serine and glutamine are also present in significant quantities in some types of silk.

The table below shows the typical amino acids present in spider silk.

Amino Acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Glycine	$-H$
Alanine	$-CH_3$
Serine	$-CH_2OH$
Glutamine	$-CH_2CH_2CONH_2$

(a) **(i)** Glycine exists as crystalline solids. Draw the zwitterionic structure of glycine and account for the high melting point of glycine. **[2]**

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3. **(a)** **(ii)** Write an equation to show the reaction between alanine and aqueous sodium carbonate. **[1]**

(iii) Suggest a chemical test to distinguish between serine and glutamine. **[2]**

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(b) Natural spider silk has excellent mechanical properties. In a recent study, researchers discovered that graphene-based materials can be used to boost the properties of spider's silk up to three times the strength and ten times the toughness of the unmodified silks.

Graphene is the thinnest material known to exist, yet it is stronger than steel. It is made from only carbon and is a single layer of graphite just one atom thick as shown in Figure **3.1** below.

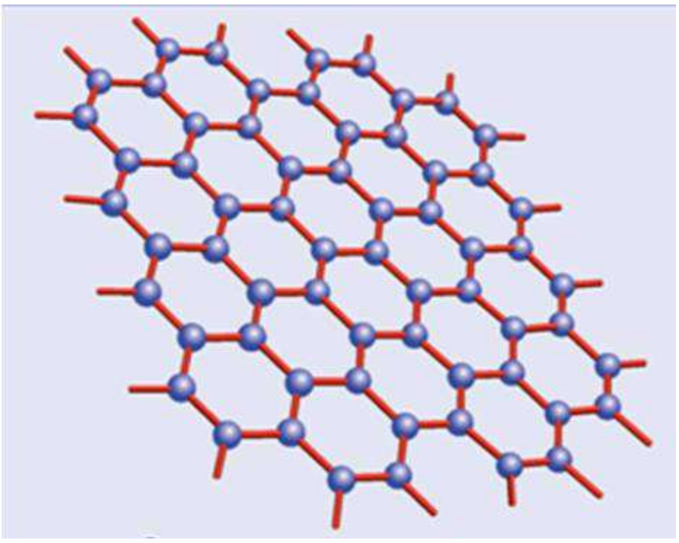

Figure **3.1**

3. **(b)** **(i)** With reference to structure and bonding, explain why graphene is strong. **[1]**

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(ii) Since its discovery in 2004, graphene has been widely studied and manufactured as replacement materials for many touchscreen products. Suggest why graphene is a suitable touchscreen material in mobile phones. **[1]**

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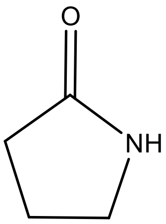
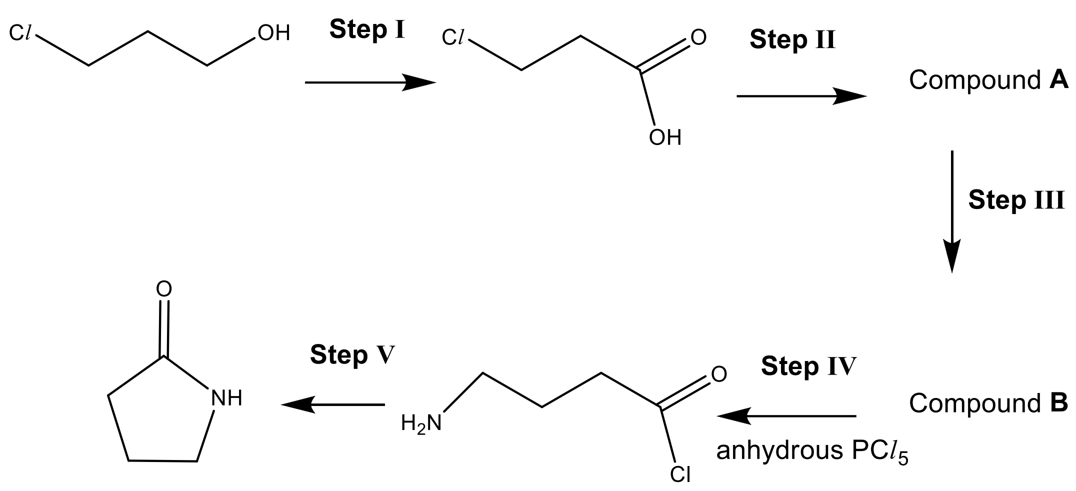
(c) Spider makes an excellent treat for a colony of marauding ants. To protect their homes, spiders coat their webs using a chemical called 2-pyrrolidone, which acts as a deterrent to many insects.

2-Pyrrolidone is a 5-membered cyclic amide (commonly known as lactam). It is a colourless liquid that is miscible with water and most common organic solvents.



2-Pyrrolidone

3. **(c)** 2-pyrrolidone can be synthesised using 3-chloropropan-1-ol as the starting organic compound as shown in the reaction scheme below:



(i) State the type of reaction in **Step V**. **[1]**

…………………………………………………………………………………………

(ii) Suggest reagents and conditions for **Step I**, **II** and **III**. **[3]**

Step I : …………………………………………………………………

Step II : …………………………………………………………………

Step III : …………………………………………………………………

(iii) Draw the structures of intermediate compounds **A** and **B.** **[2]**

A	**B**

3. **(c)** **(iv)** With the aid of an equation, explain why anhydrous condition is necessary for the reaction in **Step IV**. **[1]**

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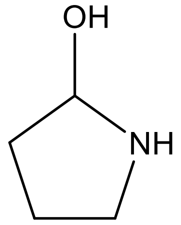
(v) 2-pyrrolidirol can be synthesised from 2-pyrrolidone.



2-pyrrolidirol

Deduce whether 2-pyrrolidone or 2-pyrrolidirol has a higher pK_b. **[2]**

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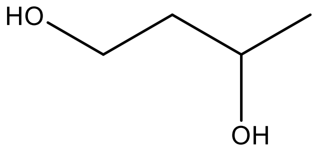
(vi) Suggest a synthesis of 3-chloropropan-1-ol from 1,3-butandiol. **[4]**



1,3-butandiol

[Total:20]

4 **(a)** Copper and iron are examples of native metals, which are found pure in its metallic form on its own or in alloys in nature.

Copper and iron form many complexes with a range of colours as shown in the table:

complex	colour	complex	colour
$[Cu(NH_3)_4]^{2+}$	dark blue	$[Fe(H_2O)_6]^{3+}$	yellow
$[Cu(H_2O)_6]^{2+}$	blue	$[Fe(CN)_6]^{3-}$	red

(i) Explain why $[Cu(H_2O)_6]^{2+}$ is blue. **[3]**

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(ii) The oxidation state of iron in both $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ complexes is the same. However, they have different colours. Explain this observation. **[1]**

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4. **(a)** **(iii)** Draw **fully labelled** diagrams of the following:

- One of the d-orbitals at the lower energy level in $[Cu(H_2O)_6]^{2+}$. Label the diagram “lower”.
- One of the d-orbtials at the upper energy level in $[Cu(H_2O)_6]^{2+}$. Label this diagram “upper”. **[2]**

(b) *Use of the Data Booklet is relevant to this question.*

Fe^{2+} is commonly used to catalyse the reaction between $S_2O_8^{2-}$and I^-. In another similar reaction, peroxodisulfate(VI), $S_2O_8^{2-}$, reacts with tartrate ion, $[CH(OH)CO_2]_2^{2-}$, to give carbon dioxide and methanoate as shown in the following equation.

$$[CH(OH)CO_2]_2^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

The reaction is very slow, even when heated, hence a catalyst is used to speed up the reaction.

(i) Explain why the reaction is slow. **[1]**

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4. (b) (ii) Given that the standard electrode potential for the following half-equation is

$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons [CH(OH)CO_2]_2^{2-} + 2H_2O \qquad E^\theta = +0.56\ V$$

Using suitable equations, explain why Mn^{2+} is a suitable catalyst for this reaction. **[2]**

(iii) State the property of transition metal ions that enable them to function as a homogenous catalyst in the reaction. **[1]**

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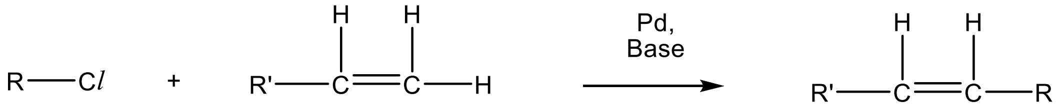
4. (c) Palladium is a transition element that is used as a catalyst in the Cassar reaction.

The Cassar reaction is a type of substitution reaction between an alkyl chloride and a terminal alkene in the presence of a base and a palladium catalyst.



[R can be a substituted alkyl group containing –OH, –NH$_2$, –NO$_2$,–COOH]

The following scheme shows the synthesis of **D** using Cassar reaction in one of the steps.

$$\mathbf{A} + \underset{C_4H_8O}{\mathbf{B}} \xrightarrow{\text{Cassar reaction}} \underset{C_5H_{11}NO}{\mathbf{C}} \xrightarrow{K_2Cr_2O_7(aq),\ H_2SO_4(aq),\ heat} \mathbf{D}$$

The table below shows the observations when **A**, **B** and **D** react with various reagents.

reaction		observations
1	**A** + HC*l*(aq)	colourless solution
2	**B** + Br$_2$(aq)	colourless solution
3	**D** + Na$_2$CO$_3$(aq)	Gas forms white ppt with Ca(OH)$_2$

(i) Name the functional group that reaction **1** shows to be present in **A** **[1]**

……………………………………………………………………………………

(ii) State the type of reaction that takes place in reaction **2** and name the functional group present in **B** **[1]**

……………………………………………………………………………………

(iii) **C** is able to exhibit cis-trans isomerism. Draw the structures of **A**, **B**, **C** and **D**. **[4]**

A	**B**
C	**D**

4. (c) (iv) Draw the structure of the product when $CH_3CH(CH_2Cl)CH_2CH_2CH{=}CH_2$ undergoes the Cassar reaction. **[1]**

(d) A solution containing Cu^{2+} and Zn^{2+} can be separated by selective precipitation.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

Aqueous hydrogen sulfide behaves as a dibasic acid.

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq) \quad K_{a1} = 8.9 \times 10^{-8}\ mol\ dm^{-3}$$

$$HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq) \quad K_{a2} = 1.2 \times 10^{-13}\ mol\ dm^{-3}$$

Metal sulfides are precipitated by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \rightleftharpoons MS(s)$$

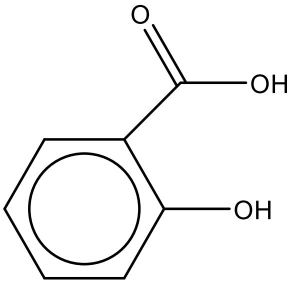
Relevant K_{sp} values are given in the table below.

Salt	K_{sp} / mol^2 dm^{-6}
CuS	6.3×10^{-36}
ZnS	1.6×10^{-24}

(i) Given that a solution contains 0.0010 mol dm^{-3} Zn^{2+} and 0.0010 mol dm^{-3} Cu^{2+}, determine the maximum sulfide concentration for each cation so that no precipitation occurs. **[1]**

4. **(d)** **(ii)** Given that $[H^+] = \sqrt{\dfrac{K_{a1}K_{a2}[H_2S]}{[S^{2-}]}}$ and using your answer in **(c)(i)**, calculate the maximum pH that must be maintained to separate Zn^{2+} and Cu^{2+} ions, given that the concentration of H_2S in the solution is 0.0010 mol dm^{-3}. **[2]**

(e) The Trinder spot test is a diagnostic test used in medicine to determine exposure to salicylates, in particular, salicylic acid. The test involved the Trinder reagent which is mixed with a patient's urine. A coloured complex is formed if salicylates are present.



Salicylic acid

(i) Suggest the compound that is present in the Trinder reagent added to salicylic acid and state the observation when if the test is positive.

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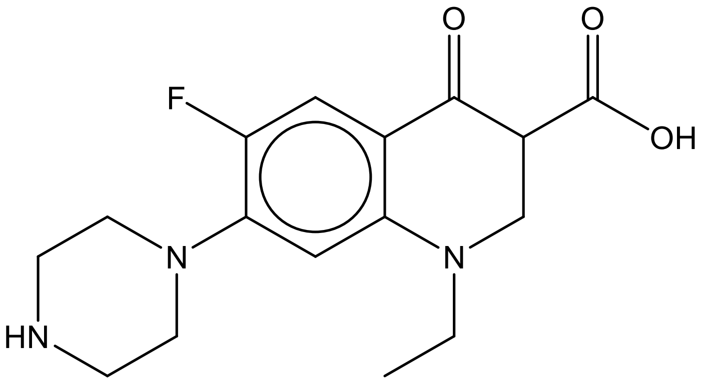
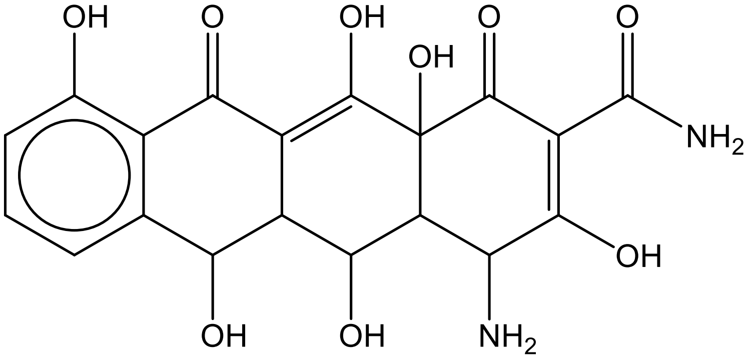
……………………………………………………………………………………..…. **[2]**

4. (e) Another variation of the Trinder spot test has also been used to determine the presence of norfloxacin and oxytetracycline.



norfloxacin



oxytetracycline

(ii) State the number stereoisomers present in oxytetracycline. **[1]**

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(iii) Suggest a chemical test to distinguish between oxytetracycline and norfloxacin. **[2]**

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[Total:25]

5. Sodium alginate is a natural polymer extracted from brown seaweed. Figure **5.1** shows the simplified representation of a sodium alginate polymer.

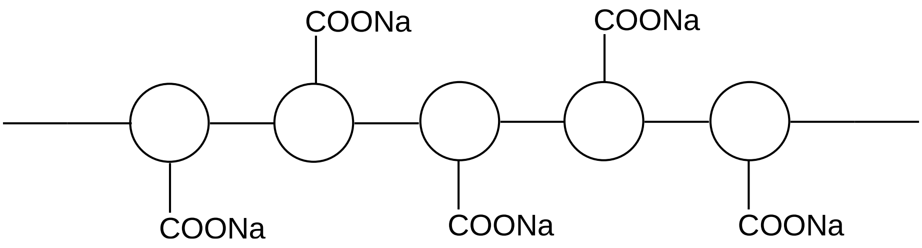

Figure **5.1** : simplified representation of sodium alginate polymer

In food chemistry, sodium alginate serves as a gel-forming agent as it can react with calcium salts to make "popping boba" in the bubble tea industry. This process is commonly known as spherification.

During spherification, a solution of sodium alginate is added to a solution of calcium salt. Na^+ ions are exchanged with Ca^{2+} ions and the cross linked calcium alginate polymers forms as shown in Figure **5.2**.

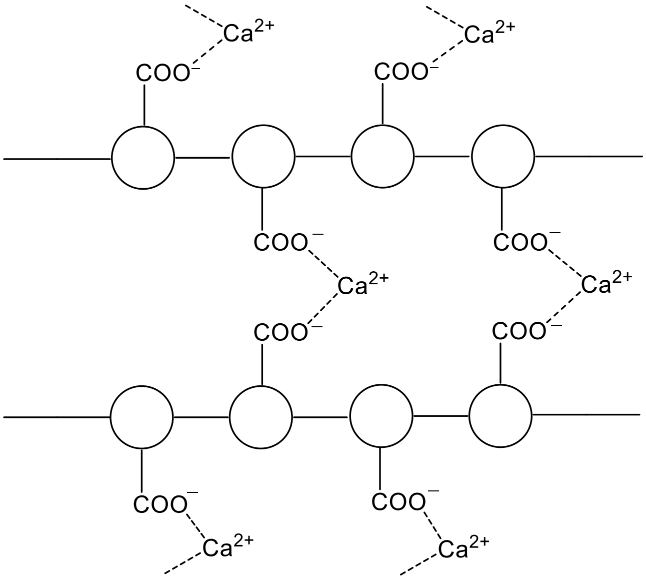

Figure **5.2**: simplified representation of cross-linked calcium alginate polymer

(a) **(i)** Cross-linking is the general term for the process of forming chemical bonds to join two polymer chains together. Explain, in terms of bonding, why Ca^{2+} ions are able to cross-link the alginate polymers but Na^+ ions are unable to do so. **[1]**

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5. **(a)** **(ii)** Explain why calcium alginate has a low solubility in water. **[1]**

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(b) During spherification, the pH of the flavoured liquid used is important. Below a pH of 3.6, sodium alginate tends to react and the resultant solution will thicken which makes it difficult to form spheres.

Although Ca^{2+} is crucial in helping the alginate to gel, excess Ca^{2+} present can also cause the liquid to gel prematurely which is undesirable.

Table **5.3** shows the pH of various flavoured liquid.

Table **5.3**

Flavoured Liquid	**pH**
cranberry juice	2.3
blueberry juice	3.4
tomato juice	4.6
watermelon juice	5.2
aloe vera juice	6.1

(i) Cranberry juice is not suitable for spherification to work.

Suggest the type of reaction that takes place when sodium alginate is added to cranberry juice and hence explain why spherification will not occur in presence of cranberry juice. **[2]**

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5. **(b)** **(ii)** A bubble tea shop wanted to make a "popping boba" by mixing 250 cm^3 of aloe vera juice with 300 cm^3 of blueberry juice. By determining the pH of the mixture, deduce if the spherification would happen. **[3]**

(iii) Hard water is water that has a high mineral content. It is formed when water percolates through deposits of limestone which are made up of calcium and magnesium carbonates and bicarbonates.

Suggest why spherification does not work well in hard water. **[1]**

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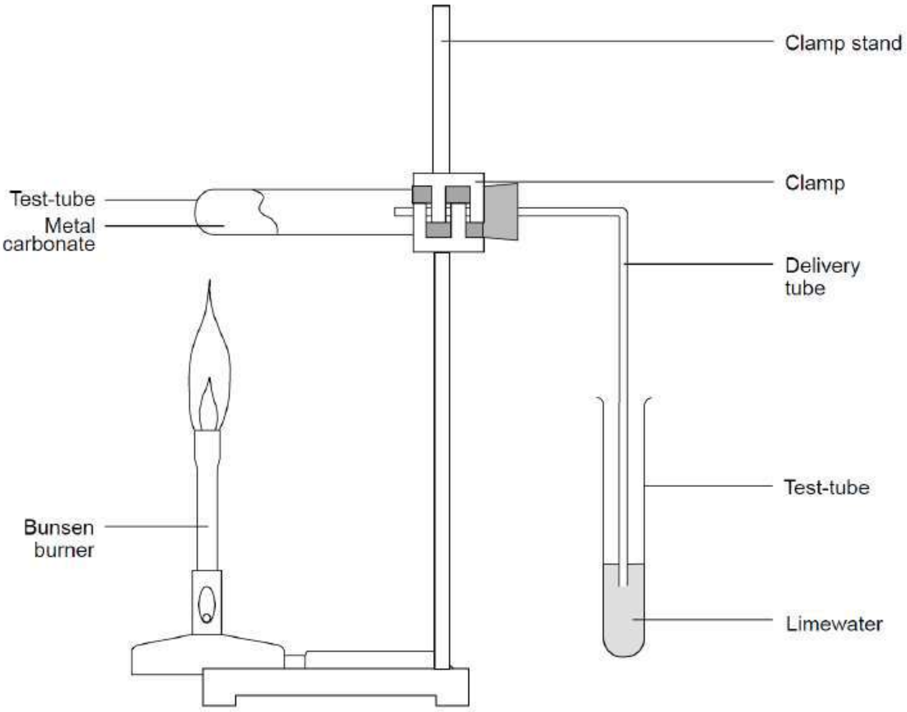
(iv) Draw the dot-cross diagram for calcium bicarbonate $Ca(HCO_3)_2$. **[2]**

5. **(c)** A student set up the following experiment to investigate the thermal stability of magnesium and calcium carbonates:



Each of the metal carbonate is heated strongly for 5 min and the time taken for a white precipitate to form in limewater is recorded in the following table:

Metal carbonate	Time taken (s)
X	70
Y	40

(i) What are the identities of **X** and **Y**? **[1]**

X: ……………………………

Y: ……………………………

(ii) Explain the results. **[2]**

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[Total:13]

~END OF PAPER~

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examination

H2 Chemistry (9729) **18 September 2019**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Answer 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.

Section A

Answer **all** questions. Marks **[60]**

Section B

Answer **one** question. Marks **[20]**

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.

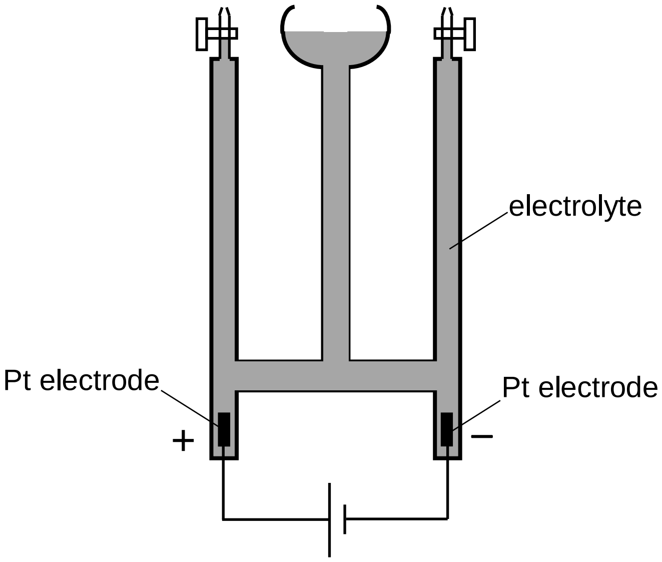
This document consists of **14** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** Use of the Data Booklet is relevant to this question.

The Hoffmann voltameter is used to electrolyse concentrated iron (III) chloride solution. The setup of the Hoffmann voltameter is shown below.



(i) Describe the observations at the cathode and anode. Explain your answer with the aid of suitable ion-electron equations. **[2]**

(ii) State the difference in the observations at the anode when dilute aqueous iron (III) chloride solution is used instead. Explain your answer using relevant E^{θ} data. **[2]**

(b) The electrolysis of a hot aqueous solution of Na**X** yielded a reddish brown gas, $\mathbf{X_2}$, at the anode and hydrogen gas at the cathode. The red litmus paper turned blue when dipped into the solution at the cathode.

(i) Suggest the identity of the reddish brown gas $\mathbf{X_2}$. **[1]**

(ii) Write an ion-electron equation for the reaction at the cathode. **[1]**

(iii) Some of the $\mathbf{X_2}$ dissolved in the alkaline medium to form $\mathbf{X^-}$ and $\mathbf{XO_3^-}$ ions. Write a balanced equation to represent the reaction of $\mathbf{X_2}$ in alkaline medium. **[1]**

(iv) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between sodium chloride and sodium iodide. **[2]**

(c) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. **[2]**

(d) When methylcyclopentane is treated with a small quantity of chlorine in the presence of ultraviolet light, 4 mono-chlorinated constitutional isomers are produced. Draw the structures of the isomers and state the ratio in which they are formed. **[3]**

(e) $SiCl_4$ reacts readily with water to form a solution of pH 2. However, SiO_2 does not react with water and only reacts with hot concentrated alkali such as NaOH.

(i) Explain why $SiCl_4$ reacts readily with water, but SiO_2 only reacts with hot concentrated NaOH. Use relevant equations to explain your answer. **[3]**

(ii) Using Cl_2(g) as an example, define the term *bond energy*. **[1]**

(iii) Construct an energy level diagram to calculate the enthalpy change of formation of $SiCl_4$.

Your diagram should include relevant data from the *Data Booklet* together with the following data: **[3]**

Enthalpy change of atomisation of Si = +338 $kJmol^{-1}$

Enthalpy change of vapourisation of $SiCl_4$ = +29 $kJmol^{-1}$

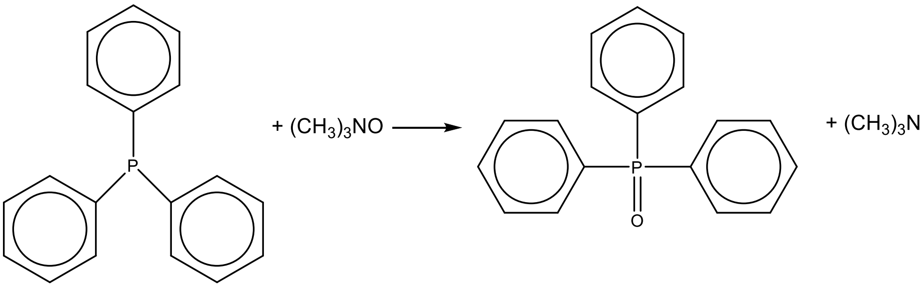
[Total: 21 marks]

2 **(a)** Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way the phosphorus-containing compound is reacting in each case. Explain your answers fully.

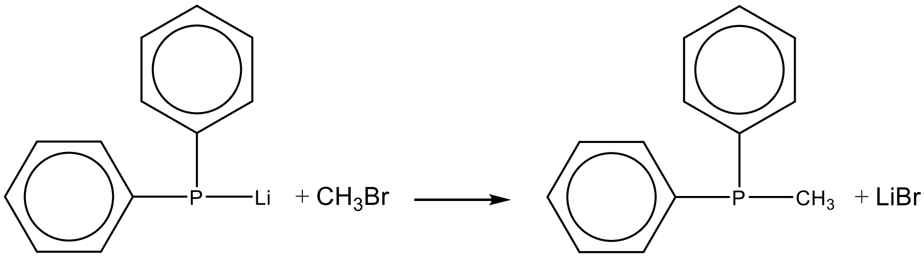
(i) $H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$ **[1]**

(ii)



[1]

(iii)



[1]

(b) 2-chloropropanoyl chloride, **W**, can be obtained from propanoic acid by heating it with Cl_2 and PCl_5.

Reaction **1** :

$CH_3CH_2CO_2H(l) + Cl_2(g) + PCl_5(s) \rightarrow \underset{\textbf{W}}{CH_3CHClCOCl(l)} + 2HCl(g) + POCl_3(l)$

$\Delta H > 0$

(i) Explain the different reactivities of the two chlorine atoms in **W** towards water. **[2]**

(ii) Explain fully why the pH of an aqueous solution of 2-chloropropanoyl chloride is 1.0 while that of an aqueous solution of propanoic acid of the same concentration is greater than 1.0. **[2]**

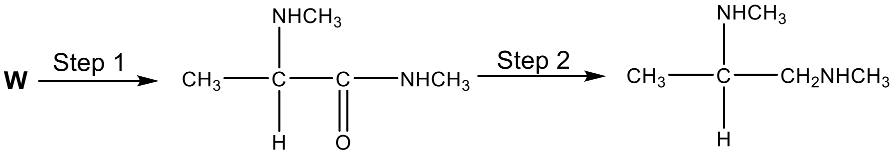
(iii) **W** can be used to produce sweet-smelling **Z**, $C_6H_8O_4$, via compounds **X** and **Y**, as shown in Fig. 2.1

$$\mathbf{W} \xrightarrow[\text{heat}]{\text{NaOH(aq)}} \mathbf{X} \xrightarrow{H_2SO_4\text{(aq)}} \mathbf{Y} \xrightarrow[\text{heat}]{\text{conc } H_2SO_4} \mathbf{Z}$$

Fig. 2.1

Suggest structures for compounds **X**, **Y** and **Z** in Fig. 2.1. **[3]**

(iv) **W** can undergo the following reaction scheme.



$$\mathbf{W} \xrightarrow{\text{Step 1}} CH_3-\underset{H}{\overset{NHCH_3}{C}}-\underset{\underset{O}{\|}}{C}-NHCH_3 \xrightarrow{\text{Step 2}} CH_3-\underset{H}{\overset{NHCH_3}{C}}-CH_2NHCH_3$$

State the reagents and conditions for Steps 1 and 2. **[2]**

(v) **V** is an isomer of **W**.

V rotates the plane of polarised light. It gives a positive test with 2,4-dinitrophenylhydrazine.

Draw the displayed formula of **V**, identifying the chiral carbon. **[1]**

(vi) Use the table of characteristic values for infra-red absorption frequencies in the *Data Booklet* to answer this question.

Infra-red adsorption frequencies can be used to identify functional groups in organic compounds. For example, propanol shows absorptions at 970–1250cm^{-1} and 3580–3620 cm^{-1}.

Use the table to suggest how infra-red absorption frequencies can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. **[1]**

(vii) Given that reaction **1** is endothermic, explain why the reaction will only take place with heating. **[2]**

[Total : 16 marks]

3 There are 2 isomers of 2-methylbutanoic acid, $CH_3CH_2CH(CH_3)COOH$ (M_r 102.0) ; one of the isomers is sweet-smelling and the other has a stinky odour.

(a) **(i)** State the stereoisomerism exhibited by 2–methylbutanoic acid and how it arises. **[2]**

(ii) Hence, explain why the isomers have different smells. **[1]**

(b) Suggest a 2 stage synthesis of 2–methylbutanoic acid from 2–bromobutane. State reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. **[3]**

(c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

When 2–methylbutanoic acid was synthesised using 2–bromobutane in a factory, both the sweet-smelling and the stinky isomers were obtained in equal proportions.

(i) The M_r of 2–methylbutanoic acid in the liquid phase is 204.0.
With the aid of a diagram, explain the above. **[2]**

(ii) 2–methylbutanoic acid has a relatively low boiling point of 176 ^{o}C at 1 atm, and hence vaporises easily. This poses a problem when adhering to safety regulations.

In a factory, during the synthesis of 2–methylbutanoic acid, the workers did not seal the chemical container properly.

Given that the enthalpy change of vaporisation of 2–methylbutanoic acid is +59.1 kJ mol^{-1}, use the following equation (Clausius–Clapeyron Equation) to determine the vapour pressure of 2–methylbutanoic acid in the factory at night when the temperature was 30.2 ^{o}C.

$$\ln P = \frac{\Delta H_{vaporisation}}{R}\left(\frac{1}{T_{b.p.}} - \frac{1}{T}\right)$$

P = vapour pressure in atm at temperature T K

$\Delta H_{vaporisation}$ = enthalpy change of vaporisation of the substance in J mol^{-1}

R = universal gas constant

$T_{b.p.}$ = boiling point of the substance in K at 1 atm

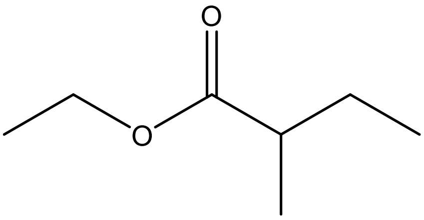
[2]

(iii) Safety protocols dictated that stinky smelling substances above 300 ppm (parts per million) is considered a safety hazard and likely to be fined. Based on your answers in **(a)(i)** and **(c)(ii)**, and given that the pressure in the factory is 1 atm, determine whether the factory would be fined.

[2]

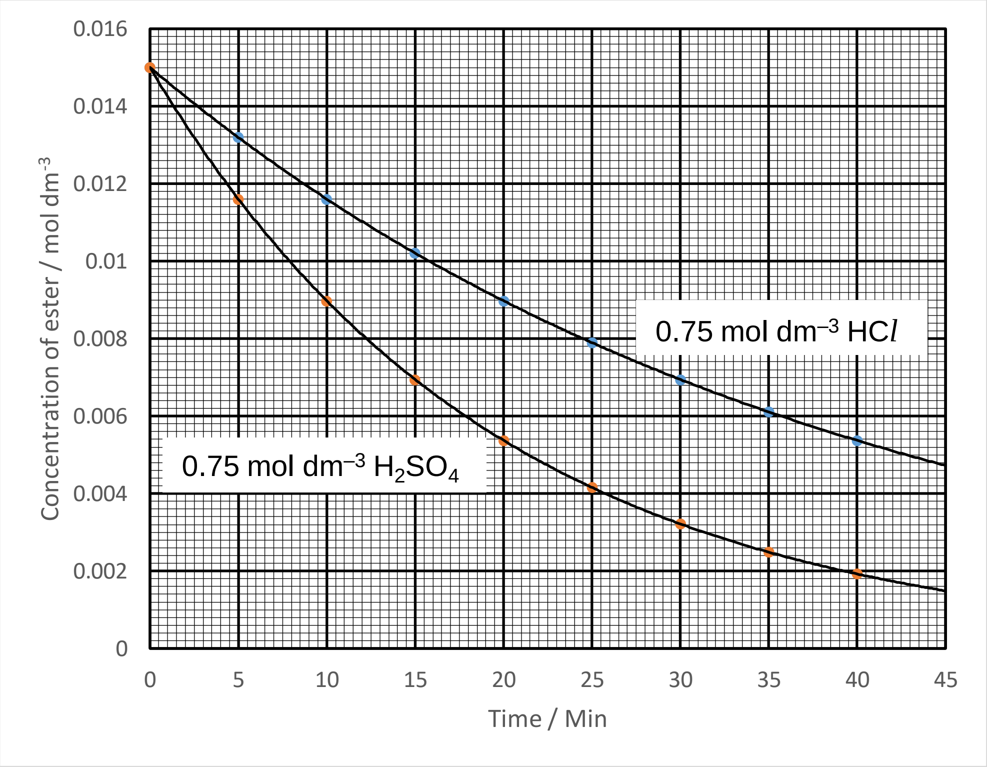
[1 x 10^{-6} atm in 1 atm = 1 ppm]

(d) Ethyl 2–methylbutanoate is an ester which is commonly found in citrus fruits, such as pineapple and oranges. It is commonly used as the starting material to form the sweet–smelling 2–methylbutanoic acid via hydrolysis.



ethyl 2-methylbutanoate

The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of the ester, ethyl 2–methylbutanoate, was carried out, using 0.75 mol dm^{-3} hydrochloric acid. The experiment was repeated using 0.75 mol dm^{-3} sulfuric acid. The following graphs were obtained.



(i) Using the graphs above, deduce the order of reaction with respect to [H^+] and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate. **[3]**

(ii) Calculate the rate constant for the hydrolysis of ethyl 2-methylbutanoate, including its units. **[2]**

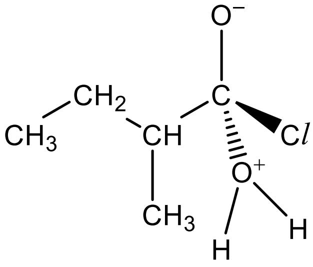
(iii) In the absence of an acid, the hydrolysis of the ester is very slow.
With the aid of a relevant diagram, explain how the rate constant would change if the acid was removed. **[3]**

(e) Ethyl 2-methylbutanoate can also be formed using 2-methylbutanoyl chloride and ethanol.

The reaction takes place under anhydrous conditions as 2-methylbutanoyl chloride undergoes hydrolysis in water to form 2-methylbutanoic acid.

The hydrolysis of 2-methylbutanoyl chloride occurs via a two-stage mechanism:

- The first stage (the addition stage of the reaction) involves a nucleophilic attack on the partial positive carbon atom by one of the lone pairs of electrons on the oxygen atom of a water molecule, giving intermediate **E**.



intermediate **E**

The second stage (the elimination stage) happens in two steps.

1. The carbon-oxygen double bond reforms with a chloride ion as the side product.
2. A hydrogen ion is removed by the chloride ion to give 2-methylbutanoic acid and hydrogen chloride.

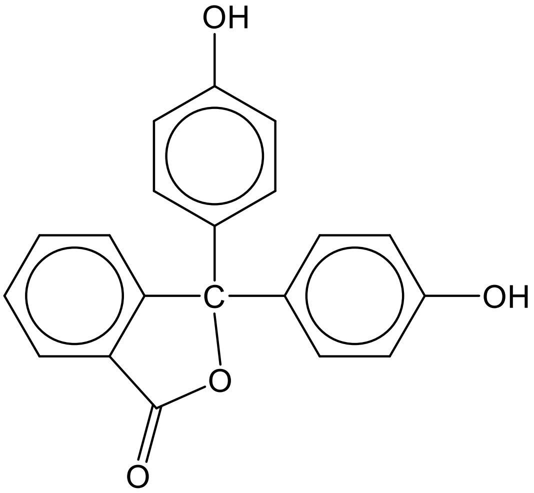
Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. **[3]**

[Total: 23 marks]

Section B

Answer **one** question from this section.

4 Phenolphthalein, a type of triarylmethane dye, is a common indicator used in acid-base titrations.



Phenolphthalein

In its uncharged form, aqueous phenolphthalein is colourless. At pH of 8.2 and above, both phenol groups are deprotonated to form a pink solution.

(a) The pK_b for trimethylamine, $(CH_3)_3N$, at 25 °C is 4.19.

(i) Trimethylamine can behave as a Lewis base. Use the reaction of trimethylamine with aluminium chloride to illustrate this behaviour, writing the equation for the reaction that occurs. **[1]**

(ii) Calculate the pH of an aqueous solution of 0.20 mol dm^{-3} trimethylamine solution. **[1]**

(iii) Calculate the pH of the resulting solution when 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution and 5 cm^3 of 0.10 mol dm^{-3} HC*l* solution are mixed. **[2]**

(iv) Calculate the pH of the resultant solution when 20 cm^3 of 0.10 mol dm^{-3} HC*l* solution is added to 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution. **[2]**

(v) Explain why phenolphthalein would not be a suitable indicator for the titration of trimethylamine with HC*l*. **[1]**

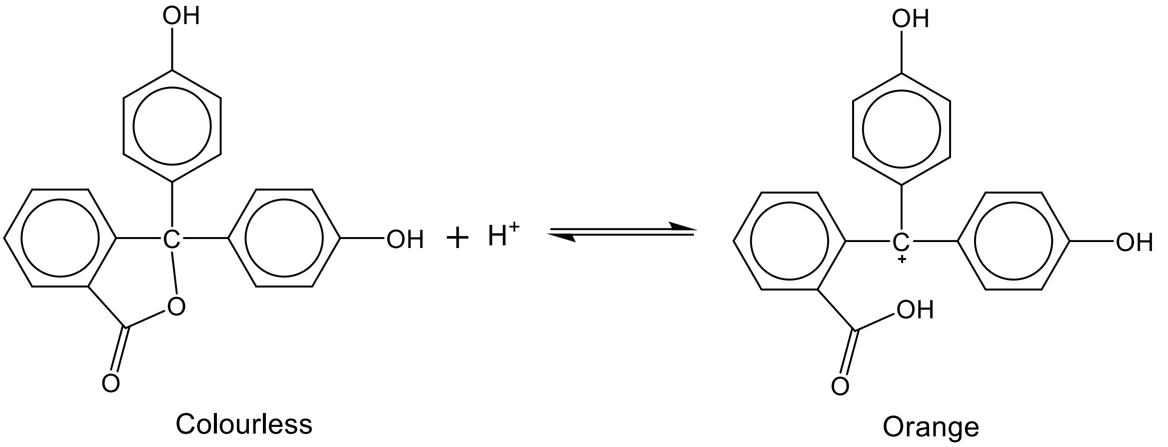
(vi) Methylamine has a pK_b of 3.36. Suggest a reason for the difference in basicity between methylamine and trimethylamine. **[1]**

(b) Draw the structural formula of the product formed when phenolphthalein reacts with each of the following reagents:

(i) excess Br_2 in the presence of $AlBr_3$. **[2]**

(ii) sodium hydroxide with heat. **[2]**

(c) Under extremely acidic conditions (pH < 0), phenolphthalein can be protonated to form an orange solution. This is an endothermic process.



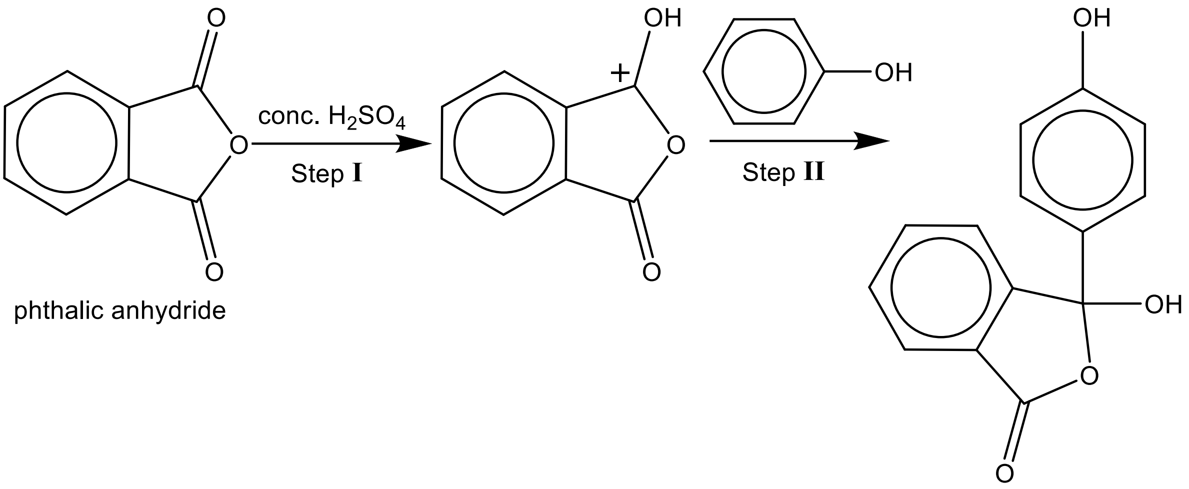
$\Delta H > 0$

Use Le Chatelier's Principle to explain the following observations.

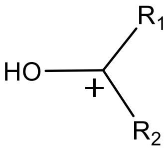
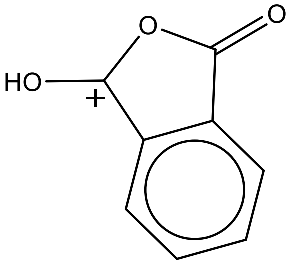
(i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. **[1]**

(ii) A solution of orange phenolphthalein solution was placed in an ice bath and turned colourless. **[1]**

(d) Part of the process in synthesising phenolphthalein involves the reaction of phthalic anhydride according to the reaction scheme below.

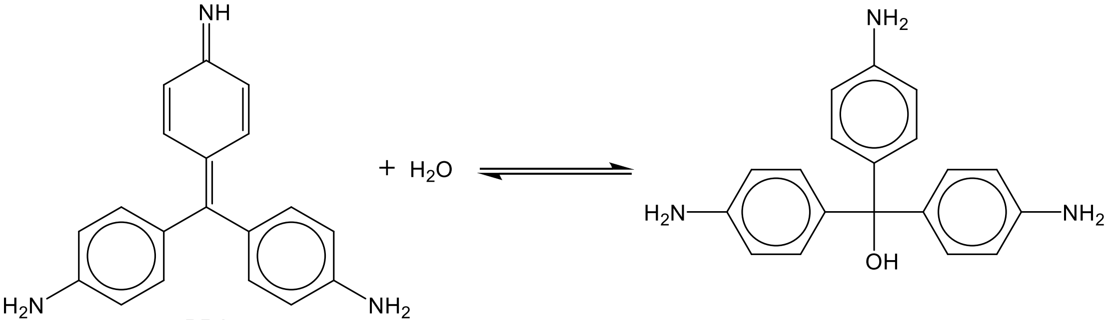


(i) Name and describe the type of mechanism in Step **II**.

You may use  to represent 

[3]

(e) Pararosaniline (PRA), another triarylmethane dye, reacts with water to form acidified pararosaniline (APRA).



0.0040 mol of PRA was dissolved in 25.0 cm^3 of water and the solution allowed to reach equilibrium. After equilibrium was reached, the concentration of APRA was found to be 0.10 mol dm^{-3}.

Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O] = 55.5$ mol dm^{-3} throughout. **[3]**

[Total: 20 marks]

5 Manganese is a highly abundant transition metal in the Earth’s crust.

(a) The atomic radii of transition elements is relatively invariant. Explain. **[2]**

(b) Manganese sulfate, $MnSO_4$, is often added to soils to promote plant growth as manganese is an important trace element crucial to photosynthesis and chloroplast formation.

Data concerning $MnSO_4$ at 298 K, are given in the table below.

Enthalpy change of formation $MnSO_4$ / kJ mol^{-1}	−1365
Enthalpy change of hydration of Mn^{2+} / kJ mol^{-1}	−1851
Enthalpy change of hydration of SO_4^{2-}/ kJ mol^{-1}	−1004
Lattice energy of $MnSO_4$ / kJ mol^{-1}	−2747

(i) Define the term *standard enthalpy change of solution*. **[1]**

(ii) Calculate the enthalpy change of solution of $MnSO_4$ at 298 K. **[1]**

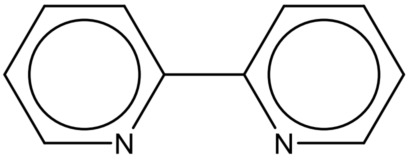
(iii) Using your answer in **(b)(ii)**, calculate the amount of heat evolved when 0.005 mol of $MnSO_4$ is dissolved in 60.0 cm^3 of water at 298 K. Hence, determine the final temperature of the solution.
(You may assume that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}) **[2]**

(c) To promote plant growth, 0.0530 mol dm^{-3} $MnSO_4$ solution is added to the soil. In addition, the pH of the soil must be carefully controlled. The pH of the soil cannot exceed 6.5, because it would cause the precipitation of solid manganese (II) hydroxide, which would prevent the plants from absorbing the necessary amount of manganese.

(i) Using the above information, calculate the K_{sp} of manganese (II) hydroxide. **[2]**

(ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. **[1]**

(d) Manganese can also form complexes. One such complex is $[Mn(C_{10}H_8N_2)_3]^{2+}$, where $C_{10}H_8N_2$ is the bipyridine molecule. Bipyridine acts as a bidentate ligand and has the structure shown below.



Bipyridine

(i) Describe and explain the features of the bipyridine molecule that enable it to act as a ***bidentate*** ligand. Hence, state the type of bond formed between the ligand and the central manganese ion. **[2]**

(ii) State the shape of the $[Mn(C_{10}H_8N_2)_3]^{2+}$ complex and draw its structure. **[2]**

(e) Compound **A** has the molecular formula $C_{10}H_{13}Cl$. It reacts with NaOH under aqueous conditions and heat to form **B**, $C_{10}H_{14}O$. **A** does not react with aqueous Br_2.

B does not react with hot acidified potassium dichromate. **B** reacts with hot acidified potassium manganate to form **C**, $C_{10}H_{12}O_3$.

In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**, $C_{10}H_8O_2$.

Deduce the structures of **A** – **D**, and explain the chemistry of the reactions described. **[7]**

[Total: 20 marks]

END OF PAPER

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **27 Aug 2019**

Paper 4 Practical **2.5 hours**

Candidates answer on the Question Paper

Additional Materials : As listed in the Confidential Instructions
: Insert

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 an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Shift
Laboratory

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 **21** and **22**.
The number of marks is given in the brackets [ ] at the end of each question or part question.

For Examiner's use:

Question	Practical	Planning	Total
Marks	44	11	55

This document consists of **22** printed pages.

1 **To standardise a 0.03 mol dm^{-3} of iron(III) chloride solution and determine the concentration of sodium thiosulfate solution.**

(a) Planning

FA1 is a standard solution containing 0.03 mol dm^{-3} of $FeCl_3$ solution.

You are to design an experiment to show how **FA1** is prepared using solid $FeCl_3$.

You are provided with :

a solid sample of approximately 1.50 g of $FeCl_3$ (M_r = 162.3),

250 cm^3 volumetric flask and

the usual laboratory apparatus

In your plan, you should include details on:

- the mass of $FeCl_3$(s) you use with justification,
- the apparatus you would use, and
- the procedures which you would follow.

Do not carry out this plan as FA1 is provided for you to continue with 1(b).

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.... [3]

1 **(b)** In addition to **FA1**, you are also provided with the following:

FA2 is 0.060 mol dm^{-3} potassium iodide, KI.

FA3 is aqueous sodium thiosulfate, $Na_2S_2O_3$.

When **FA1** is combined with **FA3**, a complex, $[Fe(S_2O_3)_2]^-$, is formed.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^-(aq)$

To 1 cm^3 of **FA3** in a test–tube, add 2–3 drops of **FA1** and shake them thoroughly. State the colour of the complex formed.

Colour : ………………………… [1]

(c) A student aimed to determine the concentration of **FA3** using volumetric analysis involving the use of **FA1** and **FA2.**

Reaction 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Using the above reactions, the student planned and carried out the following procedure.

1. Fill a 50.00 cm^3 burette with **FA3** solution.
2. Using a 10 cm^3 measuring cylinder, measure 5 cm^3 of **FA1** and place it in a 100 cm^3 conical flask.
3. Using another 10 cm^3 measuring cylinder, measure 5 cm^3 of **FA2** into the conical flask.
4. Run **FA3** from the burette into the conical flask. Near the endpoint, when the brown solution becomes pale, add 2 drops of starch.
5. Continue adding **FA3** slowly, the endpoint is reached when the solution **first becomes colourless**.
6. Record the titration results, to an appropriate level of precision, in an appropriate table and repeat the experiment once more.

1 (c) (i) Carry out the student's procedure **twice only** to obtain two titration readings. **Your titre values need not be consistent**.

> Note: After the end point is reached, you may observe the appearance of the coloured mixture again. There is no need to titrate any further.

Record your titration in an appropriate table in the space below.

[2]

(ii) Planning

A teacher commented that it is appropriate for the student to use 5 cm^3 instead of 25 cm^3 of **FA1** for this titration. Justify the teacher's comment using suitable calculations.

Assume the concentration of **FA3** is 0.006 mol dm^{-3}.

[2]

1 (c) (iii) **Planning**

Justify whether the amount of **FA2** that the student used in step **3** of the procedure in **1(c)** is sufficient to determine the concentration of **FA3**.

[1]

(iv) The student did the titration several times but could not get consistent titre values of **FA3**. Based on your observation during titration, suggest a reason why.

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(v) Suggest another reason why the results obtained are not reliable.

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1 **(c)** **(vi)** The student performed the titration and had a titration value of 18.50 cm^3. Given the errors (uncertainties) associated with each reading using a measuring cylinder and burette are ±0.1 cm^3 and ±0.05 cm^3 respectively, calculate the maximum total percentage error (uncertainty) from the apparatus in the titration.

[3]

[Total: 14 marks]

2 **To investigate the kinetics of the reaction between iron(III) ions and iodide ions**

In this experiment, you are investigating the rate of reaction between iron(III) ions and iodide ions.

You are provided with:

FA1 is 0.03 mol dm^{-3} of $FeCl_3$ solution

FA2 is 0.060 mol dm^{-3} potassium iodide, KI

FA3 is sodium thiosulfate, $Na_2S_2O_3$

The reaction is started by mixing a 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**.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^{-}(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

When all the thiosulfate have 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.

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 10.

For each of the five experiments, you will need to include the

- volume of **FA2**, $\mathbf{V_{FA2}}$,
- volume of water, $\mathbf{V_{water}}$,
- calculated squared volume of **FA2**, $(\mathbf{V_{FA2}})^2$,
- reaction time, ***t*** to nearest second, and
- calculated rate in mol dm^{-3} s^{-1}

Record all calculated values to 3 significant figures.

2 (a) Method

Experiment 1

1. Use the measuring cylinders to measure the following:
    - 20 cm^3 of **FA1**
    - 20 cm^3 of **FA3**
    - 1 cm^3 of starch indicator
2. Using another measuring cylinder, measure 10 cm^3 of **FA2**.
3. Pour the measured **FA1** and starch into a dry 100 cm^3 beaker.
4. Pour in the **FA3**, followed by **FA2** immediately into the same beaker. Start the stopwatch on adding **FA2**.
5. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
6. The mixture turns brown and then yellow before turning a blue–black colour. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
7. Record the time to the nearest second in the space on page 10.
8. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

Experiment 2

9. Repeat step **1** in **Experiment 1**.
10. Using a measuring cylinder, add 2 cm^3 of **FA2.** Make up the volume to 10 cm^3 using deionised water using another measuring cylinder.
11. Pour the measured **FA1**, starch and deionised water into a dry 100 cm^3 beaker.
12. Pour in the **FA3**, followed by **FA2** immediately into the same beaker. Start the stopwatch on adding **FA2**.
13. Stir the mixture and place the beaker on the printed page on page 2 of the insert.

14. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
15. Record the time to the nearest second in the space on page 10. The timing should not exceed 6 minutes.
16. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

Experiments 3−5

Carry out three further experiments to investigate the effect of changing the concentration of **FA2** by altering the volume of aqueous potassium iodide, **FA2**, used.

You should use a volume of **FA2** that is at least 2 cm^3 and the total volume of the reaction mixture must always be 51 cm^3.

2 (a) With reference to **1(b)**, consider the colour change observed when **FA2** was added to the solution prepared in step **6** of **Experiment 1** before the blue–black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved.

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.... [2]

2 **(b)** Show, by means of calculation, that the change in the concentration of I^-, $\Delta[I^-]$, which occurred when the blue–black colour appeared was 2.35×10^{-3} mol dm^{-3}.

Assume the concentration of $Na_2S_2O_3$ to be 0.006 mol dm^{-3}.

[1]

(c) **Results**

The rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{\Delta[\,I^-]}{\text{reaction time}}$$

Calculate the rate of reaction for each experiment and complete your table.

[4]

2 (d) (i) Plot a graph of rate on the y–axis against $(V_{FA2})^2$ on the x–axis on the grid in **Figure 2.1**. Draw the best fit line taking account of all the plotted data points.

Figure 2.1

[4]

2 **(d)** **(ii)** Explain why the volume of **FA2** in each experiment can be used as the [I⁻].

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(iii) Deduce the order of reaction with respect to [I⁻]. Use evidence from your graph to support your deduction.

Order of reaction with respect to [I⁻] : ………… [1]

(e) **(i)** Use your graph and the formula in **2(c)** to calculate the time that the reaction would have taken if 5.0 cm^3 of **FA2** had been used. Show your working clearly.

time = ... [2]

2 **(e)** **(ii)** Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions in the reaction mixture if 5.0 cm^3 of **FA2** had been used.

initial $[Fe^{3+}]$ = ...

initial $[I^-]$ = ... [1]

(iii) Given that the reaction is first order with respect to $[Fe^{3+}]$, calculate the rate constant.

rate constant = ... [2]

(f) At the end of Experiment **1**, a student washed the beaker and used it immediately for Experiment **2**. State and explain how the student's action would affect the time ***t*** for Experiment **2**.

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.... [2]

2 **(g)** List 1 possible source of experimental errors and suggest the corresponding improvement to reduce the experimental error.

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[Total: 22 marks]

3 Qualitative Analysis

You are provided the following reagents and the *Qualitative Analysis Notes* on page 21 and 22.

FA1 is 0.03 mol dm^{-3} of $FeCl_3$ solution

FA4 is 6% volume H_2O_2

FA5 is 0.00215 mol dm^{-3} of **X**$^-$ solution

(a) You are to perform the tests described in **Table 3.1** and record your observations in the same table.

Your answers should include

- details of colour changes throughout the tests 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 3.1

Test	Observations
i. To 5 cm^3 of **FA1**, add aqueous silver nitrate in excess. Filter the mixture. Separate the filtrate into three test tubes for **(ii)**, **(iii)** and **(iv)**. Place the filter funnel containing the residue on a new test tube, add aqueous ammonia over the residue. Add HNO_3 dropwise to the filtrate until no more change.	

	Test	Observations
ii.	To a new test tube containing 1 cm^3 of **FA4**, add a few drops of filtrate from the first test tube from **(i)**. Wait and observe the effervescence. Test for the identity of the gas.	
iii.	To the second test tube containing 1 cm^3 of filtrate from **(i)**, add aqueous sodium hydroxide till excess. Add 1 cm^3 of **FA4**.	
iv.	To the last test tube containing 1 cm^3 of filtrate from **(i)**, add 1 cm^3 of **FA5**.	
v.	To a new test tube containing a fresh sample of **FA1**, test the pH of the solution with a Universal Indicator paper. Add aqueous ammonia dropwise. Add **FA1** dropwise to dissolve the precipitate formed. Stop adding **FA1** once the precipitate disappears.	

[6]

3 **(b)** With reference to the observation made in test **(i),** identify the ppt and explain its solubility in aqueous ammonia.

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(c) In the presence of strong base,

$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$

Electrode Reaction	$E^\ominus$/V
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2$	–0.56
$O_2 + 2H_2O + 2e \rightleftharpoons H_2O_2$	+0.68
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.23
$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^-$	–0.08

With reference to the electrode potential given, explain the difference in the observation for effervescence made when **FA4** is added in test **(ii)** and **(iii)**.

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(d) Write an equation to explain the colour of the Universal Indicator paper on addition of **FA1** before adding aqueous ammonia.

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3 **(e)** The pH of the resultant solution in test **(v)** is 7. Explain the chemistry behind the changes of pH in test **(v)** when aqueous ammonia is added dropwise followed by **FA1**.

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(f) Predict what happen when the resultant solution in test **(v)** is added to phenol.

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3 (g) Planning

Thermometry is sometimes used to determine the number of ligands attached to the central metal atom or ion. One of such monodentate ligand is X^- present in **FA5**.

A student performed an experiment to determine the structural formula of the hexa–coordinated complex.

$$[Fe(H_2O)_6]^{3+} + nX^- \rightarrow [Fe(H_2O)_{6-n}X_n]^{3-n} + nH_2O \qquad \Delta H < 0$$

He used varying volumes of **FA1** and **FA5** only, while keeping the total volume of the mixture at 80 cm^3. He recorded the change in temperature.

(i) Outline how you would:

- determine the effect of changing the volumes of **FA1** and **FA5** on the temperature change of the experiment and hence,
- vary the volumes of **FA1** and **FA5** to form the needed hexa–coordinated complex, $[Fe(H_2O)_{6-n}X_n]^{3-n}$.

You are provided with the same solutions, which were used in **3(a)** described. **There is no need to perform the experiment.**

No details regarding the use of specific apparatus are required.

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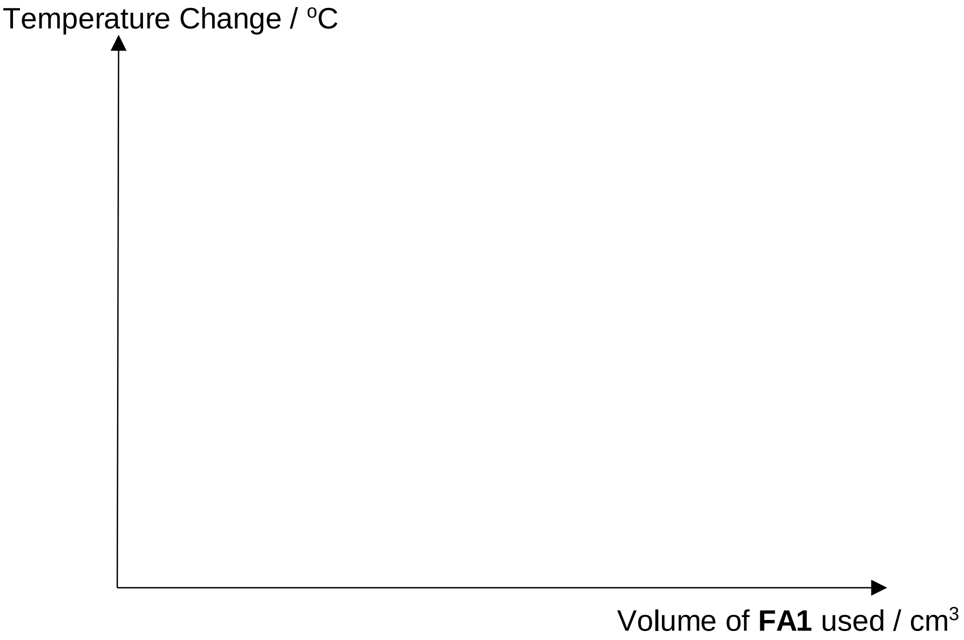
(ii) The student plotted a graph and concluded that n=1 in the structural formula of $[Fe(H_2O)_{6-n}X_n]^{3-n}$. On the axes of **Figure 3.1**, sketch a graph that the student would obtain from your experiment in **3(g)(i)** to draw this conclusion. Indicate the volume of **FA1** that the student would use to reach this conclusion on the x-axis of the graph.

Figure 3.1



[2]

[Total: 19 marks]

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

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 Preliminary Examination

H2 Chemistry (9729) **19 Sep 2019**

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 (including this page).

1 Which statement about one mole of sodium metal is always true?

A It has the same mass as one mole of ^{12}C.

B It has the same number of atoms as 18 g of water.

C It has the same number of atoms as $\frac{1}{12}$ mole of ^{12}C.

D It has the same number of atoms as 12 dm^3 of fluorine gas at r.t.p.

Ans: D
12/24 = 0.5 mol of F_2 = 1.0 mol of F atoms = 6.02×10^{23} H atoms

2 0.84 g of an oxide **M**O of a metal **M** was dissolved in excess sulfuric acid. 25.0 cm^3 of 0.12 mol dm^{-3} potassium manganate(VII) solution was required to oxidise $\mathbf{M}^{2+}$ to $\mathbf{M}^{3+}$.

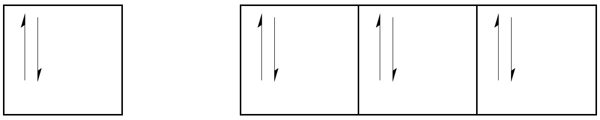
What is the relative atomic mass of **M**?

A 36.0 **B** 40.0 **C** 52.0 **D** 56.0

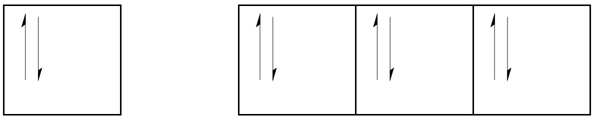
Ans: B
Amt of MnO_4^- = 25/1000 x 0.12 = 0.003 mol
Amt of e gained by MnO_4^- = Amt of e lost by M^{2+} = 5 x 0.003 = 0.015 mol
M_r of MO = 0.84/0.015 = 56
A_r of M = 56-16 = 40

3 **X** and **Y** are elements found in the first three periods of the Periodic Table. The outermost shell electronic configurations of two species are given as follows:

$\mathbf{X}^{2-}$:



$\mathbf{Y}^{2+}$:



What can best be deduced from the above information?

A **X** has a larger proton number than **Y**.

B **X** has more unpaired electrons than **Y** at the ground state.

C **X** exists as a gas while **Y** is a solid at standard condition.

D $\mathbf{X}^{2-}$ and $\mathbf{Y}^{2+}$ are isoelectronic.

Ans: B
Since **X** and **Y** are elements in the first three periods and their valence electronic configurations consist of s and p subshells, there are likely to be in period 2 or period 3.

X has the valence shell electronic configuration ns^2 np^4 so it is a Group 16 element and it can be in Period 2 or Period 3. **X** can be O or S.
Y has the valence shell electronic configuration of $(n+1)s^2$ and it should be in Period 3. **Y** can be Mg.

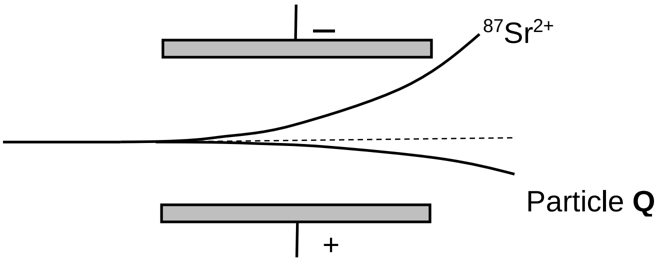
Option A: Since **Y** is Mg, X can have a smaller or larger proton than **Y**, depending on whether X is O or S

Option B: **X** would have 2 unpaired electrons while **Y** has no unpaired electrons.

Option C: **X** can be oxygen which is a gas but it may also be sulfur which is a solid at standard condition.

Option D: If **X** is S, S^{2-} is not isoelectronic with Mg^{2+}.

4 In an experiment, a sample of gaseous $^{87}Sr^{2+}$ was passed through an electric field. The angle of deflection for $^{87}Sr^{2+}$ was observed to be 2°.



The experiment was repeated with gaseous sample of particle **Q**.

Which of following could be **Q**?

A $^{74}As^{3-}$ **B** $^{19}F^{-}$ **C** $^{79}Se^{2-}$ **D** $^{127}Te^{2-}$

Ans: D

Angle of deflection = k(charge/mass)

k = 2 x 87/2 = 87

Angle of deflection of $^{74}As^{3-}$ = 87(3/74) = 3.5°

Angle of deflection of $^{19}F^{-}$ = 87(1/19) = 4.6°

Angle of deflection of Se^{-} = 87(2/79) = 2.2°

Angle of deflection of Te^{2-} = 87(2/127) = 1.4°

5 $BeCl_2$ reacts with CH_3NH_2 to form compound **Z** (M_r = 142.0).

Which of the following statements are correct?

1 The hybridisation state of N in **Z** is sp^3.

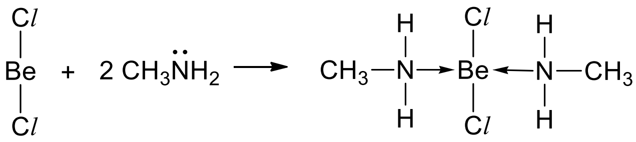
2 Hydrogen bonds exist between molecules of compound **Z**.

3 1 mol of compound **Z** is formed from 1 mol of $BeCl_2$ and 2 mol of CH_3NH_2.

A 1, 2 and 3 **B** 1 and 2 only

C 1 and 3 only **D** 3 only

Ans: C



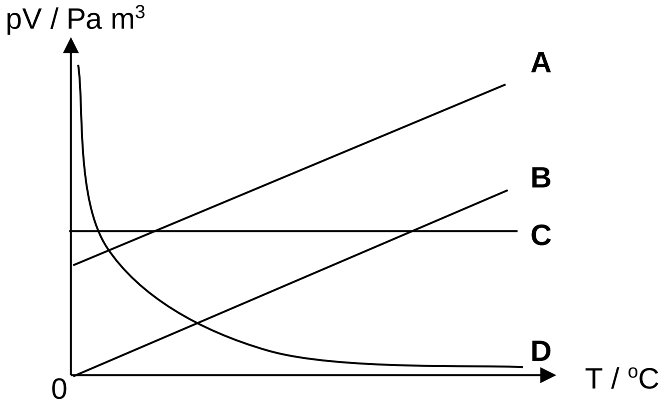
$$BeCl_2 + 2\,CH_3\ddot{N}H_2 \longrightarrow CH_3\text{—}NH_2\rightarrow BeCl_2\leftarrow NH_2\text{—}CH_3$$

Option 1 is correct as N has a sp^3 hybridisation state and hence tetrahedral shape around N in compound **Z.**

Option 2 is wrong since there is no lone pair on the N after bonded to Be, hence between the molecules, H-bond no longer exist.

Option 3 is correct as Be in $BeCl_2$ has only 4 electrons and it can accommodate another 4 electrons to react octet configuration.

6 Which of the following graphs correctly describes the variation of pV with temperature for a fixed amount of an ideal gas?



Ans: A

pV = nRT. For an ideal gas, pV α T, hence straight line.

But since the scale is in °C, pV = 0 only when T = -273 °C.

7 The conversion of graphite into diamond is an endothermic reaction.

$$C(graphite) \longrightarrow C(diamond)$$

Which of the following statements are correct?

1 The carbon-carbon bonds in graphite are stronger than that in diamond.

2 The activation energy of the conversion of graphite to diamond is larger than that of the reverse reaction.

3 The enthalpy change of atomisation of diamond is less endothermic than that of graphite.

4 The enthalpy change of combustion of diamond is less exothermic than that of graphite.

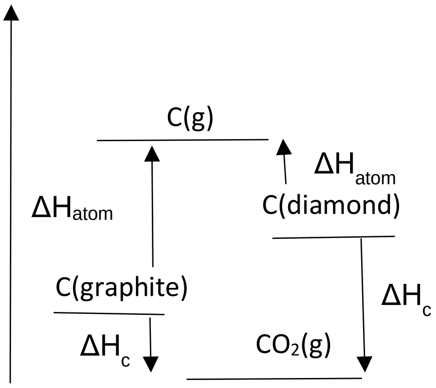
A 1 and 2 only **B** 1 and 3 only

C 1, 2 and 3 only **D** 1, 2 and 4 only

Ans: C

Option 1 is correct. Since ΔH > 0, C-C bond energy in graphite is higher than the C-C bond energy in diamond.

Option 2 is correct. Since ΔH > 0, the E_a of forward reaction is larger than that of backward reaction.



Option 3 is correct. ΔH_{atom} of diamond is less endothermic than that of graphite

Option 4 is incorrect: ΔH_c of diamond is more exothermic than that of graphite

8 Given the following enthalpy changes:

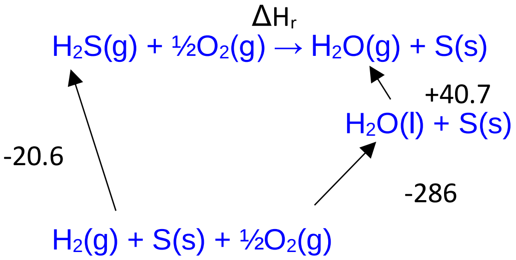
	ΔH / kJ mol^{-1}
Enthalpy change of formation of $H_2S(g)$	–20.6
Enthalpy change of formation of $H_2O(l)$	–286.0
Enthalpy change of vaporisation of $H_2O(l)$	+40.7

What is the enthalpy change (in kJ mol^{-1}) of reaction for the following reaction?

$$H_2S(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) + S(s)$$

A –224.7 **B** –265.4 **C** –306.6 **D** -347.3

Ans: A



ΔH_r = –286 + 40.7 + 20.6 = –224.7

9 Which equation corresponds to the enthalpy change stated?

A $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ $\Delta H^{\theta}_{neutralisation}$

B $Na^{+}(s) + aq \rightarrow Na^{+}(aq)$ $\Delta H^{\theta}_{hydration}(Na^{+})$

C $Al_2O_3(s) \rightarrow 2Al^{3+}(g) + 3O^{2-}(g)$ $\Delta H^{\theta}_{lattice\ energy}(Al_2O_3)$

D $O_2(g) \rightarrow 2O(g)$ $2\Delta H^{\theta}_{atomisation}(O_2)$

Ans: D

Option A: $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ $2\Delta H^{\theta}_{neutralisation}$

Option B: $Na^{+}(g) + aq \rightarrow Na^{+}(aq)$ $\Delta H^{\theta}_{hydration}(Na^{+})$

Option C: $2Al^{3+}(g) + 3O^{2-}(g) \rightarrow$ $Al_2O_3(s)$ $\Delta H^{\theta}_{lattice\ energy}(Al_2O_3)$

10 A chemical plant illegally dumped some radioactive waste in a landfill. This waste composed of two radioactive isotopes **X** and **Y**. The half-life of **X** is 4 days whereas that of **Y** is 2 days. The authorities found out about this illegal dumping only when the waste had been in the landfill for 8 days. They did an immediate analysis on a sample of the waste and found equal amounts of **X** and **Y**.

Considering that the decay of radioactive isotopes follows first-order kinetics, what is the initial molar ratio of **X** to **Y** if the waste had been in the landfill for 4 days?

	X	:	**Y**
A	1	:	2
B	1	:	4
C	2	:	1
D	4	:	1

Ans: A

Day	0	1	2	3	**4**	5	6	7	8
X	4x				**2x**				x
Y	16x		8x		**4x**		2x		x

X:Y = 2x: 4x = 1x : 2x =1:2

11 Hydrogen reacts with nitrogen monoxide to form nitrogen and steam only. The rate equation for this reaction is rate = $k[NO]^2[H_2]$.

Which could be the mechanism for this reaction?

A

$NO + 2H_2 \xrightarrow{slow} NH_2 + H_2O$

$NH_2 + NO \rightarrow N_2 + H_2O$

B

$2NO \xrightarrow{\text{slow}} N_2 + O$

$2H_2 + O \rightarrow 2H_2O$

C

$2NO + H_2 \xrightarrow{\text{slow}} N_2 + H_2O_2$

$N_2 + 2H_2 \rightarrow N_2H_4$

D

$2NO + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$

$N_2O + H_2 \rightarrow N_2 + H_2O$

Ans: D

$2NO + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$

$N_2O + H_2 \rightarrow N_2 + H_2O$

Overall: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

Rate: $k\,[NO]^2[H_2]$

Option A is wrong since Rate = $k\,[NO][H_2]^2$

Option B is wrong since rate= $k[NO]^2$

Option C is wrong since the products formed are N_2H_4 and H_2O_2 instead.

12 The table below shows the values of the ionic product of water, K_w, at two different temperatures.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
60	1.00×10^{-13}

Which of the following statements is correct for pure water?

A The ionic dissociation of water is an exothermic process.

B At 60 °C, the pH is less than 7.

C At 60 °C, the pH is more than the pOH.

D At 60 °C, the solution becomes more acidic.

Ans: B

As K_w increases with increasing temperature, the rate constant of forward reaction increases more than the rate constant of the backward reaction, hence the forward reaction is endothermic and not exothermic. Option A is wrong.

pK_w at 60°C = $-\log K_w = 13$
Hence, pH + pOH = 13, hence pH = 6.5
Option B is correct.

13 The numerical value of the equilibrium constant, K_c, for the following reaction at 25°C is 1.2×10^5.

$$CO\,(g) + 2H_2(g) \rightleftharpoons CH_3OH\,(g) \qquad \Delta H^\ominus < 0$$

Which statements about the reaction is correct?

1 The units for K_c is $mol^{-1}dm^3$.

2 $\Delta G^\ominus$ is less than zero.

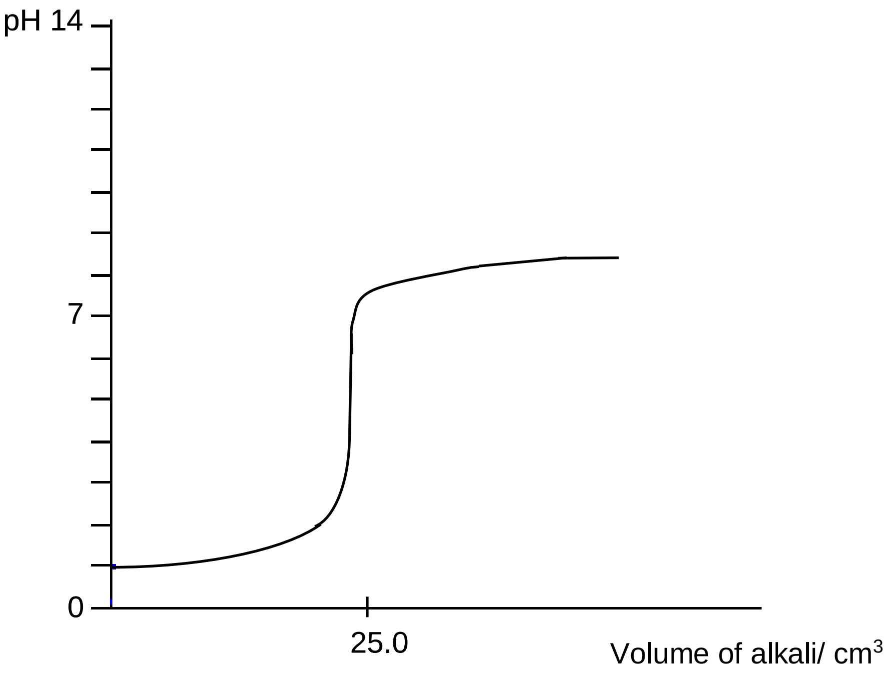
3 The equilibrium position shifts when an inert gas is added at constant volume.

A 1 and 3 only **B** 2 only

C 2 and 3 only **D** 1, 2 and 3

Ans: B
Option 1 is wrong since the units is $mol^{-2}dm^6$.
Option 2 is correct. $K_c >> 1$, hence $\Delta G^\ominus < 0$ (Correct)
Or $\Delta G^\ominus = -RT\ln K = -(8.31)(298)\ln(1.2X10^5) = -29$ kJ mol^{-1}.
Option 3 is wrong. At constant volume, the addition of an inert gas DOES NOT AFFECT the partial pressure of the reacting gases, even though the total pressure increases. Hence there is NO shift of the equilibrium position.

14 The graph shows the change in pH when an alkali is gradually added to 25 cm^3 of an acid.



Which of the following statements about the titration is correct?

A Acidic buffer is formed after the equivalence point.

B Both phenolphthalein and methyl orange can be used as the indicator for this titration.

C This is a titration between 0.10 mol dm^{-3} of HC*l*(aq) and 0.10 mol dm^{-3} of NH_3(aq).

D The maximum buffer capacity occurs when 12.5 cm^3 of alkali is added.

Ans: C

Option A: Basic buffer occurs after the equivalence point.

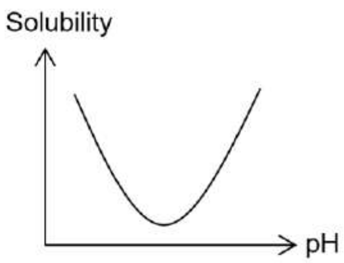
Option B: Only methyl orange is suitable for a strong acid- weak base titration.

Option C: Strong acid-weak base titration leads to an acidic salt.
pH of equivalence point is less than 7. (Correct)

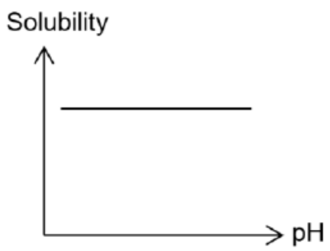
Option D: Since this is a SA-WB titration, MBC occurs at 2V$_{\text{equilvalence}}$ instead of ½V$_{\text{equivalence}}$.

15 CaF_2 is a sparingly soluble salt and is added to a weakly acidic solution of HF. The pH of the solution is adjusted by adding NaOH. Which diagram shows how the solubility of CaF_2 will vary with the pH of the solution at constant temperature?

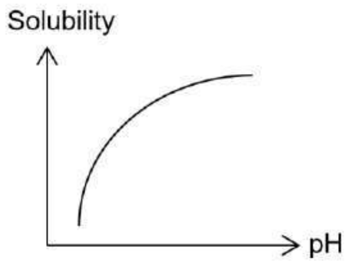
A



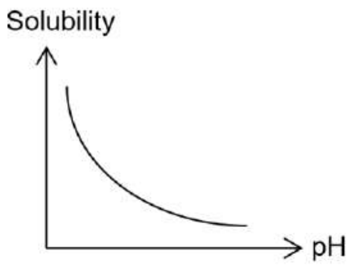
B



C



D



Ans: D
CaF_2 (s) $\rightleftharpoons$ Ca^{2+} (aq) + $2F^-$(aq) ----Eqm 1
HF (aq) $\rightleftharpoons$ H^+ (aq) + F^-(aq) ---- Eqm 2
When pH is very high, the H^+ is neutralised by the OH^-, hence eqm 2 is shifted to RHS to produced more F^-. This will cause the POE of Eqm 1 to shift to LHS, reducing the solubility of CaF_2 (s).

16 Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?

A Ammonium ethanoate is completely ionised in aqueous solution.

B Ammonium ethanoate is strongly acidic in aqueous solution.

C Ammonia is a stronger base than water.

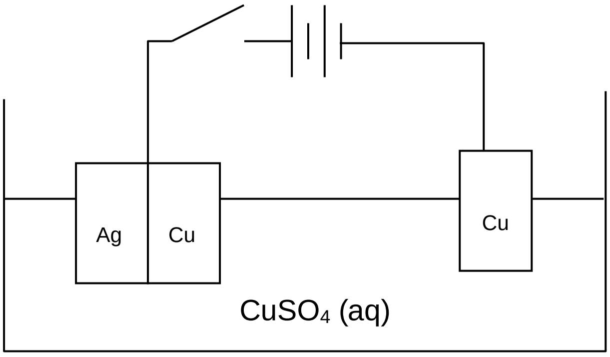
D Liquid ammonia is more polar solvent than water.

Ans: C

A more basic solvent is able to extract the H^+ more readily and therefore increase the strength of the acid.

17 Use of *Data Booklet* is relevant to this question.

The following circuit with a switch was set up as shown in the diagram:



Which electrode reactions will occur when the switch is closed?

	Anode reaction	Cathode reaction
A	Silver dissolves preferentially	Hydrogen is evolved
B	Copper dissolves preferentially	Copper is precipitated
C	Silver dissolves preferentially	Copper is precipitated
D	Silver and copper both dissolve together	Hydrogen is evolved

Ans : B

Cu has a more negative $E^\ominus$ value than Ag would oxidise preferentially to form Cu^{2+};

Cu^{2+} has a more positive $E^\ominus$ value than H_2O, would be preferentially reduced to form Cu.

18 Some relevant redox half-equations are given below:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\ominus = +1.33\ V$$
$$S + 2H^+ + 2e^- \rightleftharpoons H_2S \qquad E^\ominus = +0.14\ V$$

Which of the following statements are true when hydrogen sulfide is bubbled into acidified aqueous sodium dichromate(VI)?

1 The solution turns orange to green.

2 White precipitate is observed.

3 The reaction has a positive entropy change.

A 1 only **B** 1 and 2 only

C 1, 2 and 3 **D** None of the statements are true

Ans: A

$E^{\ominus}_{cell}$ = +1.33 – (+0.14) = +1.19 V

Since $E^{\ominus}_{cell} > 0$ V, the reaction between acidified aqueous sodium dichromate(VI) and hydrogen sulfide is thermodynamically feasible.

Option 1 is correct

Option 2 is wrong since S appears as yellow solid.

Option 3 is wrong since there is a decrease in number of gas molecules and hence entropy change should be negative.

19 Elements **X**, **Y** and **Z** are in Period 3 of the Periodic Table.

- The oxide of **X** gives an aqueous solution of pH less than pH 7.
- The oxide of **Y** reacts with both strong acids and strong alkalis.
- The oxide of **Z** gives an aqueous solution which is strongly alkaline.

What is the order of increasing atomic radius for these elements?

A **X** < **Y** < **Z**

B **X** < **Z** < **Y**

C **Y** < **Z** < **X**

D **Z** < **Y** < **X**

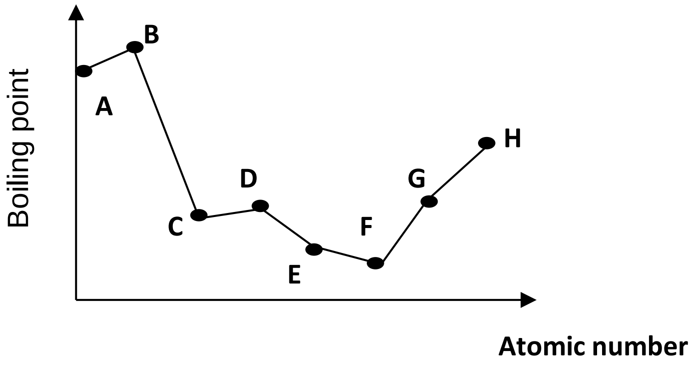
Ans: A

X could be phosphorus(0.110)/sulfur(0.104)

Y is aluminum (0.143nm)

Z is sodium (0.186 nm)

20 The graph below shows the variation in the boiling points for eight consecutive elements in the Periodic Table, all with atomic number between 10 and 20.



Which of the following statements is correct?

A Element **G** does not conduct electricity.

B Element **D** forms only one acidic oxide.

C Element **A** and beryllium are in the same group

D Element **C** forms a chloride which hydrolyse readily to give a strongly acidic solution.

Ans : D

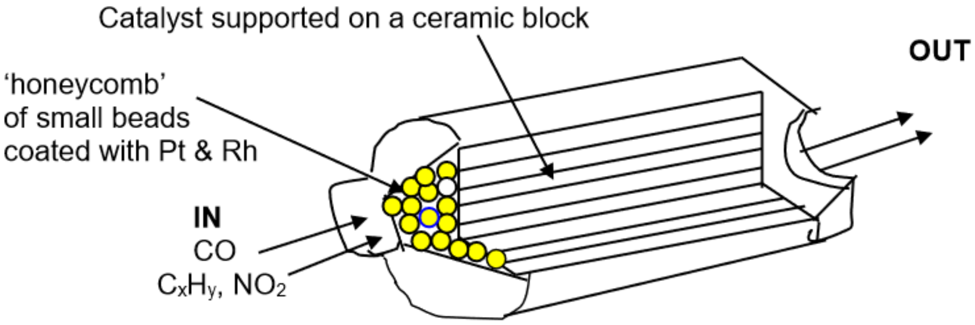
Option A: Element G is potassium, it can conduct electricity.

Option B: Element D is sulfur, it forms more than one acidic oxide (SO_2, SO_3).

Option C: Element A is aluminium, it is in Group 13.

Option D: Element C is phosphorus, its chloride hydrolyse completely to give HCl and H_3PO_4.

21 A catalytic converter is part of the exhaust system in modern cars.



Which of the following statements are true concerning the reactions and processes in the catalytic converter?

1 $CO_2 + NO \rightarrow CO + NO_2$

2 $2CO + 2NO \rightarrow 2CO_2 + N_2$

3 $C_xH_y + (2x + \frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x + \frac{y}{4})N_2$

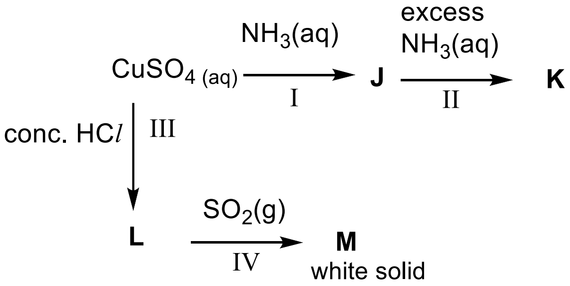
4 Platinum and rhodium catalyse the reactions

A	1, 2, 3 and 4	**B**	1 and 2 only
C	2 and 3 only	**D**	2, 3 and 4 only

Ans: D

Option 1 is wrong as CO and NO_2 are pollutants.

22 Copper(II) sulfate solution reacted as shown in the scheme below.



Which of the following statements are correct?

1 NH_3 functions as a ligand in reaction I.

2 The coordination number of complex **L** is 4.

3 The oxidation number of Cu in **M** is +1.

A 1, 2 and 3 **B** 1 and 2 only

C 1 and 3 **D** 2 and 3 only

Ans: D

Option 1 is incorrect as NH_3 acts as a base.

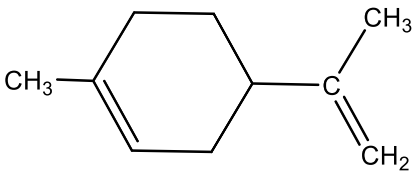
Option 2 is correct as metal complex in **L** $[CuCl_4]^{2-}$,coordination number 4.

Option 3 is correct.

$2[CuCl_4]^{2-} + SO_2 + H_2O \rightarrow CuCl(s) + 6Cl^- + SO_4^{2-} + 4H^+$

White solid is CuCl.

23 Limonene is an oil formed in the peel of citrus fruits.

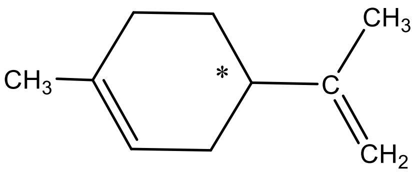


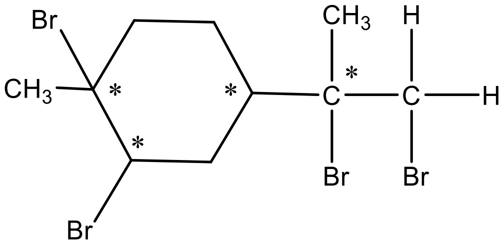
Limonene

When limonene reacts with excess bromine at room temperature in the dark, how many **more** chiral centers than limonene does the product molecule have?

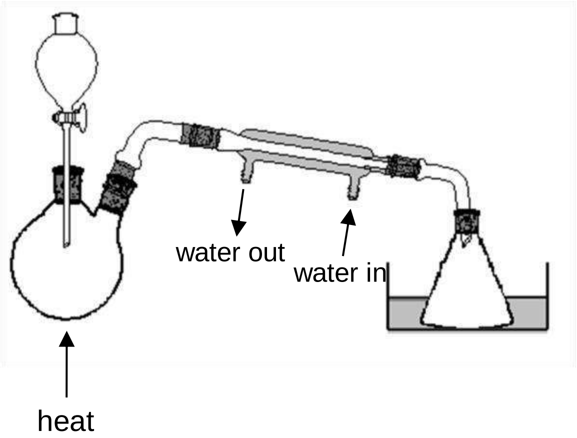
A 2 **B** 3 **C** 4 **D** 5

Ans: B





24 The diagram below shows some laboratory apparatus.



Which preparations could this apparatus be used for?

A 1,2-dibromoethane from ethene and bromine

B ethanal from ethanol, sodium dichromate(VI) and sulfuric acid

C propanone from propan-1-ol, sodium manganate(VII) and sulfuric acid

D butan-2-ol from butanone, lithium aluminum hydride in dry ether

Ans : B

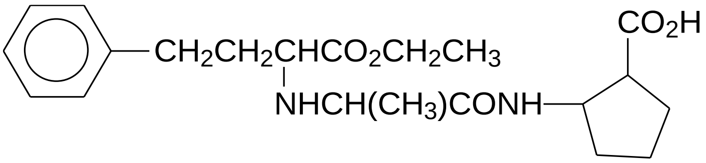
Option A is wrong since ethene is a gas, could not be prepared by heating under reflux.

Option B is correct ethanal could be prepared by heating under reflux with ethanol followed by distillation of ethanal which has a lower boiling point than ethanol.

Option C is wrong since propanone should be prepared from propan-2-ol instead of propan-1-ol,

Option D is wrong since butan-2-ol has a higher boiling point than butanone and would not be distill out first.

25 A prodrug is a molecule that can be converted into its active form in the body. An example is *Enalapril*, as shown below. The active form of *Enalapril* can be formed when enzymes in the body hydrolyse the esters found on the molecule.



Enalapril

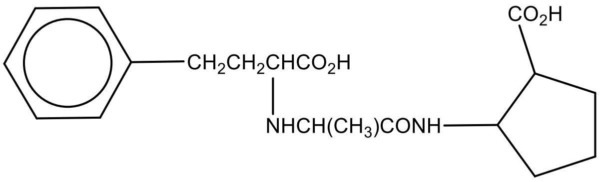
Which of the following is **not** true about *Enalapril*?

A *Enalapril* turns orange aqueous $K_2Cr_2O_7$ green when heated in an acidic medium.

B *Enalapril* does not react with 2,4–dinitrophenylhydrazine.

C *Enalapril* reacts with two moles ethanoyl chloride.

D The active form of *Enalapril* has the structure



Ans: C

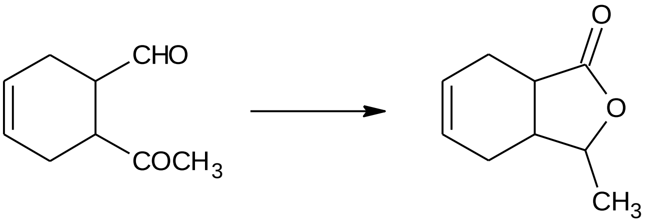
Option A: The ester in Enalapril can be hydrolysed when heated with acid and ethanol formed will be oxidised to ethanoic acid by $K_2Cr_2O_7$

Option B: No carbonyl group present.

Option C: There is only one amine group present hence it requires only 1 mol of ethanoyl chloride to react with to form amide.

Option D: The active form of *Enalapril* can be formed when enzymes in the body hydrolyse esters to form the above structure.

26 Compound **V** can be converted to compound **W** in three stages.



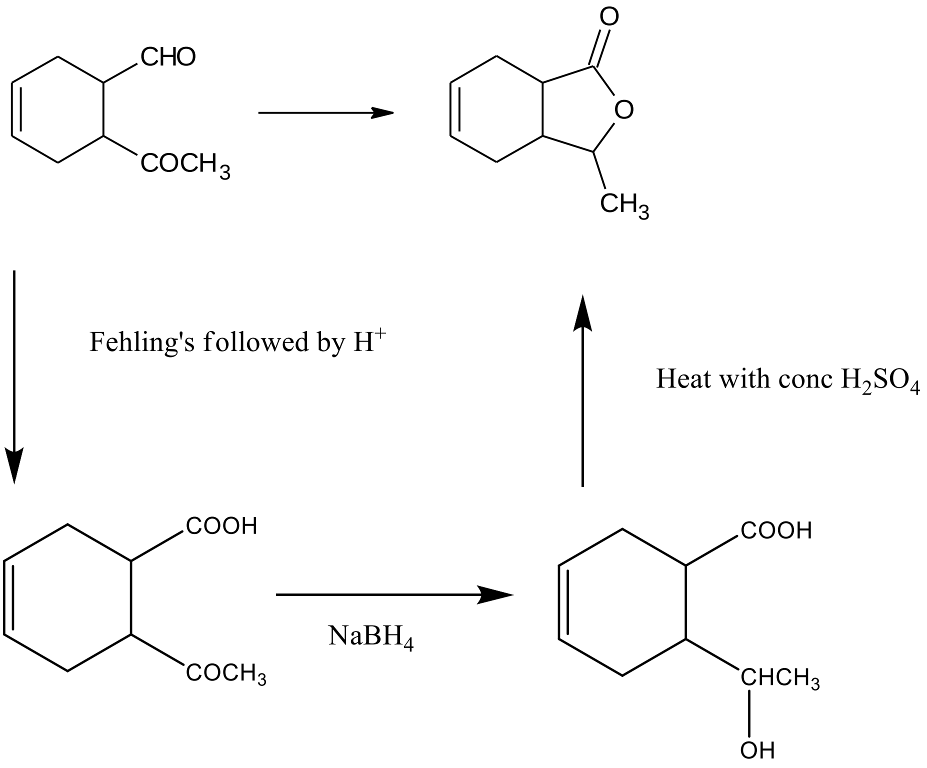
Compound **V** Compound **W**

Which sequence of reagents and conditions can be used to carry out this conversion?

	Stage 1	**Stage 2**	**Stage 3**
A	hot acidified $KMnO_4$	H_2 with Pt catalyst	heat with dilute H_2SO_4
B	hot acidified $K_2Cr_2O_7$	$NaBH_4$ in ethanol	heat with dilute H_2SO_4

C	hot Fehling’s reagent, followed by acidification	NaBH$_4$ in ethanol	heat with a few drops of conc. H_2SO_4
D	hot Tollens’ reagent, followed by acidification	LiA/H$_4$ in dry ether	heat with a few drops of conc. H_2SO_4

Ans: C

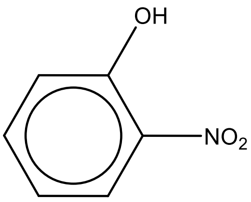


Note that KMnO$_4$ cannot be used in stage as it will oxidise alkene. LiA/H$_4$ will reduce carboxylic acid as well hence it cannot be used in stage 2. H_2SO_4 must be in conc form for the ester to form.

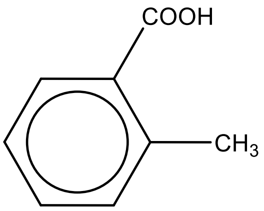
27 Phenol has a pK_a of 10.0.

Which one of the following has a higher pK_a value than phenol?

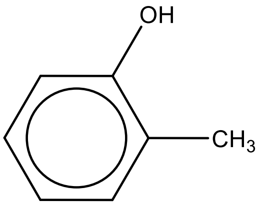
A



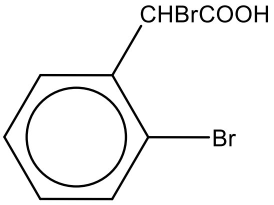
B



C



D

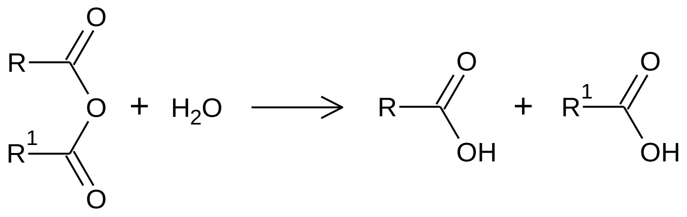


Ans: C

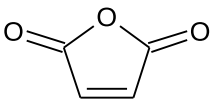
Higher pK_a implies less acidic than phenol and C is has an electron-donating $-CH_3$ group and hence the negative charge on O of the phenoxide conjugate base would be dispersed to a lesser extent.

The conjugate base is less stable, hence compound C is less acidic than phenol.

28 An acid anhydride is a carboxylic acid derivative that undergoes hydrolysis in water similar to acyl chlorides and esters. A mixture of carboxylic acids is produced in the case of the anhydride.



Based on the information above, which of the following can be deduced when maleic anhydride undergoes hydrolysis in the presence of water labelled with the ^{18}O isotope?



maleic anhydride

A The resulting product is non-planar.

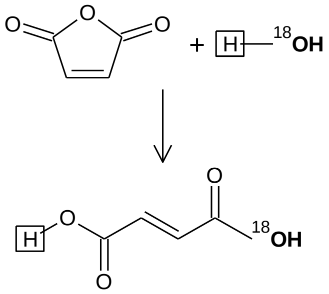
B The product is labelled with the ^{18}O isotope.

C Two carboxylic acid molecules are produced for every molecule of maleic anhydride.

D The reaction is faster than when maleic anhydride undergoes hydrolysis in the presence of water labelled with the ^{16}O isotope.

Ans: B

Option B: One ^{18}O atom from heavy water is inserted into every product molecule of maleic anhydride hydrolysis.



Option C is wrong since a single dicarboxylic acid molecule is produced for every molecule of maleic anhydride hydrolysed.

Option A is wrong as the resulting product is planar since the C are all sp^2 hybridised.

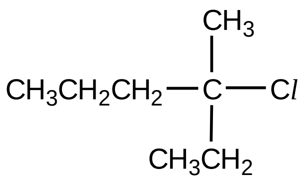
Option D: not enough information is given to deduce that.

29 Which of the following reactions will **not** form a racemic mixture of products?

A CH_3COCH_3 with HCN in trace amounts of NaOH

B $CH_3CH_2CH_2COCH_3$ with HCN in trace amounts of NaCN

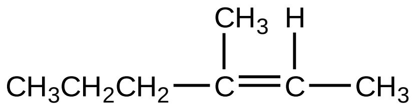
C



$CH_3CH_2CH_2-C(CH_3)(CH_2CH_3)-Cl$

with KOH(aq), heat under reflux

D



$CH_3CH_2CH_2-C(CH_3)=C(H)-CH_3$

with HBr(g)

Ans: A

Option A: Product formed does not have chiral carbon.

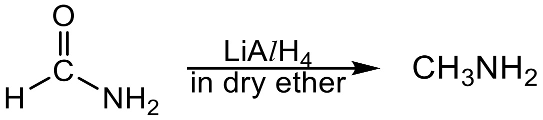
Option B: Nucleophile can attack the trigonal planar carbonyl carbon from either side.

Option C: S_N1 reaction so a trigonal planar intermediate formed as it is a 3° alkyl halide

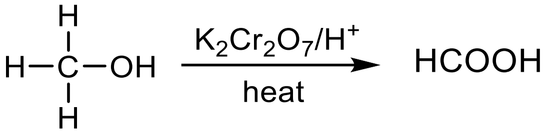
Option D: Carbocation intermediate is trigonal planar so Br^- can attack from the top or front

30 In which reaction will the oxidation number of carbon change by 4?

1



2



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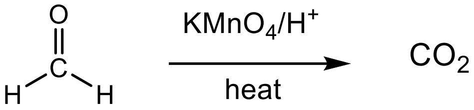
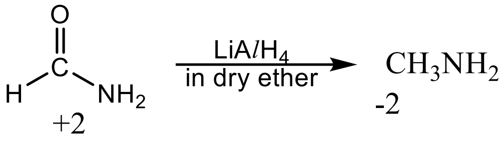
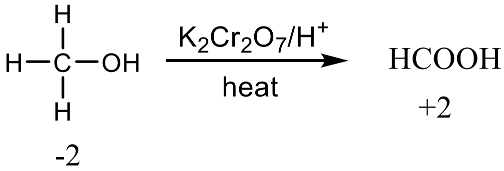


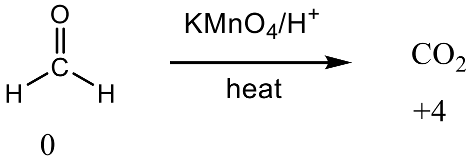
A 1, 2 and 3 **B** 2 only

C 1 and 3 only **D** 1 only

Ans: A







End of Paper

Prelims Paper 2 Answers

1. **(a)** **P**, **Q**, **R and S** are consecutive elements in Period 4.

The table below shows the first four ionisation energies (in kJ mol^{-1}) of the elements.

Element	**1st I.E.**	**2nd I.E.**	**3rd I.E.**	**4th I.E.**	**5th I.E.**
P	908	1730	3828	5980	7970
Q	577	1980	2960	6190	8284
R	762	1540	3300	4390	9020
S	947	1798	2735	4837	6043

(i) Explain why the second ionisation energy of **Q** is higher than that of **R**. **[2]**

Q is in group 13, there is a great jump in IE from 3rd IE to 4th IE

Q: $4s^2 4p^1$ Q$^+$: $4s^2$

R: $4s^2 4p^2$ R$^+$: $4s^2 4p^1$

Q: the second electron is removed from the **4s** orbital, whereas for R, the second electron is removed from the **4p** orbital. The **4p** orbital is **further** away from the nucleus than the 4s and **experiences additional shielding effect** by the two 4s electrons. These factors **outweigh the effect of increase in nuclear charge** from Q to R, resulting in a weaker attraction by nucleus. **Less energy** is required to **remove an electron** from 4p than the 4s orbital.

(ii) Explain why **P** is not considered to be a transition metal like most of the d-block metals. **[1]**

They **do not** form stable ions with a partially filled d subshell. **[1]**

(b) The idea of covalent bonding was first described in 1916 by an American physical chemist Gilbert Newton Lewis. HCOC*l* is an example of a polar covalent molecule.

(i) Explain what is *covalent bonding*. **[1]**

Covalent bonding is the electrostatic attraction between a shared pair of electrons and the positively charged nuclei.

(ii) State what is meant by the term *polar* when applied to a covalent bond. **[1]**

A polar covalent bond is one in which the electron density is unequally shared due to the difference in electronegativity of atoms bonded, resulting in ∂+ and ∂- across bond.

(iii) State and explain with reference to the Valence Shell Electron Pair Repulsion theory, the shape of HCOC*l* molecule. **[2]**

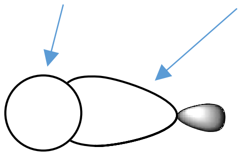
3 bond pair no lone pair so trigonal planar. The 3 electrons bond pairs arrange themselves to maximise stability and minimise electronic repulsion.

(iv) The molecule of HCOC*l* contains both σ (sigma) and π (pi) bonds. Draw labelled diagrams to show how orbitals overlap to form

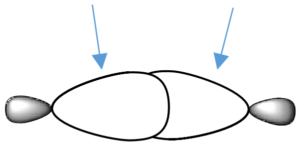
- a σ (sigma) bond
- a π (pi) bond

σ (sigma) bond is formed from **head-on overlap** of

s orbital of H and sp^2 of C or sp^2 of O and sp^2 of C

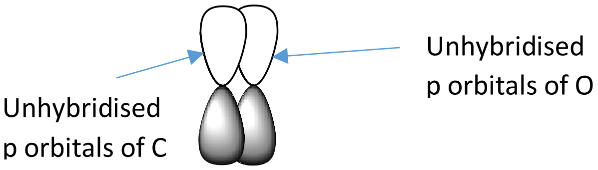


or



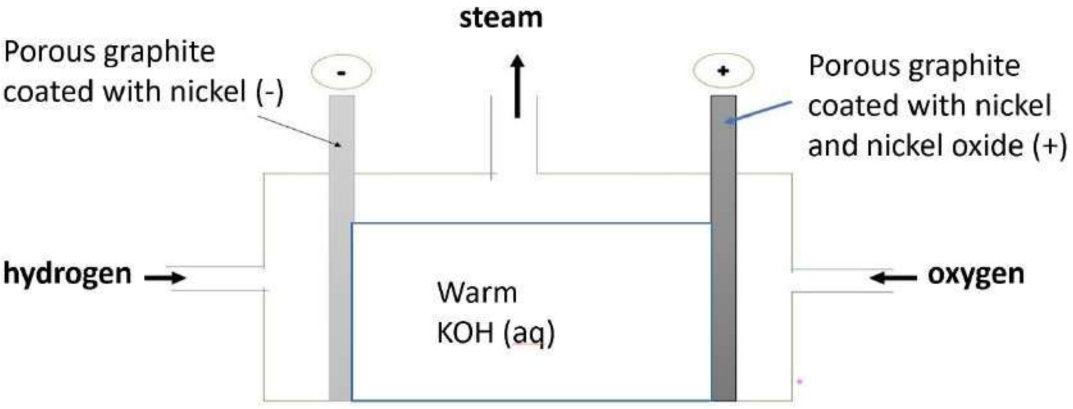
[2]

π (pi) bond is formed from **side-on overlap** of unhybridised p orbitals.



[Total:9]

2 Below is a labelled diagram of a hydrogen-oxygen fuel cell in an alkaline electrolyte.



(i) Write the half equations for both electrodes and hence the overall equation. **[2]**

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

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

Overall equation : $2H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$

(ii) Calculate $\Delta G^\ominus$ for the above reaction and state whether it is spontaneous. **[3]**

$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$

$= 0.40-(-0.83)$

$= +1.23\text{ V}$

$\Delta G^\ominus = -nFE^\ominus_{cell}$

$= -\,4 \times 96500 \times 1.23$

$= -\,474780\text{ Jmol}^{-1}$

$= -475\text{ kJmol}^{-1}$

It is spontaneous.

(iii) The hydrogen-oxygen fuel cell produces 1.5 A of current. Hydrogen gas is contained in a 1 dm^3 tank at a pressure and temperature of 200 atm and 20 ^oC respectively. Determine the number of days the fuel cell can operate before the hydrogen gas runs out. Give your answer to the nearest whole number. You may assume there is an unlimited supply of O_2. **[3]**

$PV = nRT$

$200 \times 1.01325 \times 10^5 \times 1 \times 10^{-3} = n \times 8.31 \times 293$

n (amt of H_2 gas) = 8.322 mol

no. moles of electrons given out = 2n = 16.64

Q = 16.64 x 96500 = 1605760C

Q = It

t = 1605760/1.5 = 1070506 s

=1070506/86400 = 12.39 days

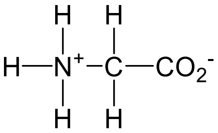
12 days

[Total:8]

3. Spider silk is a protein fiber. Major amino acids in the silk proteins are alanine and glycine. Serine and glutamine are also present in significant quantities in some types of silk. The table below shows the typical amino acids present in spider silk.

Amino Acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Glycine	–H
Alanine	$–CH_3$
Serine	$–CH_2OH$
Glutamine	$–CH_2CH_2CONH_2$

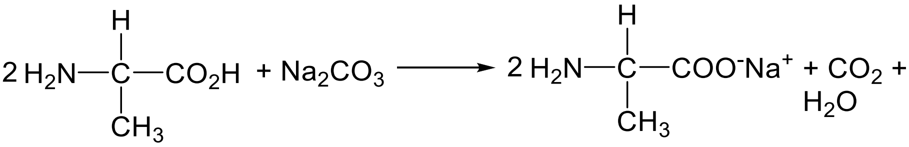
(a) **(i)** Glycine exists as crystalline solids. Draw the zwitterionic structure of glycine and account for the high melting point of glycine. **[2]**



$H_3N^+–CH_2–CO_2^-$

Crystalline solid of glycine has giant ionic lattice structure with strong electrostatic forces of attraction exists between the zwitterions. A lot of energy is required to overcome these strong ionic bonds between zwitterions.

(ii) Write an equation to show the reaction between alanine and aqueous sodium carbonate. **[1]**



$2\,H_2N–CH(CH_3)–CO_2H + Na_2CO_3 \longrightarrow 2\,H_2N–CH(CH_3)–COO^-Na^+ + CO_2 + H_2O$

(iii) Suggest a chemical test to distinguish between serine and glutamine. **[2]**

Test: $K_2Cr_2O_7$(aq),H_2SO_4(aq), heat

Observation:

For serine, orange dichromate turns green

For glutamine, orange solution remains

OR

Test: NaOH(aq), **heat**

Observation:

For serine, no pungent gas observed and moist litmus paper remained red.

For glutamine, pungent gas evolved turns **moist** red litmus blue

(b) Natural spider silk has excellent mechanical properties. In a recent study, researchers discovered that graphene-based materials can be used to boost the properties of spider's silk up to three times the strength and ten times the toughness of the unmodified silks.

Graphene is the thinnest material known to exist, yet it is stronger than steel. It is made from only carbon and is a single layer of graphite just one atom thick as shown in Figure **3.1** below.

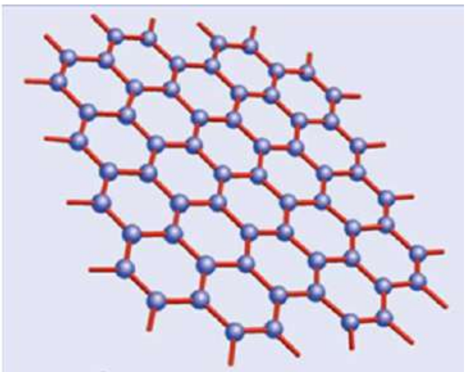


Figure **3.1**

(i) With reference to structure and bonding, explain why graphene is strong. **[1]**

Graphene is an allotrope of C and just like graphite it has giant covalent structure. Each layer of graphene is made of hexagonal "ring" of carbon atoms strongly covalently bonded. A lot of energy is required to break these strong covalent C-C bonds.

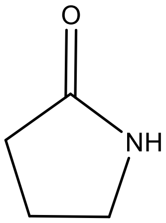
(ii) Since its discovery in 2004, graphene has been widely studied and manufactured as replacement materials for many touchscreen products. Suggest why graphene is a suitable touchscreen material in mobile phones. **[1]**

It is two-dimensional which makes it thin/light/transparent, suitable as touchscreen material.

Or it has high electrical conductivity due to presence of delocalized electrons that serve as mobile charge carriers.

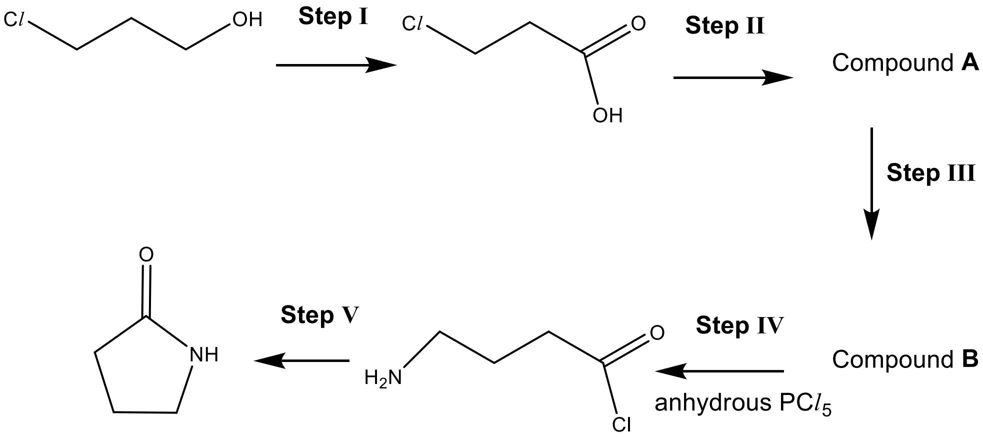
(c) Spiders are excellent treats for colonies of marauding ants. To protect their homes, spiders coat their webs using a chemical called 2-pyrrolidone, which acts as a deterrent to many insects.

2-Pyrrolidone is a 5-membered cyclic amide (commonly known as lactam). It is a colourless liquid that is miscible with water and most common organic solvents.



2-Pyrrolidone

2-pyrrolidone can be synthesised using 3-chloropropan-1-ol as the starting organic compound as shown in the reaction scheme below:



(i) State the type of reaction in **Step V**. **[1]**

(Intramolecular) condensation

(intramolecular) nucleophilic (acyl) substitution)

(ii) Suggest reagents and conditions for **Step I**, **II** and **III**. **[3]**

Step I : ……………………………………………………………………

Step II : ……………………………………………………………………

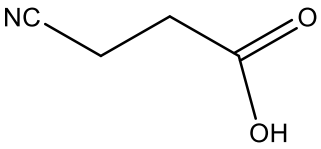
Step III : ……………………………………………………………………

Step I: $KMnO_4$(aq), H_2SO_4(aq), heat OR $K_2Cr_2O_7$, H_2SO_4(aq), heat

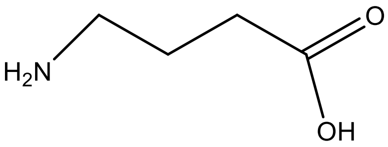
Step II: ethanolic KCN, heat

Step III: H_2, Ni, heat

(iii) Draw the structures of intermediate compounds **A** and **B.** **[2]**



A



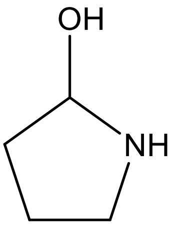
B

(iv) With the aid of an equation, explain why anhydrous condition is necessary for the reaction in **Step IV**. **[1]**

PCl_5 will hydrolyse readily in water as follows:

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

(v) 2-pyrrolidirol can be synthesised from 2-pyrrolidone.



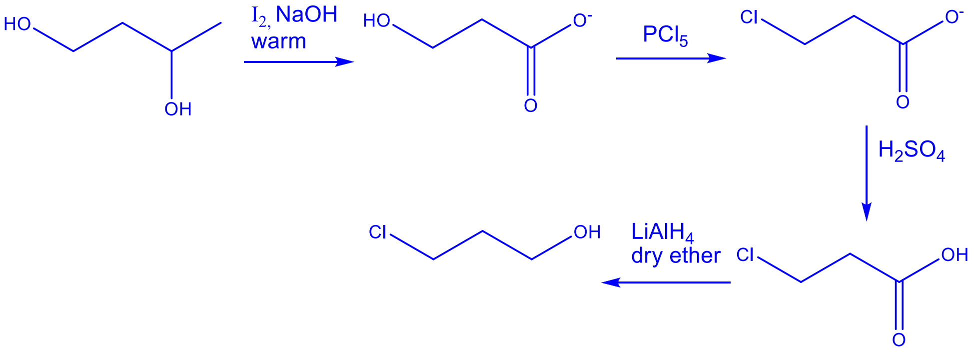
[2]

2-pyrrolidirol

Deduce whether 2-pyrrolidone or 2-pyrrolidirol has a higher pK_b.

2-pyrrolidone is less basic hence a higher pK_b as it is an amide. The lone pair of electrons on N are delocalised over the O-C-N bond and not available for protonation.

(vi) Suggest a synthesis to form 3-chloropropan-1-ol from 1,3-butanediol.



[Total:20]

4 **(a)** Copper and iron are examples of native metals, which are found pure in its metallic form on its own or in alloys in nature.

Copper and iron form many complexes with a range of colours as shown in the table:

complex	colour	complex	colour
$[Cu(NH_3)_4]^{2+}$	dark blue	$[Fe(H_2O)_6]^{3+}$	yellow
$[Cu(H_2O)_6]^{2+}$	blue	$[Fe(CN)_6]^{3-}$	red

(i) Explain why $[Cu(H_2O)_6]^{2+}$ is blue. **[3]**

In the isolated gas phase, all partially filled 3d orbitals of the transition metal ions are degenerate. In the presence of ligand such as NH_3 or CN^-, the 3d orbitals split into 2 energy level with a small energy gap between them.

An electron from the lower energy d orbital absorbs energy from the visible region (or visible spectrum) of the electromagnetic spectrum with wavelength corresponding to the energy gap is absorbed and get promoted to a higher energy d orbital.

The orange light energy is absorbed and the complementary blue colour is observed.

(ii) The oxidation state of iron in both $[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$ complexes is the same. However, they have different colours. Explain this observation.

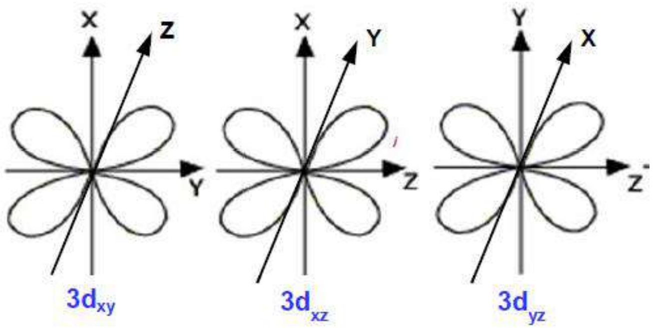
[1]

Different ligands (CN^- and H_2O) split the energy gap between the d orbitals differently. Hence different wavelength of light is absorbed and colour reflected is different.

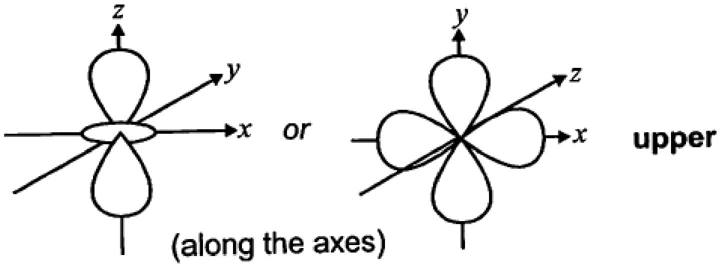
(iii) Draw **fully labelled** diagrams of the following:

- One of the d-orbitals at the lower energy level in $[Cu(H_2O)_6]^{2+}$. Label the diagram “lower”.
- One of the d-orbitals at the upper energy level in $[Cu(H_2O)_6]^{2+}$. Label this diagram “upper”. **[2]**

Lower: any



Upper: either



$3dz^2$ $3dx^2 - y^2$

(b) *Use of the Data Booklet is relevant to this question.*

Fe^{2+} is commonly used to catalyse the reaction between $S_2O_8^{2-}$and I^-. In another similar reaction, peroxodisulfate(VI), $S_2O_8^{2-}$, reacts with tartrate ion, $[CH(OH)CO_2]_2^{2-}$, to give carbon dioxide and methanoate as shown in the following equation.

$$[CH(OH)CO_2]_2^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

The reaction is very slow, even when heated, hence a catalyst is used to speed up the reaction.

(i) Explain why the reaction is slow. **[1]**

It involved two negative ions ($S_2O_8^{2-}$ and tartrate ion) which repel each other.

(ii) Given that the standard electrode potential for the following half-equation is

$$2CO_2 + 2HCO_2^- + 6H^+ + 6e^- \rightleftharpoons [CH(OH)CO_2]_2^{2-} + 2H_2O \qquad E^\theta = +0.56\ V$$

Using suitable equations, explain why Mn^{2+} is a suitable catalyst for this reaction. **[2]**

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

$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$ $E^\theta = +1.54\ V$

(Catalysed reaction using Mn^{2+})

$2Mn^{2+} + S_2O_8^{2-} \rightarrow 2Mn^{3+} + 2SO_4^{2-}$

$E^{\theta}_{cell} = 2.01 – (1.54) = + 0.47$ V

$6Mn^{3+} + [CH(OH)CO_2]_2^{2-} + 2H_2O \rightarrow 6Mn^{2+} + 2CO_2 + 2HCO_2^{-} + 6H^{+}$

$E^{\theta}_{cell} = 1.54 - 0.56 = + 0.98$ V

Alternative answer:

$S_2O_8^{2-} + 2e^{-} \rightleftharpoons 2SO_4^{2-}$ $\quad E^{\theta} = +2.01$ V

$MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad E^{\theta} = +1.52$ V

$5S_2O_8^{2-} + 2Mn^{2+} + 8H_2O \rightarrow 10SO_4^{2-} + 2MnO_4^{-} + 16H^{+}$

$E^{\theta}_{cell} = 2.01 – (1.52) = + 0.49$ V

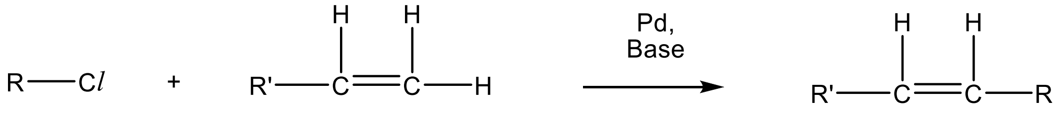
$6MnO_4^{-} + 18H^{+} + 5[CH(OH)CO_2]_2^{2-} \rightarrow 6Mn^{2+} + 14H_2O + 10CO_2 + 10HCO_2^{-}$

$E^{\theta}_{cell} = 1.52 - 0.56 = + 0.96$ V

(iii) State the property of transition metal ions that enable them to function as a homogenous catalyst in the reaction. **[1]**

Transition metal ions are able to exhibit a variety of oxidation states due to the similar energy of the 3d and 4s orbitals and hence both are able to be shared or lost.

(c) Palladium is a transition element that is used as a catalyst in the Cassar reaction. The Cassar reaction is a type of substitution reaction between an alkyl chloride and a terminal alkene in the presence of a base and a palladium catalyst.



[R can be a substituted alkyl group containing –OH, –NH₂, –NO₂ –COOH]

The following scheme shows the synthesis of **D** using Cassar reaction in one of the steps.

$$\mathbf{A} + \underset{C_4H_8O}{\mathbf{B}} \xrightarrow{\text{Cassar reaction}} \underset{C_5H_{11}NO}{\mathbf{C}} \xrightarrow{K_2Cr_2O_7(aq),\ H_2SO_4(aq),\ \text{heat}} \mathbf{D}$$

The table below shows the observations when **A**, **B** and **D** reacts with various reagents.

reaction		observations
1	**A** + HC*l*(aq)	colourless solution
2	**B** + Br_2(aq)	colourless solution
3	**D** + Na_2CO_3(aq)	Gas forms white ppt with $Ca(OH)_2$

(i) Name the functional group that reaction **1** shows to be present in **A** **[1]**

(Primary) amine

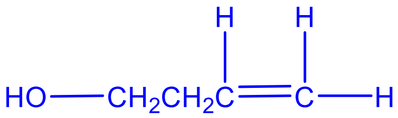
(ii) State the type of reaction that takes place in reaction **2** and name the functional group present in **B** **[1]**

Electrophilic addition. Alkene

(iii) **C** is able to exhibit cis-trans isomerism. Draw the structures of **A**, **B**, **C** and **D**. **[4]**

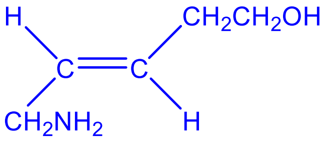
$H_2N{-}CH_2Cl$

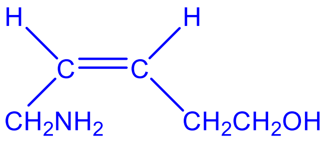
Compound A



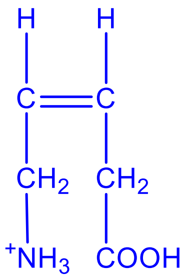
$HO{-}CH_2CH_2CH{=}CH{-}H$

Compound B



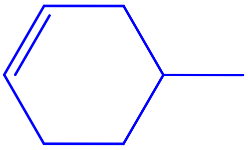


Trans isomer of compound C EITHER Cis isomer of compound C



Compound D

(iv) Draw the structure of the product when $CH_3CH(CH_2Cl)CH_2CH_2CH=CH_2$ undergoes the Cassar reaction. **[1]**



(d) A solution containing Cu^{2+} and Zn^{2+} can be separated by selective precipitation.

The reagent used is hydrogen sulfide which behaves as a dibasic (diprotic) weak acid when in aqueous solution.

Aqueous hydrogen sulfide behaves as a dibasic acid.

$$H_2S\,(aq) \rightleftharpoons H^+\,(aq) + HS^-\,(aq) \quad K_{a1} = 8.9 \times 10^{-8}\ \text{mol dm}^{-3}$$

$$HS^-\,(aq) \rightleftharpoons H^+\,(aq) + S^{2-}\,(aq) \quad K_{a2} = 1.2 \times 10^{-13}\ \text{mol dm}^{-3}$$

Metal sulfides are precipitated by the following reaction.

$$M^{2+}(aq) + S^{2-}(aq) \rightleftharpoons MS(s)$$

Relevant K_{sp} values are given in the table below.

Salt	K_{sp} / mol^2 dm^{-6}
CuS	6.3×10^{-36}
ZnS	1.6×10^{-24}

(i) Given that a solution contains 0.0010 mol dm^{-3} Zn^{2+} and 0.0010 mol dm^{-3} Cu^{2+}, determine the maximum sulfide concentration for each cation so that no precipitation occurs. **[1]**

$[S^{2-}]_{max}$ for ZnS= $\dfrac{1.6 \times 10^{-24}}{0.0010}$ = 1.6×10^{-21} mol dm^{-3}

$[S^{2-}]_{max}$ for CuS = $\dfrac{6.3 \times 10^{-36}}{0.0010}$ = 6.3×10^{-33} mol dm^{-3}

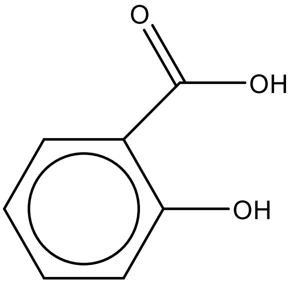
(ii) Given that $[H^+] = \sqrt{\dfrac{K_{a1}K_{a2}[H_2S]}{[S^{2-}]}}$ and using your answer in **(d)(i)**, calculate the maximum pH that must be maintained to separate Zn^{2+} and Cu^{2+} ions, given that the concentration of H_2S in the solution is 0.0010 mol dm^{-3}. **[2]**

$K_{a1}\ K_{a2} = 1.068 \times 10^{-20}$ mol^2 dm^{-6}

$[H^+] = \sqrt{\dfrac{1.068\times10^{-20}\times0.0010}{1.6\times10^{-21}}}$ = 0.08170 mol dm^{-3}

pH = – log 0.08170 = 1.09

(e) The Trinder spot test is a diagnostic test used in medicine to determine exposure to salicylates, in particular, salicylic acid. The test involved the Trinder reagent which is mixed with a patient's urine. A coloured complex is formed if salicylates are present.



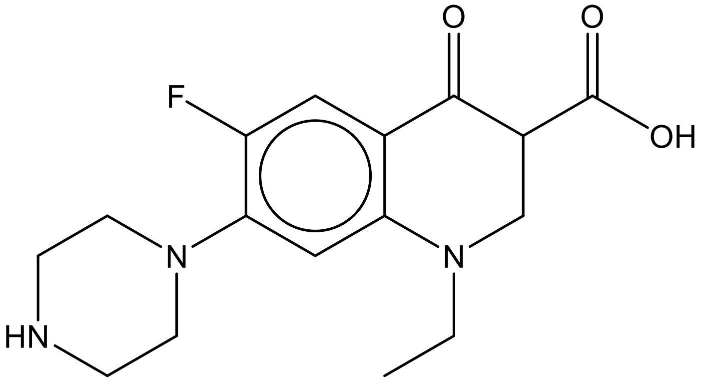
Salicylic acid

(i) Suggest the compound that is present in the Trinder reagent added to salicylic acid and state the observation when if the test is positive. **[2]**

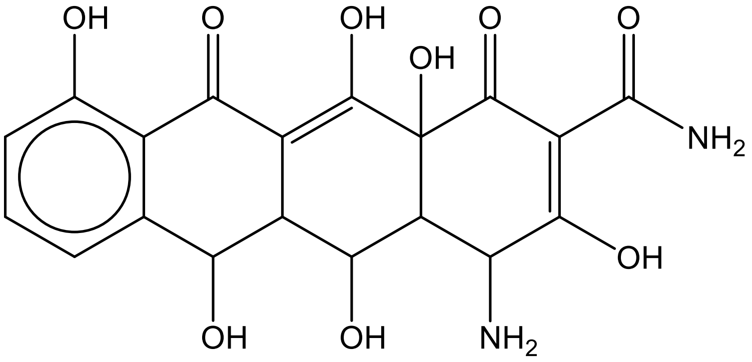
Neutral aq $FeCl_3$. [1]

Violet [1] coloration is observed.

Another variation of the Trinder spot test has also been used to determine the presence of norfloxacin and oxytetracycline.



norfloxacin



oxytetracycline

(ii) State the number of stereoisomers present in oxytetracycline. **[1]**

……………………………………………………………………………..………

$2^6 = 64$

(iii) Suggest a chemical test to distinguish between oxytetracycline and norfloxacin. **[2]**

……………………………………………………………………………..………

…………………………………………………………………………………..…

$K_2Cr_2O_7$(aq), H_2SO_4(aq), heat. Orange $K_2Cr_2O_7$ turns green for oxytetracycline but remained orange for norfloxacin.

Or

Na_2CO_3(aq). Effervescence observed and gas evolved formed white ppt in limewater for norfloxacin but no effervescence for oxytetracycline.

Or

Neutral $FeCl_3$ (aq). Violet colouration for oxytetracycline but no violet colouration for norfloxacin.

[Total:25]

5 Sodium alginate is a natural polymer extracted from brown seaweed. Figure **5.1** shows the simplified representation of a sodium alginate polymer.

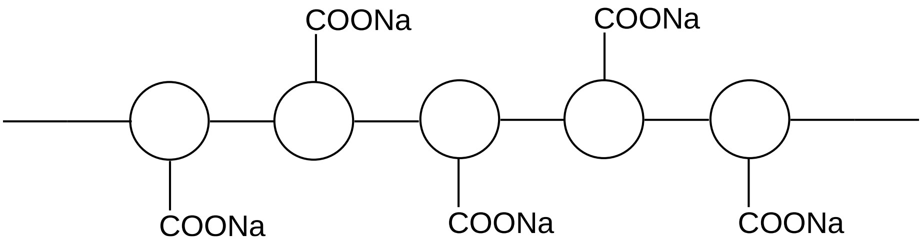


Figure **5.1** : simplified representation of sodium alginate polymer

In food chemistry, sodium alginate serves as a gel-forming agent as it can react with calcium salts to make “popping boba” in the bubble tea industry. This process is commonly known as spherification.

During spherification, a solution of sodium alginate is added to a solution of calcium salt. Na^+ ions are exchanged with Ca^{2+} ions and the cross linked calcium alginate polymers forms as shown in Figure **5.2**.

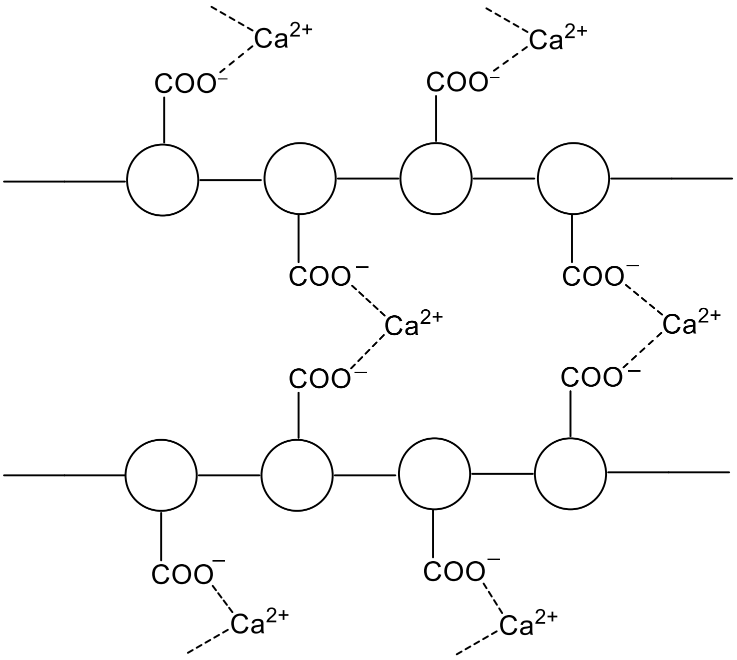


Figure **5.2**: simplified representation of cross-linked calcium alginate polymer.

(a) **(i)** Cross-linking is the general term for the process of forming chemical bonds to join two polymer chains together. Explain, in terms of bonding, why Ca^{2+} ions are able to cross-link the alginate polymers but Na^+ ions are unable to do so. **[1]**

The divalent Ca^{2+} ions are able to cross-link the alginate polymers because they can form two ionic bonds, while monovalent Na^+ ions can only form one bond. [1]

(ii) Explain why calcium alginate has low solubility in water. **[1]**

The energy released from the ion-dipole interactions between calcium alginate and the water molecules [1] is insufficient to overcome the strong ionic bonds between calcium ions and alginate ions and hydrogen bonds between the water molecules.[1]

(b) During spherification, the pH of the flavoured liquid used is important. Below a pH of 3.6, sodium alginate tends to react and the resultant solution will thicken which makes it difficult to form spheres.

Although Ca^{2+} is crucial in helping the alginate to gel, excess Ca^{2+} present can also cause the liquid to gel prematurely which is undesirable.

Table **5.3** shows the pH of various flavoured liquids.

Table **5.3**

Flavoured Liquid	pH
cranberry juice	2.3
blueberry juice	3.4
tomato juice	4.6
watermelon juice	5.2
aloe vera juice	6.1

(i) Cranberry juice is not suitable for spherification to work. **[2]**

Suggest the type of reaction that takes place when sodium alginate is added to cranberry juice and hence explain why spherification will not occur in presence of cranberry juice.

Acid-base reaction.[1]

The sodium alginate will be protonated and converted to the covalent conjugate acid molecule (alginic acid). Without Na^+, ion-exchange does not take place readily with Ca^{2+} to make the cross-linked polymer. [1]

(ii) A bubble tea shop wanted to make a "popping boba" by mixing 250 cm^3 of aloe vera juice with 300 cm^3 of blueberry juice. By determining the pH of the mixture, deduce if the spherification would happen. **[3]**

$[H^+]_{\text{aloe vera}} = 10^{-6.1} = 7.943 \times 10^{-7}$ mol dm^{-3}

Amt of H^+ in aloe vera = $7.943 \times 10^{-7} \times 250/1000$

= 1.986×10^{-7} mol

$[H^+]_{\text{blueberry}} = 10^{-3.4} = 3.981 \times 10^{-4}$ mol dm^{-3}

Amt of H^+ in blueberry juice = $3.981 \times 10^{-4} \times 300/1000$

= 1.194×10^{-4} mol [1 for both amount of H^+]

$[H^+]_{\text{mixture}} = (1.986 \times 10^{-7} + 1.194 \times 10^{-4})/0.55 = 2.175 \times 10^{-4}$ mol dm^{-3}

pH = 3.66 [1] > 3.6

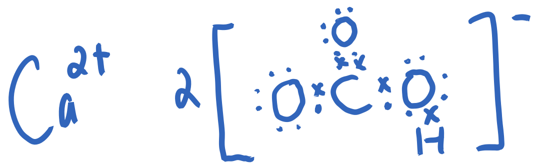
Since pH > 3.6, spherification would happen. [1]

(iii) Hard water is water that has a high mineral content. It is formed when water percolates through deposits of limestone which are made up of calcium and magnesium carbonates and bicarbonates. **[1]**

Suggest why spherification does not work well in hard water.

The presence of high concentration of calcium in hard water will solidify/gel in the sodium alginate solution **immediately/prematurely** to form calcium alginate. [1]

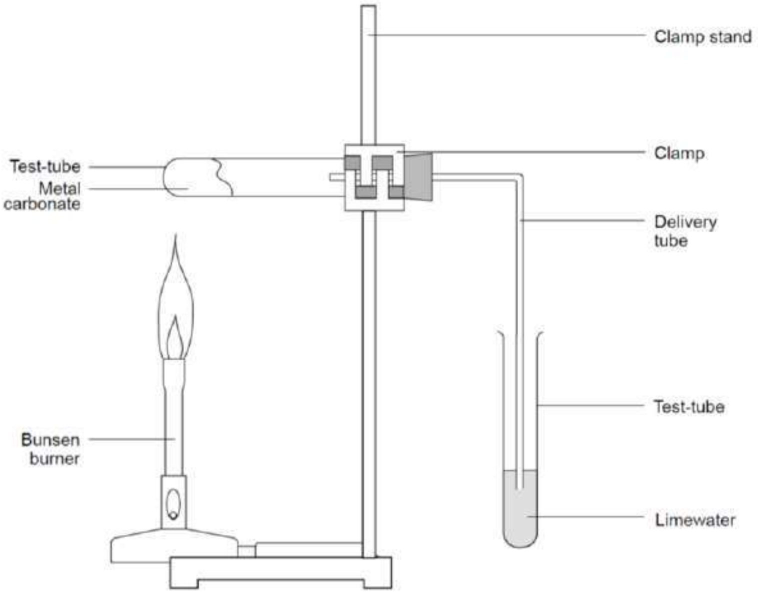
(iv) Draw the dot-cross diagram for calcium bicarbonate $Ca(HCO_3)_2$. **[2]**



[1] for ionic structure

[1] for HCO_3^{2-}

(c) A student set up the following experiment to investigate the thermal stability of magnesium and calcium carbonates:



Each of the metal carbonate is heated strongly for 5 min and the time taken for a white precipitate to form in limewater is recorded in the following table:

Metal carbonate	Time taken (s)
X	70
Y	40

(i) What is the identity of **X** and **Y**? **[1]**

X: Calcium carbonate

Y: Magnesium carbonate

(ii) Explain the results. **[2]**

Magnesium carbonate decomposes more easily and releases CO_2 faster to form white ppt in limewater because size of Mg^{2+} is smaller than Ca^{2+} but charge remains. Hence charge density of Mg^{2+} is larger than Ca^{2+} [1]. Electron cloud of carbonate in $MgCO_3$ will be distorted to a larger extent/polarising power of Mg^{2+} is more, weakening the C-O bond more [1].

[Total:13]

NAME		**Class**	

ST ANDREW’S JUNIOR COLLEGE

JC2 Preliminary Examination

H2 Chemistry (9729) **18 September 2019**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Answer 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.

Section A

Answer **all** questions. Marks **[60]**

Section B

Answer **one** question. Marks **[20]**

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.

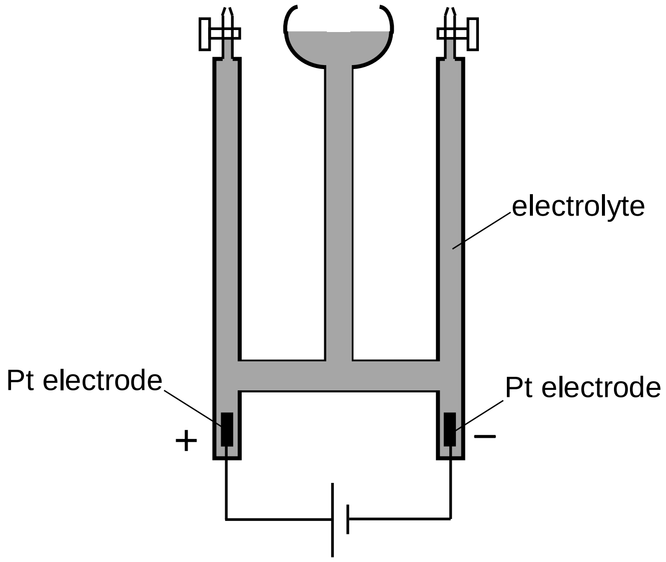
This document consists of **14** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** Use of the Data Booklet is relevant to this question.

The Hoffmann voltameter is used to electrolyse concentrated iron (III) chloride solution. The setup of the Hoffmann voltameter is shown below.



(i) Describe the observations at the cathode and anode. Explain your answer with the aid of suitable ion-electron equations. **[2]**

Anode (+): $2Cl^{-} \longrightarrow Cl_2 + 2e$

Greenish-yellow gas was evolved at the anode.

Cathode (-): $Fe^{3+} + e \longrightarrow Fe^{2+}$

The yellow solution turned green

(ii) State the difference in the observations at the anode when dilute aqueous iron (III) chloride solution is used instead. Explain your answer using relevant E^{θ} data. **[2]**

Anode (+): $2H_2O \longrightarrow O_2 + 4H^{+} + 4e$ (equation not required)

Colourless gas is evolved

the **E°(O_2/H_2O) is +1.23V** which is **more negative** (less positive) / **preferentially oxidised** compared to E°(Cl_2/Cl^{-}) = +1.36V.

(b) The electrolysis of a hot aqueous solution of Na**X** yielded a reddish brown gas, $\mathbf{X_2}$, at the anode and hydrogen gas at the cathode. The red litmus paper turned blue when dipped into the solution at the cathode.

(i) Suggest the identity of the reddish brown gas $\mathbf{X_2}$. **[1]**

Br_2

(ii) Write an ion-electron equation for the reaction at the cathode. **[1]**

Cathode: $2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Comments:

- Many students chose the SHE equation. This is not correct as H+ was not mentioned to be present.

(iii) Some of the $\mathbf{X_2}$ dissolved in the alkaline medium to form $\mathbf{X^-}$ and $\mathbf{XO_3^-}$ ions. Write a balanced equation to represent the reaction of $\mathbf{X_2}$ in alkaline medium. **[1]**

$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$

(iv) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between sodium chloride and sodium iodide. **[2]**

Add Br_2 (aq).

For KCl, orange Br_2 is not decolourised.

For KI, orange solution of Br_2 turns brown.

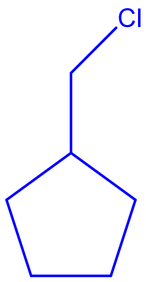
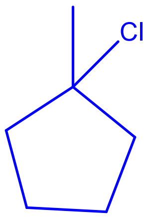
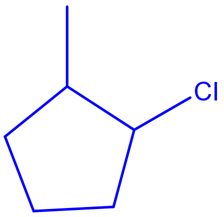
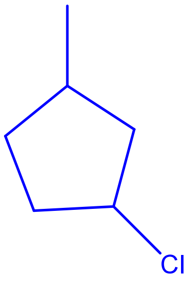
$2I^- + Br_2 \rightarrow I_2 + 2Br^-$

(c) Describe and explain how the thermal stability of the hydrogen halides varies down Group 17. **[2]**

Down the group, **size of halogen increases**, leading to **less effective orbital overlap** between H and X.

Bond energy of H – X decreases / **H-X bond is longer and weaker** and is easily broken. Thus, **thermal stability of hydrogen halides decreases** down the group.

(d) When methylcyclopentane is treated with a small quantity of chlorine in the presence of ultraviolet light, 4 mono-chlorinated constitutional isomers are produced. Draw the structures of the isomers and state the ratio in which they are formed. **[3]**

3 : 1 : 4 : 4

(e) $SiCl_4$ reacts readily with water to form a solution of pH 2. However, SiO_2 does not react with water and only reacts with hot concentrated alkali such as NaOH.

(i) Explain why $SiCl_4$ reacts readily with water, but SiO_2 only reacts with hot concentrated NaOH. Use relevant equations to explain your answer. **[3]**

$SiCl_4$ has energetically available vacant orbitals to accept lone pair of electrons from H_2O and undergo complete hydrolysis.

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$

SiO_2 is an acidic oxide and reacts with basic/ionic NaOH.
$SiO_2(s) + 2NaOH\ (conc.) \rightarrow Na_2SiO_3(aq) + H_2O(l)$

SiO_2 is a giant covalent structure with strong covalent bonds, requiring a lot of energy to overcome/break, and hence does not reacts with / not soluble in water.

(ii) Using $Cl_2(g)$ as an example, define the term *bond energy*. **[1]**

Bond energy is the enthalpy change to break one mole of Cl-Cl bonds in gaseous state.

OR

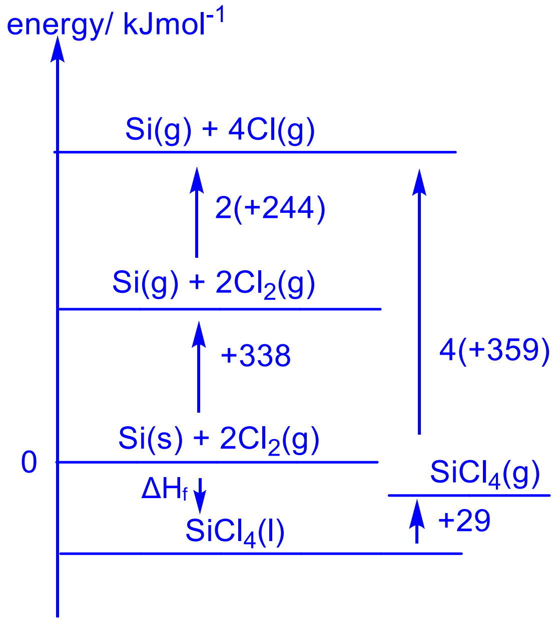
$Cl_2(g) \rightarrow 2Cl(g)$

(iii) Construct an energy level diagram to calculate the enthalpy change of formation of $SiCl_4$.

Your diagram should include relevant data from the *Data Booklet* together with the following data: **[3]**

Enthalpy change of atomisation of Si = +338 $kJmol^{-1}$

Enthalpy change of vapourisation of $SiCl_4$ = +29 $kJmol^{-1}$



ΔH_f = +338 + 2(244) – 4(359) – (29) = -639 $kJmol^{-1}$

[Total: 21 marks]

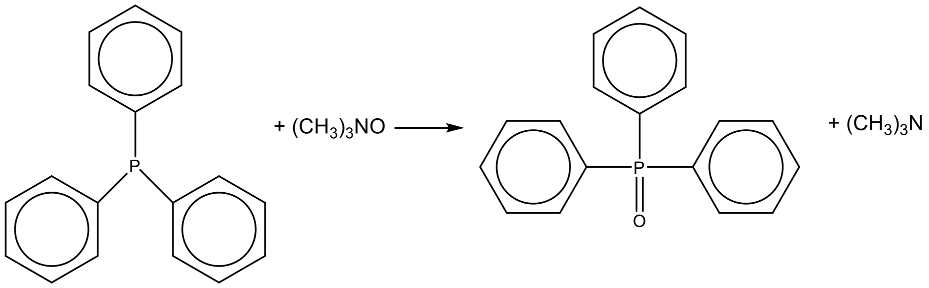
2 **(a)** Phosphorus-containing compounds can react in various ways: as an acid, as a base, as an electrophile, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way the phosphorus-containing compound is reacting in each case. Explain your answers fully.

(i) $H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+$ **[1]**

Acid . <u>donate proton (or H^+)</u> to the water molecule.

(ii)



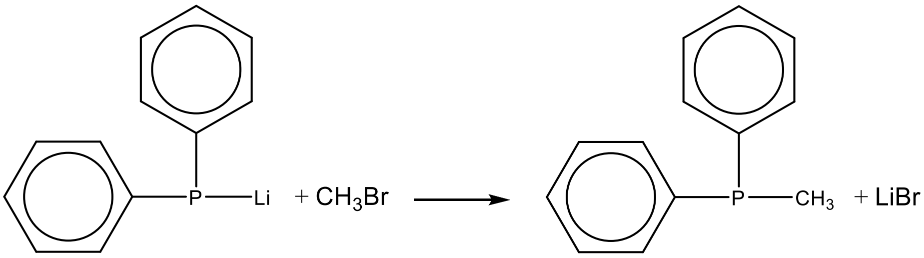
[1]

Reducing agent.

It was oxidised due to the <u>addition of O</u> or Oxidation state of P decreased from +3 to +5 OR

$(CH_3)_3NO$ was reduced since there was a loss of O or Oxidation state of N decreased from -1 to –3

(iii)



[1]

Nucleophile.

The lone pair of electrons on the P attacks the electron deficient C of CH_3Br via nucleophilic substitution.

(b) 2-chloropropanoyl chloride, **W**, can be obtained from propanoic acid by heating it with Cl_2 and PCl_5.

Reaction **1** :

$$CH_3CH_2CO_2H(l) + Cl_2(g) + PCl_5(s) \rightarrow \underset{\textbf{W}}{CH_3CHClCOCl(l)} + 2HCl(g) + POCl_3(l)$$

$\Delta H > 0$

(i) Explain the different reactivities of the two chlorine atoms in **W** towards water. **[2]**

The carbonyl carbon of acyl chloride is bonded to 2 electronegative O and C*l* making it highly electron deficient, while the carbon of the alkyl chloride is only bonded to C*l*. Hence, acyl chloride is more susceptible to the attack of nucleophiles (water).

(ii) Explain fully why the pH of an aqueous solution of 2-chloropropanoyl chloride is 1.0 while that of an aqueous solution of propanoic acid of the same concentration is greater than 1.0. **[2]**

Aqueous 2-chloropropanoyl chloride is more acidic than aqueous propanoic acid. 2-chloropropanoyl chloride hydrolyses fully in water to form a carboxylic acid and HC*l* which is a strong acid which dissociates fully in water. Propanoic acid dissociates partially in water.

OR

$$CH_3CHC\mathit{l}COC\mathit{l} + H_2O \longrightarrow CH_3CHC\mathit{l}COOH + H^+ + C\mathit{l}^-$$

$$CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$$

(iii) **W** can be used to produce sweet-smelling **Z**, $C_6H_8O_4$, via compounds **X** and **Y**, as shown in Fig. 2.1

$$\mathbf{W} \xrightarrow[\text{heat}]{\text{NaOH(aq)}} \mathbf{X} \xrightarrow{H_2SO_4\text{(aq)}} \mathbf{Y} \xrightarrow[\text{heat}]{\text{conc } H_2SO_4} \mathbf{Z}$$

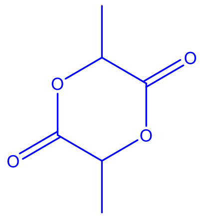
Fig. 2.1

Suggest structures for compounds **X**, **Y** and **Z** in Fig. 2.1. **[3]**

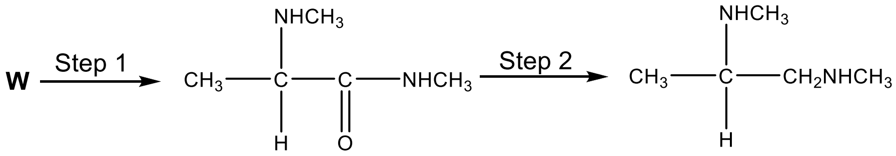
X: $CH_3CH(OH)CO_2^-Na^+$

Y: $CH_3CH(OH)CO_2H$

Z:



(iv) **W** can undergo the following reaction scheme.



State the reagents and conditions for Steps 1 and 2. **[2]**

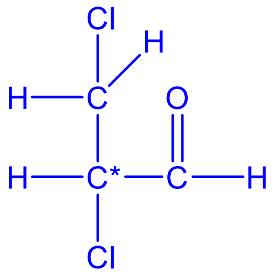
Step 1: (excess) CH_3NH_2, heat

Step 2: $LiA\mathit{l}H_4$, dry ether

(v) **V** is an isomer of **W**.

V rotates the plane of polarised light. It gives a positive test with 2,4-dinitrophenylhydrazine.

Draw the displayed formula of **V**, identifying the chiral carbon. **[1]**



(vi) Use the table of characteristic values for infra-red absorption frequencies in the *Data Booklet* to answer this question.

Infra-red adsorption frequencies can be used to identify functional groups in organic compounds. For example, propanol shows absorptions at 970–1250cm^{-1} and 3580–3620 cm^{-1}.

Use the table to suggest how infra-red absorption range can be used to distinguish 2-chloropropanoyl chloride from propanoic acid. **[1]**

2-chloropropanoyl chloride will have an absorption at 700–800cm^{-1} but propanoic acid would not have.

OR

Propanoic acid will have an absorption at 1210–1440cm^{-1} but 2-chloropropanoyl chloride would not have.

OR

Propanoic acid will have an absorption at 3580–3650cm^{-1} but 2-chloropropanoyl chloride would not have.

(vii) Given that reaction **1** is endothermic, explain why the reaction will only take place with heating. **[2]**

$\Delta G = \Delta H - T\Delta S$

ΔH is positive and $\underline{\Delta S \text{ will be positive as more gaseous molecules formed}}$ [1]. Hence$\underline{\text{, a high temperature is required such that } |T\Delta S| > |\Delta H| \text{ so } \Delta G < 0}$ [1]

[Total : 16 marks]

3 There are 2 isomers of 2-methylbutanoic acid, $CH_3CH_2CH(CH_3)COOH$ (M_r 102.0) ; one of the isomers is sweet-smelling and the other has a stinky odour.

(a) **(i)** State the stereoisomerism exhibited by 2–methylbutanoic acid and how it arises. **[2]**

Enantiomerism

Any of the following 2 explanations

- the mentioning of two non–superimposable mirror images
- explanation in terms of diagram illustrating non–superimposable enantiomer

(ii) Hence, explain why the isomers have different smells. **[1]**

Either

Different enantiomers interact differently with the chiral molecules in the human body

OR

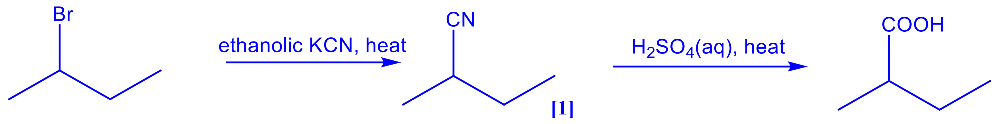
Different enantiomers have different biological properties

(b) Suggest a 2 stage synthesis of 2–methylbutanoic acid from 2–bromobutane. State reagents and conditions needed for each step, and show clearly the structure of any intermediate compounds. **[3]**

Step 1: alcoholic KCN, heat

Step 2: aqueous H_2SO_4, heat

Intermediate: $CH_3CH(CN)CH_2CH_3$



Allow for any strong acid solutions (e.g. dil HC*l*)

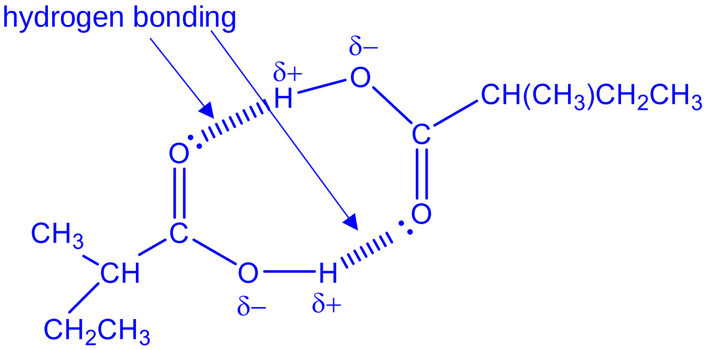
(c) Safety regulations set by many countries state that a factory would be fined, if stinky smelling compounds reached unsafe levels. The factory would have to stop production and undergo cleansing.

When 2–methylbutanoic acid was synthesised using 2–bromobutane in a factory, both the sweet-smelling and the stinky isomers were obtained in equal proportions.

(i) The M_r of 2–methylbutanoic acid in the liquid phase is 204.0.

With the aid of a diagram, explain the above. **[2]**

2–methylbutanoic acid is a polar covalent molecule with hydrogen bonding between its molecules.



(ii) 2–methylbutanoic acid has a relatively low boiling point of 176 °C at 1 atm, and hence vaporises easily. This poses a problem when adhering to safety regulations.

In a factory, during the synthesis of 2–methylbutanoic acid, the workers did not seal the chemical container properly.

Given that the enthalpy change of vaporisation of 2–methylbutanoic acid is +59.1 kJ mol^{-1}, use the following equation (Clausius–Clapeyron Equation) to determine the vapour pressure of 2–methylbutanoic acid in the factory at night when the temperature was 30.2 °C.

$$\ln P = \frac{\Delta H_{\text{vaporisation}}}{R}\left(\frac{1}{T_{\text{b.p.}}} - \frac{1}{T}\right)$$

P = vapour pressure in atm at temperature T K

$\Delta H_{\text{vaporisation}}$ = enthalpy change of vaporisation of the substance in J mol^{-1}

R = universal gas constant

$T_{\text{b.p.}}$ = boiling point of the substance in K at 1 atm

[2]

$$\ln P = \frac{59100}{8.31}\left(\frac{1}{273 + 176} - \frac{1}{273 + 30.2}\right)$$

$$P = 4.92 \times 10^{-4} \text{ atm}$$

(iii) Safety protocols dictated that stinky smelling substances above 300 ppm (parts per million) is considered a safety hazard and likely to be fined. Based on your answers in **(a)(i)** and **(c)(ii)**, and given that the pressure in the factory is 1 atm, determine whether the factory would be fined.

[2]

[1 x 10^{-6} atm in 1 atm = 1 ppm]

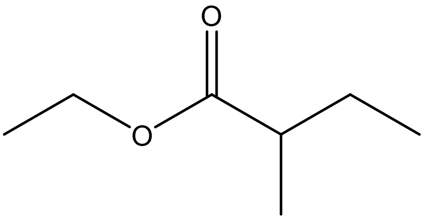
Mole fraction of the odorous 2–methylbutanoic acid

$= \frac{1}{2}\left(\frac{4.92 \times 10^{-4}}{1}\right) \times 10^{6}$

= 246 ppm **[1]**

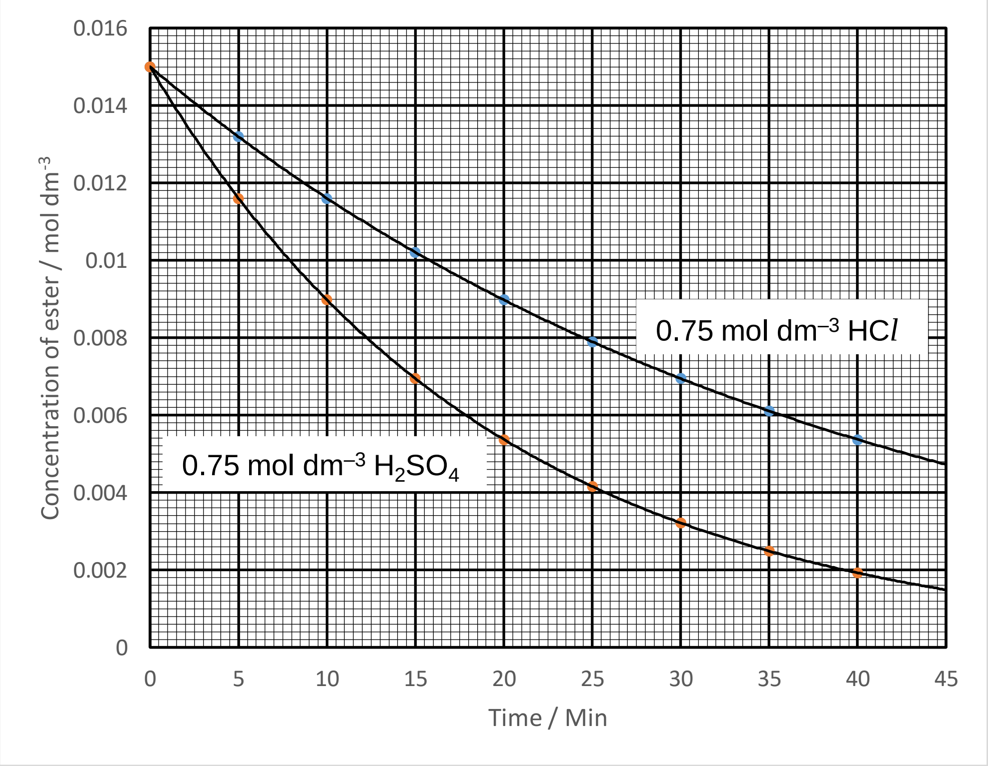
No, the factory would not be fined.

(d) Ethyl 2–methylbutanoate is an ester which is commonly found in citrus fruits, such as pineapple and oranges. It is commonly used as the starting material to form the sweet–smelling 2–methylbutanoic acid via hydrolysis.



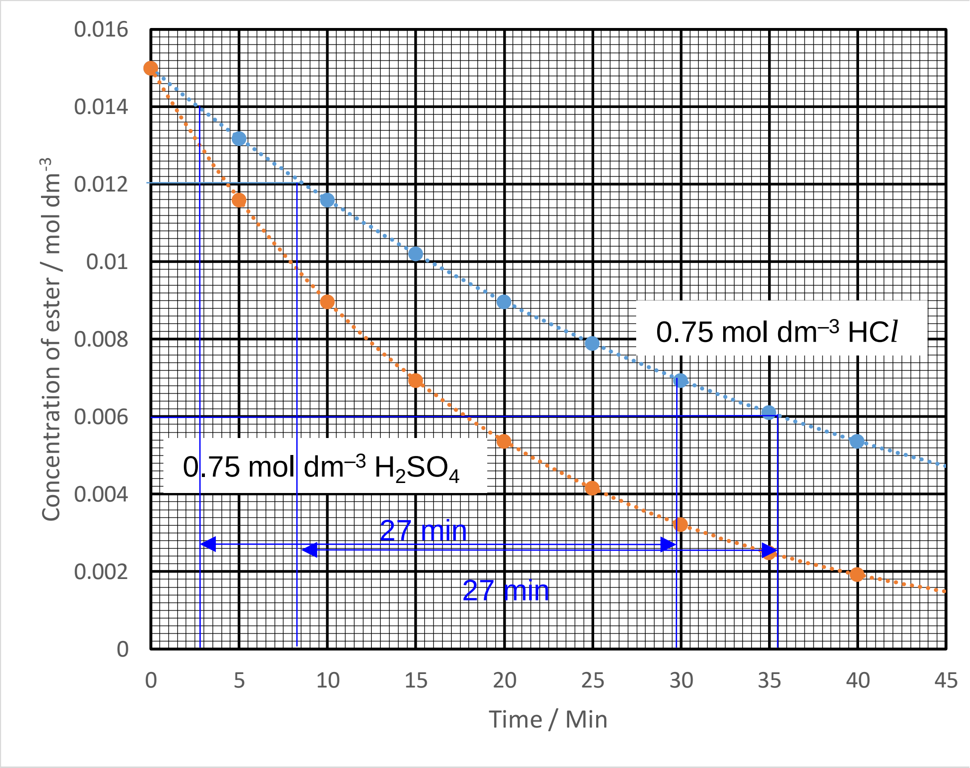
ethyl 2-methylbutanoate

The rate equation for the hydrolysis of esters was determined by a series of experiments. The hydrolysis of the ester, ethyl 2–methylbutanoate, was carried out, using 0.75 mol dm^{-3} hydrochloric acid. The experiment was repeated using 0.75 mol dm^{-3} sulfuric acid. The following graphs were obtained.

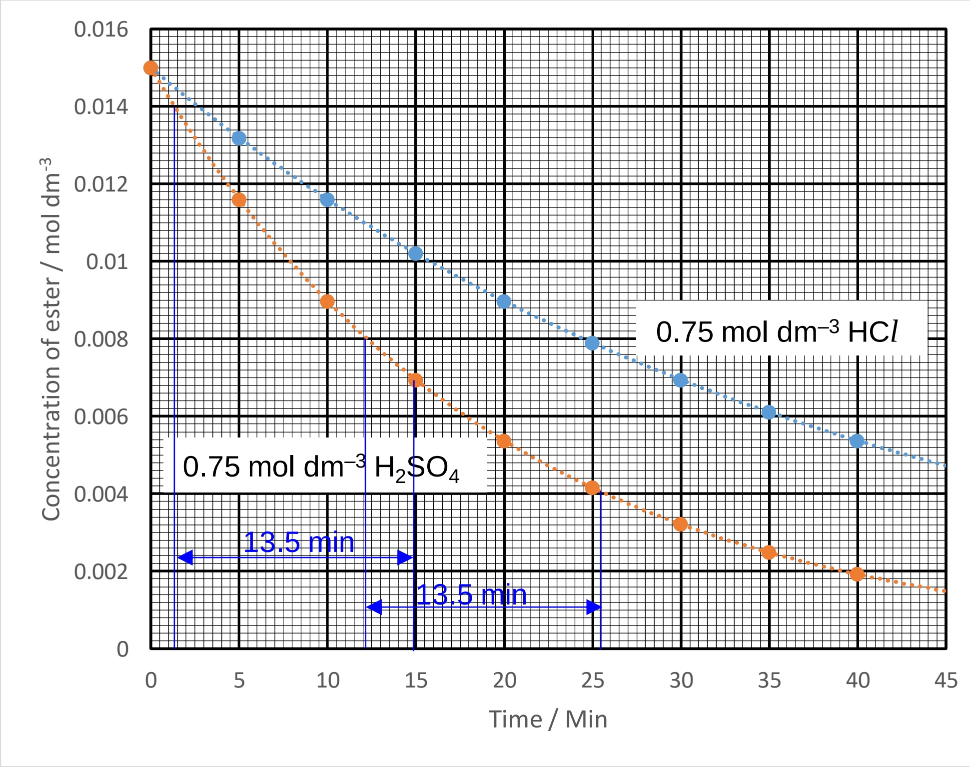


(i) Using the graphs above, deduce the order of reaction with respect to [H^+] and [ester]. Hence, write the rate equation of the hydrolysis of the ester, ethyl 2–methylbutananoate. **[3]**

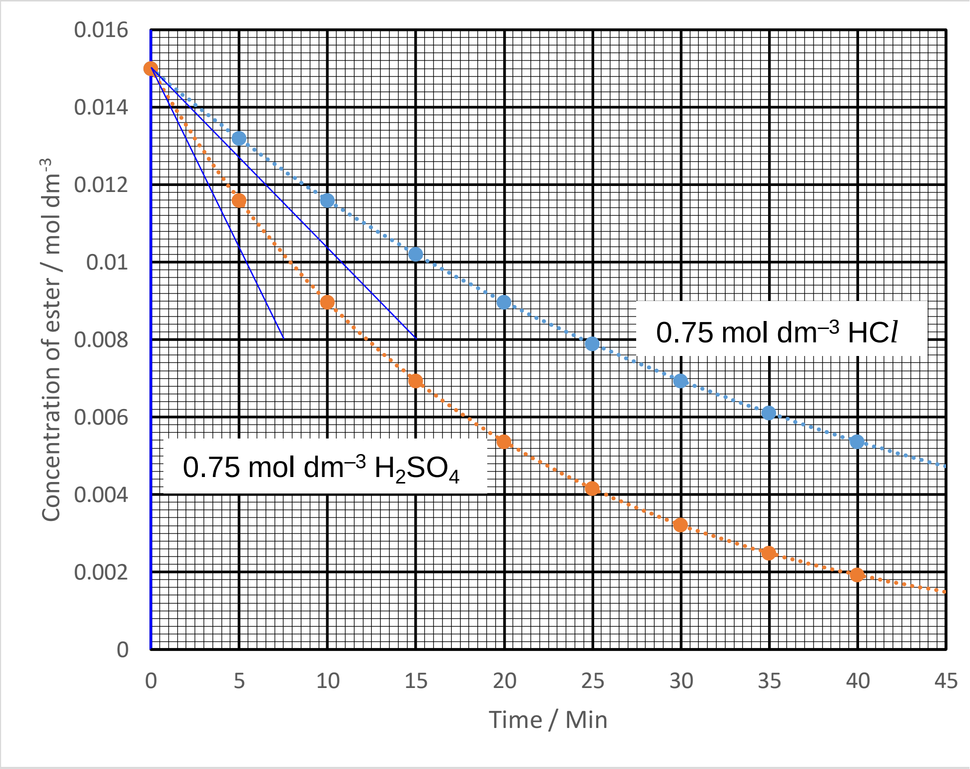
Half-life drawings for HC*l* curve.



Half-life drawings for H_2SO_4 curve.



Gradients of the lines



Change in concentration of ester = 0.007 mol dm^{-3}

Time taken for HC*l* curve = 15 min

Time taken for H_2SO_4 curve = 7.5 min

Rate for HC*l* curve = 4.67 × 10^{-4} mol dm^{-3} min^{-1}

Rate for H_2SO_4 curve = 9.33 × 10^{-4} mol dm^{-3} min^{-1}

Half life of line using HC*l* is 27 minutes, and half life of line using H_2SO_4 is 13.5 minutes. Order of reaction with respect to [ester] is 1.

Half life of the 2 lines decrease to half when [H^+] was doubled, order of reaction with respect to [H^+] is 1.

rate = k[H^+][ester]

(ii) Calculate the rate constant for the hydrolysis of ethyl 2-methylbutanoate, including its units. **[2]**

$$k = \frac{\ln 2}{t_{1/2}[H^+]}$$

$= \frac{\ln 2}{27(0.75)}$ (values used here must be correct, part (i) $t_{1/2}$)

$= 0.0342$ [1] $\text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$ (may also use $t_{1/2}$ for H_2SO_4)

If student calculates $k' = 0.0257\ \text{min}^{-1}$

Can use initial rates from one experiment – ecf from gradient in (i)

Rate $= k[H^+][\text{Ester}]$

$4.67 \times 10^{-4} = k(0.75)(0.015)$ – using HCl values

$k = 0.0415\ \text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$

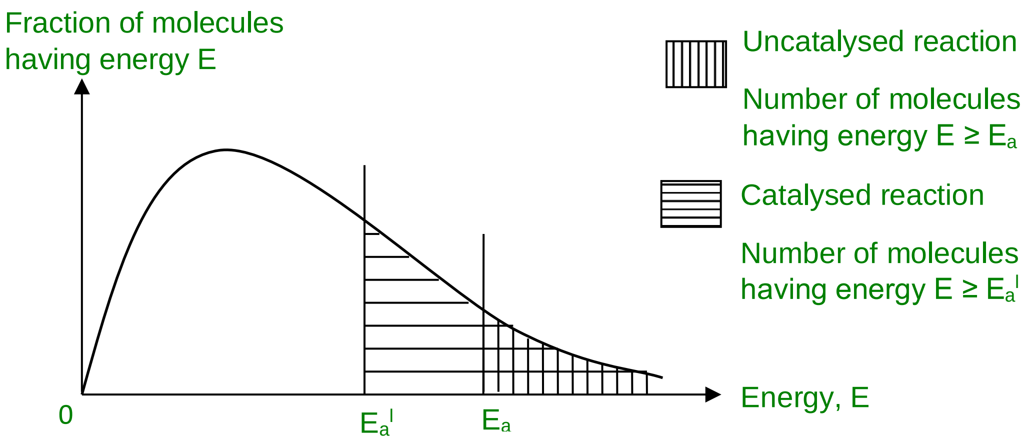
OR

$9.33 \times 10^{-4} = k(1.5)(0.015)$ – using H_2SO_4 values

$k = 0.0415\ \text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$

(iii) In the absence of an acid, the hydrolysis of the ester is very slow.

With the aid of a relevant diagram, explain how the rate constant would change if the acid was removed. **[3]**



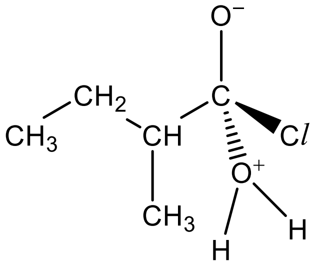
With the absence of the catalyst, the activation energy was larger than the catalysed reaction pathway. The proportion of particles with energy equal to or greater than the activation energy is smaller.[1] The frequency of effective collisions decreases and hence the rate constant decreases[1].

(e) Ethyl 2-methylbutanoate can also be formed using 2-methylbutanoyl chloride and ethanol.

The reaction takes place under anhydrous conditions as 2-methylbutanoyl chloride undergoes hydrolysis in water to form 2-methylbutanoic acid.

The hydrolysis of 2-methylbutanoyl chloride occurs via a two-stage mechanism:

- The first stage (the addition stage of the reaction) involves a nucleophilic attack on the partial positive carbon atom by one of the lone pairs of electrons on the oxygen atom of a water molecule, giving intermediate **E**.



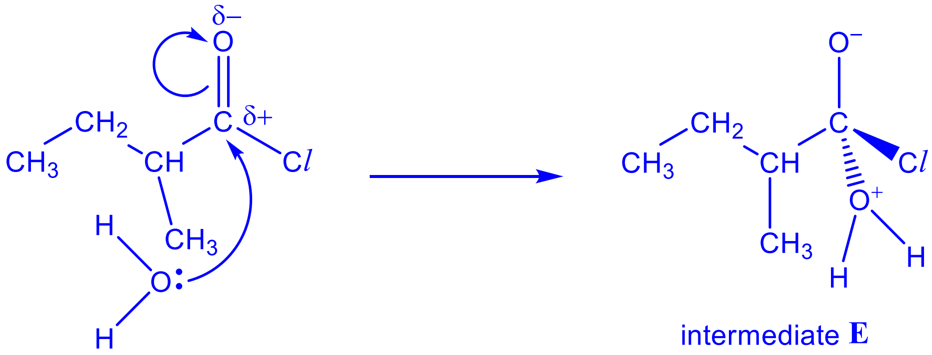
intermediate **E**

The second stage (the elimination stage) happens in two steps.

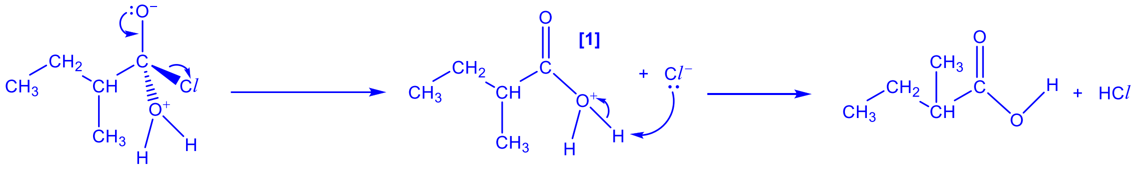
1. The carbon-oxygen double bond reforms with a chloride ion as the side product.
2. A hydrogen ion is removed by the chloride ion to give 2-methylbutanoic acid and hydrogen chloride.

Outline the mechanism for this reaction, given that intermediate **E** is formed after the first stage. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows. **[3]**

First stage



Second stage

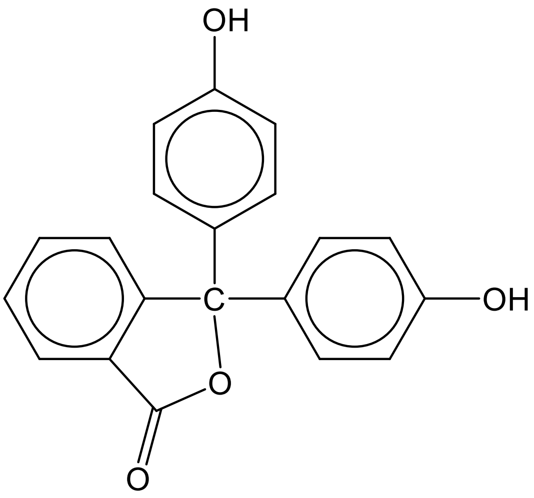


[Total: 23 marks]

Section B

Answer **one** question from this section.

4 Phenolphthalein, a type of triarylmethane dye, is a common indicator used in acid-base titrations.



Phenolphthalein

In its uncharged form, aqueous phenolphthalein is colourless. At pH of 8.2 and above, both phenol groups are deprotonated to form a pink solution.

(a) The pK_b for trimethylamine, $(CH_3)_3N$, at 25 °C is 4.19.

(i) Trimethylamine can behave as a Lewis base. Use the reaction of trimethylamine with aluminium chloride to illustrate this behaviour, writing the equation for the reaction that occurs. **[1]**

$(CH_3)_3N + AlCl_3 \rightarrow (CH_3)_3N{-}AlCl_3$

(ii) Calculate the pH of an aqueous solution of 0.20 mol dm^{-3} trimethylamine solution. **[1]**

$K_b = 10^{-4.19} = 6.46 \times 10^{-5}$ mol dm^{-3}

$[OH^-] = \sqrt{6.46 \times 10^{-5} \times 0.2} = 3.59 \times 10^{-3}$ mol dm^{-3}

pOH = 2.44, pH = 11.56

(iii) Calculate the pH of the resulting solution when 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution and 5 cm^3 of 0.10 mol dm^{-3} HC*l* solution are mixed. **[2]**

Amount of trimethylamine remaining = $2 \times 10^{-3} - 5 \times 10^{-4} = 1.5 \times 10^{-3}$ mol

Amount of salt formed = 5×10^{-4} mol

$\text{pOH} = \text{p}K_b + \lg \text{[salt]/[base]} = 4.19 + \lg\left(\left[\frac{5 \times 10^{-4}}{\frac{15}{1000}}\right] / \left[\frac{1.5 \times 10^{-3}}{\frac{15}{1000}}\right]\right) = 3.71$

pH = 10.29

(iv) Calculate the pH of the resultant solution when 20 cm^3 of 0.10 mol dm^{-3} HCl solution is added to 10 cm^3 of 0.20 mol dm^{-3} trimethylamine solution. **[2]**

Amt of salt formed = 2×10^{-3} mol

[salt] = $2 \times 10^{-3} / (10+20) = 0.0667$ mol dm^{-3}

[conj. Acid] = [salt] = 0.0667 mol dm^{-3}

K_a of conj acid = $K_w/K_b = 1.55 \times 10^{-10}$ mol dm^{-3}

$[H^+] = \sqrt{1.55 \times 10^{-10} \times 0.0667} = 3.21 \times 10^{-6}$

pH = 5.49

(v) Explain why phenolphthalein would not be a suitable indicator for the titration of trimethylamine with HCl. **[1]**

The working range of phenolphthalein does not coincide with the equivalence point pH / region of rapid pH change in the titration curve / vertical section of the titration curve.

OR

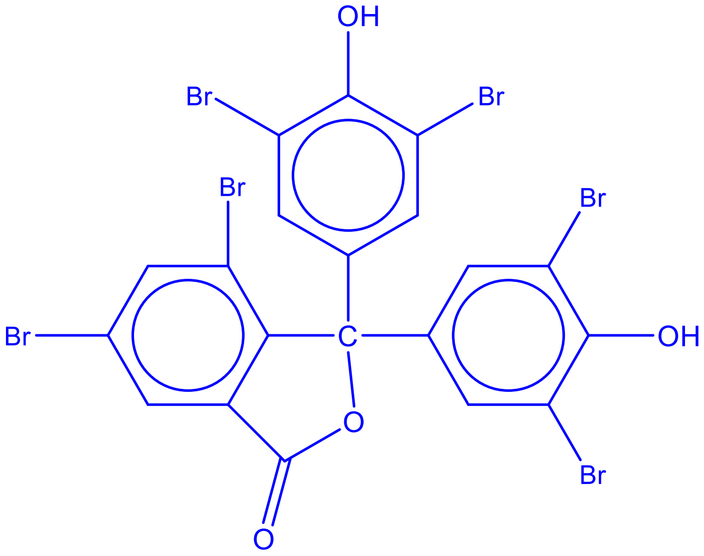
Phenolphthalein will turn colourless at pH 8.2 before the equivalence point is reached.

(vi) Methylamine has a pK_b of 3.36. Suggest a reason for the difference in basicity between methylamine and trimethylamine. **[1]**

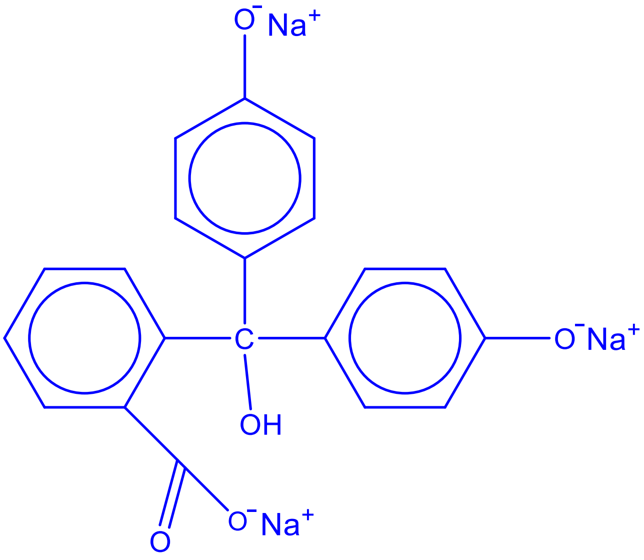
Trimethylamine is less basic than methylamine due to the steric effects of the 3 bulky methyl groups, hence it cannot accept protons easily.

(b) Draw the structural formula of the product formed when phenolphthalein reacts with each of the following reagents:

(i) excess Br_2 in the presence of $AlBr_3$. **[2]**

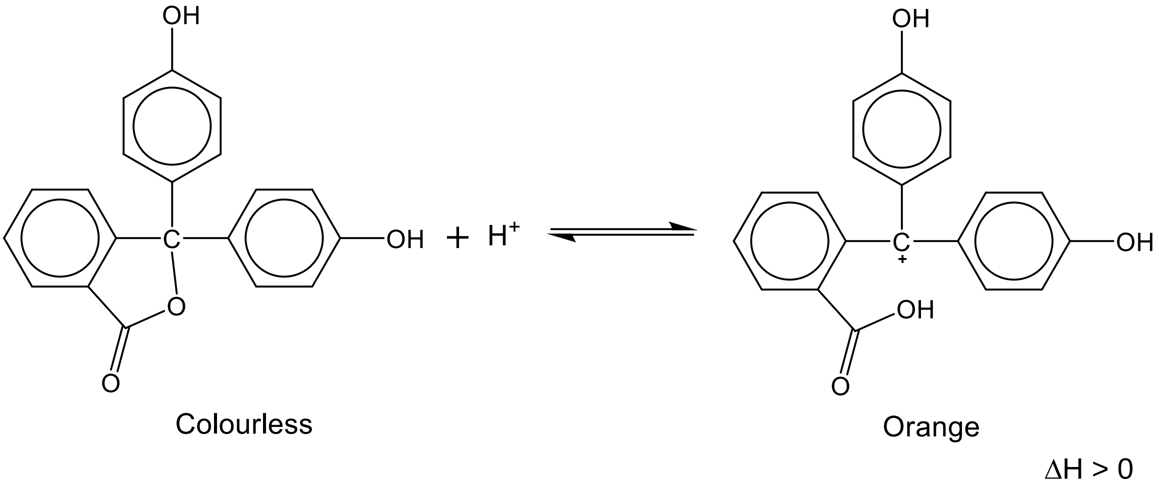


(ii) sodium hydroxide with heat. **[2]**



(c) Under extremely acidic conditions (pH < 0), phenolphthalein can be protonated to form an orange solution. This is an endothermic process.

+



Use Le Chatelier's Principle to explain the following observations.

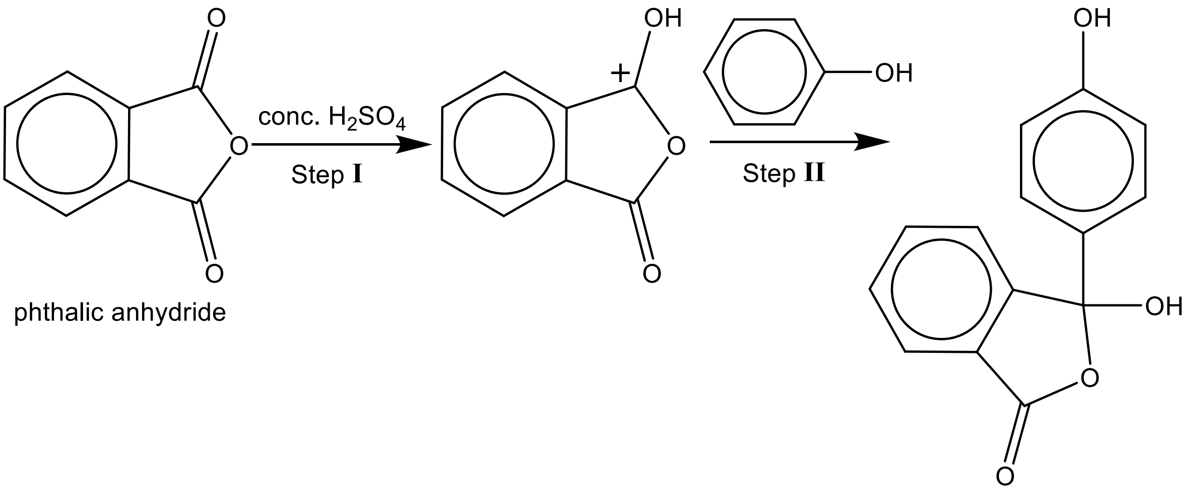
(i) An aqueous solution of phenolphthalein changed from colourless to orange when concentrated sulfuric acid was added to it. **[1]**

The addition of concentrated sulfuric acid increases the concentration of H^+. By LCP, the position of equilibrium will shift right to reduce the concentration of H^+ ions, thus forming more orange phenolphthalein.

(ii) A solution of orange phenolphthalein solution was placed in an ice bath and turned colourless. **[1]**

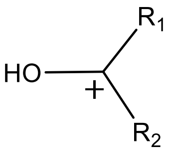
When a solution of phenolphthalein was cooled, the position of equilibrium will shift left to produce heat by favouring the exothermic backwards reaction. Hence more colourless phenolphthalein is formed and the solution turns colourless.

(d) Part of the process in synthesising phenolphthalein involves the reaction of phthalic anhydride according to the reaction scheme below.

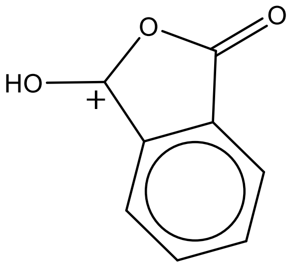


(i) Name and describe the type of mechanism in Step **II**.

You may use

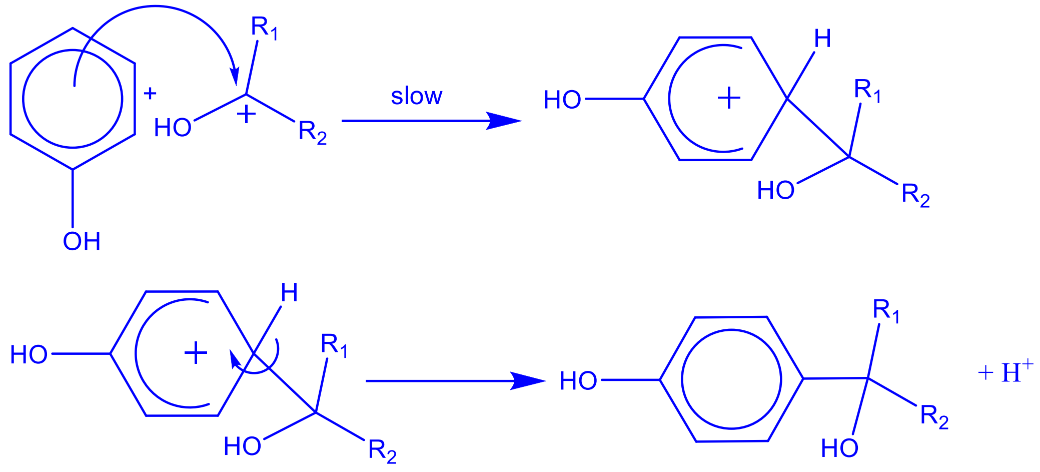


to represent

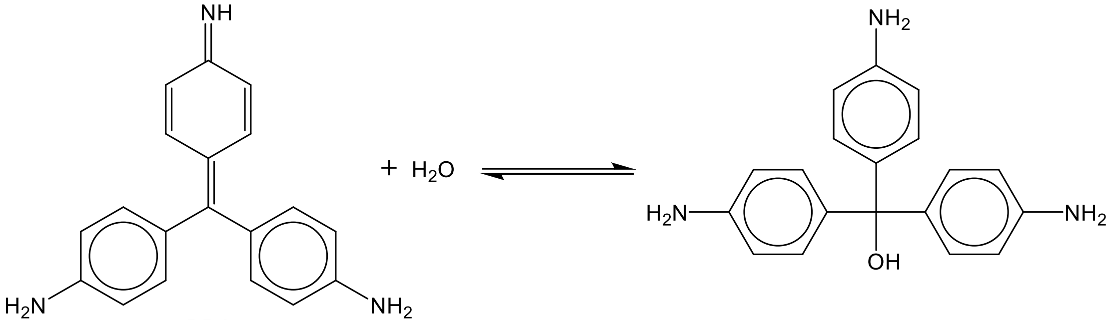


[3]

Electrophilic substitution



(e) Pararosaniline (PRA), another triarylmethane dye, reacts with water to form acidified pararosaniline (APRA).



PRA

APRA

0.0040 mol of PRA was dissolved in 25.0 cm^3 of water and the solution allowed to reach equilibrium. After equilibrium was reached, the concentration of APRA was found to be 0.10 mol dm^{-3}.

Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O] = 55.5$ mol dm^{-3} throughout. **[3]**

$K_c = [APRA] / \{[PRA][H_2O]\}$

$[PRA]_{initial} = 0.004 / 25 \times 1000 = 0.16$ mol dm^{-3}

	PRA	+	H_2O <->	APRA
Initial / mol dm^{-3}	0.16		55.5	0
Change / mol dm^{-3}	-0.10		0	+0.10
Final / mol dm^{-3}	0.06		55.5	0.10

K_c = 0.10 / (0.06 x 55.5) = 0.0300 mol^{-1} dm^3

[Total: 20 marks]

5 Manganese is a highly abundant transition metal in the Earth's crust.

(a) The atomic radii of transition elements is relatively invariant. Explain. **[2]**

Electrons are added to **inner** 3d subshell. The inner 3d electrons **effectively shield** the outer 4s electrons from the nucleus, **cancelling the effect** of the increasing nuclear charge due to increasing proton number across the period.

Thus, the **increase** in effective nuclear charge becomes **insignificant**.

Hence atomic radii remains relatively invariant.

(b) Manganese sulfate, $MnSO_4$, is often added to soils to promote plant growth as manganese is an important trace element crucial to photosynthesis and chloroplast formation.

Data concerning $MnSO_4$ at 298 K, are given in the table below.

Enthalpy change of formation $MnSO_4$ / kJ mol^{-1}	−1365
Enthalpy change of hydration of Mn^{2+} / kJ mol^{-1}	−1851
Enthalpy change of hydration of SO_4^{2-}/ kJ mol^{-1}	−1004
Lattice energy of $MnSO_4$ / kJ mol^{-1}	−2747

(i) Define the term *standard enthalpy change of solution*. **[1]**

The enthalpy change when **one mole of a substance is completely dissolved in a large excess of water** to form an infinitely dilute solution at **298 K and 1 bar**.

(ii) Calculate the enthalpy change of solution of $MnSO_4$ at 298 K. **[1]**

$\Delta H_{soln}^{\ominus} = \Delta H_{hyd}^{\ominus} - \text{L.E.} = (-1851 - 1004) - (-2747) = -108$ kJ mol^{-1}

(iii) Using your answer in **(b)(ii)**, calculate the amount of heat evolved when 0.005 mol of $MnSO_4$ is dissolved in 60.0 cm^3 of water at 298 K. Hence, determine the final temperature of the solution.

(You may assume that the specific heat capacity of water is 4.18 J g^{-1} K^{-1}) **[2]**

Heat evolved = 0.005 x 108 = 0.54 kJ

Q = mcΔT

ΔT = Q/mc = (0.54x 10^3)/(60x4.18) = 2.15 °C / K

T = 298 + 2.15 = 300 K (3s.f.)

(c) To promote plant growth, 0.0530 mol dm^{-3} $MnSO_4$ solution is added to the soil. In addition, the pH of the soil must be carefully controlled. The pH of the soil cannot exceed 6.5, because it would cause the precipitation of solid manganese (II) hydroxide, which would prevent the plants from absorbing the necessary amount of manganese.

(i) Using the above information, calculate the K_{sp} of manganese (II) hydroxide. **[2]**

pOH = 14 – 6.5 = 7.5

$[OH^-] = 3.16 \times 10^{-8}$ mol dm^{-3}

$Mn(OH)_2(s) \rightarrow Mn^{2+}(aq) + 2OH^-(aq)$

$K_{sp} = [Mn^{2+}][OH^-]^2 = (0.0530) \times (3.16 \times 10^{-8})^2 = 5.29 \times 10^{-17}$ mol^3 dm^{-9}

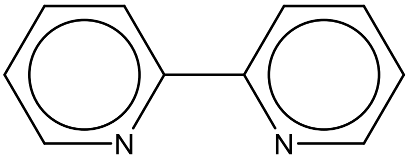
(ii) While the pH of the soil cannot exceed 6.5 in order to promote manganese intake in plants, it cannot fall too low either. Suggest a reason. **[1]**

The soil would be too acidic and may damage the roots of plants.

OR

Too much manganese would be absorbed and it is biologically toxic when in excess amounts.

(d) Manganese can also form complexes. One such complex is $[Mn(C_{10}H_8N_2)_3]^{2+}$, where $C_{10}H_8N_2$ is the bipyridine molecule. Bipyridine acts as a bidentate ligand and has the structure shown below.



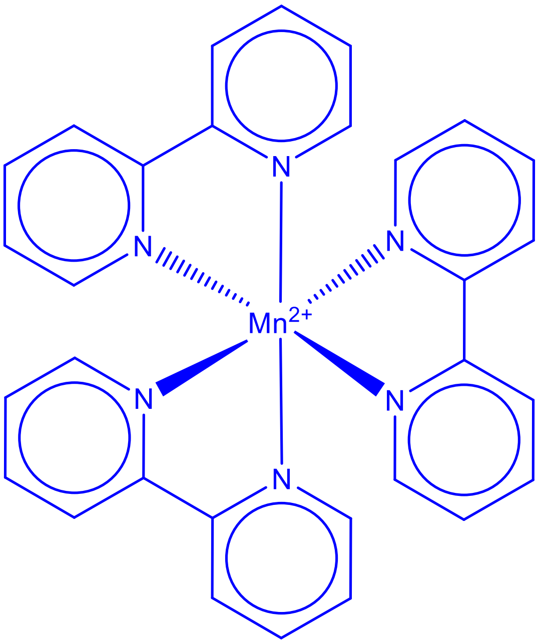
Bipyridine

(i) Describe and explain the features of the bipyridine molecule that enable it to act as a ***bidentate*** ligand. Hence, state the type of bond formed between the ligand and the central manganese ion. **[2]**

There are two nitrogen atoms, each with a lone pair of electrons, which can be donated to vacant low-lying orbitals of the manganese ion to form 2 dative bonds.

(ii) State the shape of the $[Mn(C_{10}H_8N_2)_3]^{2+}$ complex and draw its structure. **[2]**

Shape: Octahedral



(e) Compound **A** has the molecular formula $C_{10}H_{13}Cl$. It reacts with NaOH under aqueous conditions and heat to form **B**, $C_{10}H_{14}O$. **A** does not react with aqueous Br_2.

B does not react with hot acidified potassium dichromate. **B** reacts with hot acidified potassium manganate to form **C**, $C_{10}H_{12}O_3$.

In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**, $C_{10}H_8O_2$.

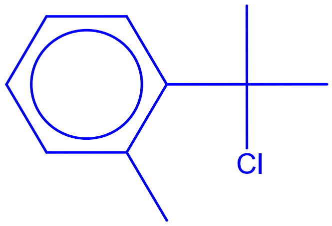
Deduce the structures of **A** – **D**, and explain the chemistry of the reactions described. **[7]**

Observations	**Deductions**
Reacts with NaOH under aqueous conditions to form B, $C_{10}H_{14}O$.	Cl is substituted by OH Nucleophilic substitution. Alcohol formed. A is alky chloride
A does not react with aqueous Br_2.	No alkene present.
B does not react with acidified potassium dichromate.	OH group cannot be oxidised, alcohol is a tertiary alcohol

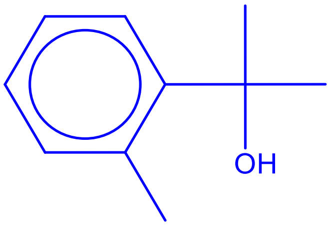
B reacts with hot acidified potassium manganate to form **C**, $C_{10}H_{12}O_3$.	Since –OH group is tertiary alcohol and cannot be oxidised, it does not react with $KMnO_4$. Hence, must be some other form of oxidation. Cannot be alkene due to earlier test. Since 2 H was lost and 2 O was added, then most likely to be <u>side chain oxidation</u> of CH_3 on benzene to form -<u>COOH</u>. Benzene ring present.
In the presence of concentrated sulfuric acid, **C** reacts to form a sweet smelling compound **D**, $C_{10}H_8O_2$.	<u>Condensation reaction.</u> D is an <u>ester</u>. Internal condensation occurred between the OH group and the COOH group. This implies the <u>two groups must be next to each other on the benzene ring</u>.

Structures

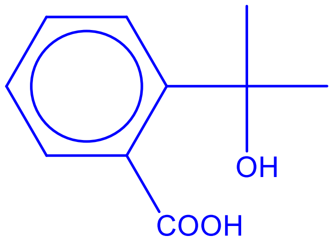
A



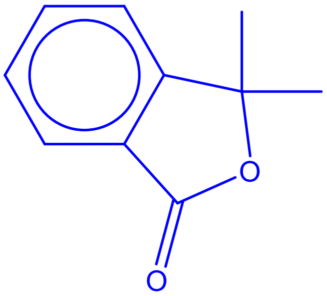
B



C



D



[Total: 20 marks]

END OF PAPER

H2 Chemistry SAJC Prelims Paper 4 Review

1 **To standardise a 0.03 mol dm^{-3} of iron(III) chloride solution and determine the concentration of sodium thiosulfate solution.**

(a) Planning

FA1 is a standard solution containing 0.03 mol dm^{-3} of $FeCl_3$ solution.

You are to design an experiment to show how **FA1** is prepared using solid $FeCl_3$.

You are provided with :

a solid sample of approximately 1.50 g of $FeCl_3$ (M_r = 162.3),

250 cm^3 volumetric flask and

the usual laboratory apparatus

In your plan, you should include details on:

- the mass of $FeCl_3$(s) you use with justification,
- the apparatus you would use, and
- the procedures which you would follow.

Do not carry out this plan as FA1 is provided for you to continue with 1(b).

To make standard solution, a 250 cm^3 volumetric flask is used.

Amount of $FeCl_3$ in 250 cm^3 = 0.03 x 250 / 1000 = 7.50 × 10^{-3} mol

Mass of $FeCl_3$ = 7.50 × 10^{-3} x 162.3 = 1.22 g

Procedure:

1. Weigh accurately about 1.22 g (2 d.p) of $FeCl_3$ into a dry clean weighing bottle.
2. Dissolve the solid using distilled water (~ 50 cm^3) in a 100 cm^3 beaker.
3. Transfer the solution after ensuring all the solid has dissolved. Rinse the weighing bottle and beaker with water and transfer all washings into a 250 cm^3 volumetric flask to ensure quantitative transfer
4. Top up the solution with distilled water to the 250 cm^3 mark.
5. Stopper and shake well to obtain a homogenous solution. Label this solution **FA 1.**

procedures 1-5.

[3]

(b) In addition to **FA1**, you are also provided with the following:

FA2 is 0.060 mol dm^{-3} potassium iodide, KI.

FA3 is aqueous sodium thiosulfate, $Na_2S_2O_3$.

When **FA1** is combined with **FA3**, a complex, $[Fe(S_2O_3)_2]^-$, is formed.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^-(aq)$

To 1 cm^3 of **FA3** in a test–tube, add 2–3 drops of **FA1** and shake them thoroughly. State the colour of the complex formed.

(Pale) purple/ lilac /Pink/ violet. [1]

(c) A student aimed to determine the concentration of **FA3** using volumetric analysis involving the use of **FA1** and **FA2.**

Reaction 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Using the above reactions, the student planned and carried out the following procedure.

1. Fill a 50.00 cm^3 burette with **FA3** solution.
2. Using a 10 cm^3 measuring cylinder, measure 5 cm^3 of **FA1** and place it in a 100 cm^3 conical flask.
3. Using another 10 cm^3 measuring cylinder, measure 5 cm^3 of **FA2** into the conical flask.
4. Run **FA3** from the burette into the conical flask. Near the endpoint, when the brown solution becomes pale, add 2 drops of starch.
5. Continue adding **FA3** slowly, the endpoint is reached when the solution **first becomes colourless**.
6. Record the titration results, to an appropriate level of precision, in an appropriate table and repeat the experiment once more.

(i) Carry out the student's procedure **twice only** to obtain two titration readings. **Your titre values need not be consistent**.

Note: After the end point is reached, you may observe the appearance of the coloured mixture again. There is no need to titrate any further.

Record your titration in an appropriate table in the space below.

	1	2
Final burette reading/ cm^3	14.50	28.60
Initial burette reading/ cm^3	0.00	14.50
Volume of **FA3**/ cm^3	14.50	14.10

[2]

(ii) Planning

A teacher commented that it is appropriate for the student to use 5 cm^3 instead of 25 cm^3 of **FA1** for this titration. Justify the teacher's comment using suitable calculations.

Assume the concentration of **FA3** is 0.006 mol dm^{-3}.

Reaction 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

No. of moles of 5 cm^3 of **FA1** = 5 / 1000 x 0.03 = 1.5×10^{-4} mol
No. of moles of I_2 = 1.5×10^{-4} / 2 = 7.5×10^{-5} mol
No. of moles of $S_2O_3^{2-}$ = 7.5×10^{-5} x 2 = 1.5×10^{-4} mol

If the concentration of **FA3** is 0.006 mol dm^{-3},

Approximate titre volume = 1.5×10^{-4} / 0.006 x 1000 = 25 cm^3

OR

If 25 cm^3 of **FA1** = 25/ 1000 x 0.03 = 7.5×10^{-4} mol

No. of moles of $S_2O_3^{2-}$ = 7.5×10^{-4} mol
Approximate titre volume = 7.5×10^{-4} / 0.006 x 1000 = 125 cm^3

If 25 cm^3 of **FA1** is used, the titre value will be 5 times (125 cm^3) and exceeds the capacity of the burette. It results in high inaccuracy as refilling of burette is required.

[2]

(iii) **Planning**

Justify whether the amount of **FA2** that the student used in step **3** of the procedure in **1(c)** is sufficient to determine the concentration of **FA3**.

No. of moles of KI required = 1.5×10^{-4} mol
Minimum volume of **FA2** = 1.5×10^{-4} / 0.06 x 1000 = 2.5 cm^3
To ensure excess **FA2** (KI), add 5 cm^3 of KI (accept 3 – 5 cm^3). [1]

(iv) The student did the titration several times but could not get consistent titre values of **FA3**. Based on your observation during titration, suggest a reason why.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^-(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

After the dark blue colouration disappear to get the colourless solution, the purple colour reappeared because the position of equilibrium of reaction 1 shift left due to the decrease in $[S_2O_3^{2-}]$ during the titration. This result in the increase in the $[Fe^{3+}]$ which reacts with excess KI to produce more I_2. The presence of I_2 in starch is revealed as the reappearance of blue black colouration. Hence, it is difficult to judge the correct end point and titration results is consistent.

[1]

(v) Suggest another reason why the results obtained are not reliable.

The limiting reagent $FeCl_3$ was measured using a 10 cm^3 measuring cylinder which has a **low precision**. Hence, the amount measured in each titration may vary slightly.

OR

The volume of **FA1** and **FA2** used are small, this would results in high percentage error. [1]

(vi) The student performed the titration and had a titration value of 18.50 cm^3. Given the errors (uncertainties) associated with each reading using a measuring cylinder and burette are ±0.1 cm^3 and ±0.05 cm^3 respectively, calculate the maximum total percentage error (uncertainty) from the apparatus in the titration.

Percentage uncertainty (error) in using the **measuring cylinder**
= (± 0.1 / 5.0) x 100 % = ± **2.00 %**

Each measuring cylinder reading has an uncertainty (error) of ± 2.00 %.
Since two readings using measuring cylinder are made, total percentage error from measuring cylinder is **2.00 x 2 = ± 4.00 %**

Percentage uncertainty (error) in using the **burette**
= $\frac{(\pm 0.05 \text{ x } 2)}{18.50}$ x 100 % = ± **0.541 %**

Hence **maximum percentage error (uncertainty)** from the apparatus in the experiment
= (± 4.00) + (± 0.541) = ± **4.54 %** (3 significant figures) [3]

[Total: 14 marks]

2 To investigate the kinetics of the reaction between iron(III) ions and iodide ions

In this experiment, you are investigating the rate of reaction between iron(III) ions and iodide ions.

You are provided with:

FA1 is 0.03 mol dm^{-3} of $FeCl_3$ solution

FA2 is 0.060 mol dm^{-3} potassium iodide, KI

FA3 is sodium thiosulfate, $Na_2S_2O_3$

The reaction is started by mixing a 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**.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^{-}(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

When all the thiosulfate have 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.

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 10.

For each of the five experiments, you will need to include the

- volume of **FA2**, $\mathbf{V_{FA2}}$,
- volume of water, $\mathbf{V_{water}}$,
- calculated squared volume of **FA2**, $(\mathbf{V_{FA2}})^2$,
- reaction time, ***t*** to nearest second, and
- calculated rate in mol dm^{-3} s^{-1}

Record all calculated values to 3 significant figures.

(a) Method

Experiment 1

1. Use the measuring cylinders to measure the following:
    - 20 cm^3 of **FA1**
    - 20 cm^3 of **FA3**
    - 1 cm^3 of starch indicator
2. Using another measuring cylinder, measure 10 cm^3 of **FA2**.
3. Pour the measured **FA1** and starch into a dry 100 cm^3 beaker.
4. Pour in the **FA3**, followed by **FA2** immediately into the same beaker. Start the stopwatch on adding **FA2**.
5. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
6. The mixture turns brown and then yellow before turning a blue–black colour. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
7. Record the time to the nearest second in the space on page 10.
8. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

Experiment 2

9. Repeat step **1** in **Experiment 1**.
10. Using a measuring cylinder, add 2 cm^3 of **FA2.** Make up the volume to 10 cm^3 using deionised water using another measuring cylinder.
11. Pour the measured **FA1**, starch and deionised water into a dry 100 cm^3 beaker.
12. Pour in the **FA3**, followed by **FA2** immediately into the same beaker. Start the stopwatch on adding **FA2**.
13. Stir the mixture and place the beaker on the printed page on page 2 of the insert.
14. Stop the stopwatch when this blue–black colour appears and obscures the wordings.
15. Record the time to the nearest second in the space on page 10. The timing should not exceed 6 minutes.
16. Wash the beaker thoroughly with water and carefully dry the beaker with paper towel.

Experiments 3−5

Carry out three further experiments to investigate the effect of changing the concentration of **FA2** by altering the volume of aqueous potassium iodide, **FA2**, used.

You should use a volume of **FA2** that is at least 2 cm^3 and the total volume of the reaction mixture must always be 51 cm^3.

2 **(a)** With reference to **1(b)**, consider the colour change observed when **FA2** was added to the solution prepared in step **6** of **Experiment 1** before the blue–black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved.

Reaction 1: $Fe^{3+}(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)_2]^{-}(aq)$

yellow purple

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 brown solution is due to a mixture of purple complex $[Fe(S_2O_3)_2]^{-}$ and yellow $Fe^{3+}(aq)$.

Since the I_2 formed reacted immediately with thiosulfate, $[S_2O_3^{2-}(aq)]$ decreased, and the position of equilibrium in Reaction 1 shifts left.

Thus, concentration of $[Fe(S_2O_3)_2]^{-}$ decreased. Hence, the colour of the solution gradually fades until the solution became pale yellow due to Fe^{3+}.

[2]

2 **(b)** Show, by means of calculation, that the change in the concentration of I^-, $\Delta[I^-]$, which occurred when the blue–black colour appeared was 2.35×10^{-3} mol dm^{-3}.

Assume the concentration of $Na_2S_2O_3$ to be 0.006 mol dm^{-3}.

Reaction 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

$\text{Amount of } S_2O_3^{2-} = \frac{20}{1000} \times 0.006 = 1.20 \times 10^{-4}$ mol

$\Delta[I^-] = \frac{1.20\times10^{-4}}{\frac{51}{1000}} = 2.35 \times 10^{-3}$ mol dm^{-3}

[1]

(c) **Results**

The rate of the reaction can be calculated as shown.

$$\text{rate} = \frac{\Delta[I^-]}{\text{reaction time}}$$

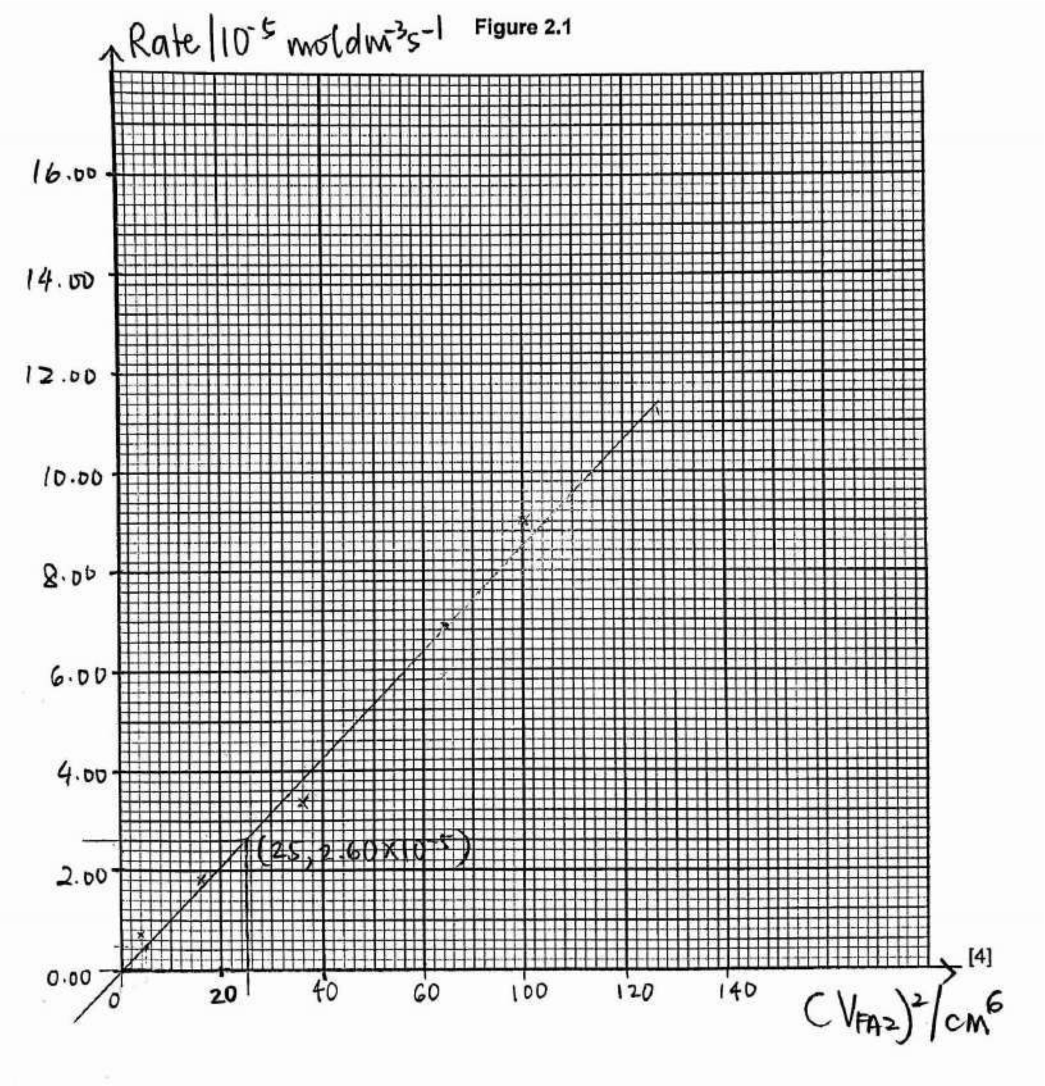
Calculate the rate of reaction for each experiment and complete your table.

Expt	V_{FA2}/ cm^3	V_{water}/ cm^3	t /s	$(V_{FA2})^2$/ cm^6	Rate / 10^{-5} mol dm^{-3} s^{-1}
1	10.0	0.0	26	100	9.04
2	2.0	8.0	304	4.00	0.773
3	4.0	6.0	128	16.0	1.84
4	6.0	4.0	69	36.0	3.41
5	8.0	2.0	34	64.0	6.91

[4]

2 (d) (i) Plot a graph of rate on the y–axis against $(V_{FA2})^2$ on the x–axis on the grid in **Figure 2.1**. Draw the best fit line taking account of all the plotted data points.

Figure 2.1



[4]

(d) (ii) Explain why the volume of **FA2** in each experiment can be used as the [I⁻].

Since total volume of the mixture is kept constant by adding deionised water, volume of **FA2** used is proportional to [I⁻]. [1]

2 **(d)** **(iii)** Deduce the order of reaction with respect to [I$^-$]. Use evidence from your graph to support your deduction.

Observe from the graph, any one of the following:

- the graph is linear/gradient and pass through origin is a constant, showing that rate ∝ squared volume/ concentration of **FA2/** state that it is a graph of rate against [I$^-$]^2.

OR

- the rate increase by xxx for every additional xxx cm^3 of **FA2** used
- when squared volume of **FA2** double, rate double (or other multiples)

✓ Therefore, the reaction is second order with respect to [I$^-$]

[1]

(e) **(i)** Use your graph and the formula in **2(c)** to calculate the time that the reaction would have taken if 5.0 cm^3 of **FA2** had been used. Show your working clearly.

If 5.0 cm^3 of **FA2** is used, $V_{FA2}{}^2$ = 25 cm^6, rate = 2.6 x 10^{-5} mol dm^{-3} s^{-1} (read from graph) [1]

Time = Δ[I$^-$]/ rate $= \frac{2.35x\ 10^{-3}}{2.6\ x\ 10^{-5}}$ = 90.4 s (to 3 sf or nearest seconds).

time = ... [2]

(d) **(ii)** Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions in the reaction mixture if 5.0 cm^3 of **FA2** had been used.

[Fe^{3+}] = $\frac{0.030\times20.0}{51.0}$ = 0.0118 mol dm^{-3}

[I$^-$] = $\frac{0.060\times5.0}{51.0}$ = 5.88 x 10^{-3} mol dm^{-3}

initial [Fe^{3+}] = ...

initial [I$^-$] = ... [1]

2 **(d)** **(iii)** Given that the reaction is first order with respect to [Fe^{3+}], calculate the rate constant.

rate = $k[Fe^{3+}][I^-]^2$

Ecf order of reaction from d(iii)

$$k = \frac{rate}{[Fe^{3+}][I^-]^2}$$

$$= \frac{2.6 \times 10^{-5}}{(0.00118) \times (5.88 \times 10^{-3})^2}$$

= 637 [1] $mol^{-2}\ dm^{6}\ s^{-1}$

rate constant = ... [2]

(f) At the end of Experiment **1**, a student washed the beaker and used it immediately for Experiment **2**. State and explain how the student's action would affect the time ***t*** for Experiment **2**.

<u>Dilution</u> of the reacting mixture will occur due to **<u>residual water</u>** left after washing.~~.~~ Time, **t**, for experiment 2 will be **<u>longer/increase</u>**.

[2]

(g) List 1 possible source of experimental errors and suggest the corresponding improvement to reduce the experimental error.

	experimental errors	improvements
1	The temperature of the set-up may not be constant throughout the experiment. A change of temperature can affect the rate and the time recorded.	Performed the experiment in a water bath with controlled temperature
2	It was difficult to start the stopwatch while reagents was added. The time for the cross to be obscured would thus be inaccurately determined.	Allow the stopwatch to run and add reagents at a convenient time.

[2]

[Total: 22 marks]

3 Qualitative Analysis

You are provided the following reagents and the *Qualitative Analysis Notes* on page 21 and 22.

FA1 is 0.03 mol dm^{-3} of $FeCl_3$ solution

FA4 is 6% volume H_2O_2

FA5 is 0.00215 mol dm^{-3} of **X^-** solution

(a) You are to perform the tests described in **Table 3.1** and record your observations in the same table.

Your answers should include

- details of colour changes throughout the tests 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 3.1

Test	Observations	Explanation (teacher's notes)
i. To 5 cm^3 of **FA1**, add aqueous silver nitrate in excess. Filter the mixture.	White ppt formed.The solution remained pale yellow/ colourless.	Cl^- is present.
Separate the filtrate into three test tubes for **(ii)**, **(iii)** and **(iv)**.	The filtrate was a pale yellow/ colourless solution. The residue was a white ppt.	The filtrate contains Fe^{3+} ions. The white ppt is $AgCl$.
Place the filter funnel containing the residue on a new test tube, add aqueous ammonia over the residue.	The white ppt was soluble aqueous ammonia to form a pale yellow/colourless solution. With HNO_3, white ppt formed and	Cl^- is present. $[Ag(NH_3)_2]^+$ is formed. It should be a colourless solution but the ppt is covered with traces of Fe^{3+}, hence the solution appears pale yellow.

Add HNO_3 dropwise to the filtrate until no more change.	white ppt insoluble in excess nitric acid in a colourless solution.	Reversal of equilibrium. HNO_3 neutralise the NH_3 and hence AgCl is formed again.
ii. To a new test tube containing 1 cm^3 of **FA4**, add a few drops of filtrate from the first test tube from **(i)**. Wait and observe the effervescence. Test for the identity of the gas.	The pale yellow solution turned light brown/orange. Effervescence of colourless, odourless gas observed. Gas relighted a glowing splinter. Oxygen evolved.	**FA4** acts an reducing agent as oxygen is evolved. Hence, hydrogen peroxide FA4 undergoes oxidation.
iii. To the second test tube containing 1 cm^3 of filtrate from **(i)**, add aqueous sodium hydroxide till excess. Add 1 cm^3 of **FA4**.	Brown/ orange ppt, insoluble in excess aqueous NaOH. The brown ppt insoluble in **FA4**. Vigorous effervescence of colourless, odourless gas is seen. The gas relighted a glowing splinter. Oxygen evolved.	Fe^{3+} is present. $Fe(OH)_3$ cannot be reduced by FA4. However, more O_2 released as H_2O_2 exists as HO_2^- and have a greater reducing ability (gets oxidised more easily by remaining Fe^{3+}).
iv. To the last test tube containing 1 cm^3 of filtrate from **(i)**, add 1 cm^3 of **FA5**.	(Blood) red solution formed.	Fe^{3+}(aq) undergoes a ligand exchange.
v. To a new test tube containing a fresh sample of **FA1**, test the pH of the solution with a Universal Indicator paper. Add aqueous ammonia dropwise. Add **FA1** dropwise to dissolve the precipitate formed. Stop adding **FA1** once the precipitate disappears.	The UI paper turned red/brown or. The pH was 1 or 2. Brown/ orange ppt formed on adding NH_3. A yellow/ orange/ light brown solution was formed on adding FA1.	Fe^{3+} solution is acidic because of appreciable hydrolysis. Ammonia is neutralised by the acidic Fe^{3+}. There are no excess Fe^{3+}. Ideally, the pH drops to 7. This is how neutral $FeCl_3$ is made.

[6]

3 **(b)** With reference to the observation made in test **(i),** identify the ppt and explain its solubility in aqueous ammonia.

The white ppt is $AgCl$.[1] The ppt is soluble in aqueous ammonia because of the formation of complex[1] , $[Ag(NH_3)_2]^+$. [2]

(c) In the presence of strong base,

$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$

Electrode Reaction	$E^\ominus$/V
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2$	–0.56
$O_2 + 2H_2O + 2e \rightleftharpoons H_2O_2$	+0.68
$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O$	+1.23
$O_2 + H_2O + 2e \rightleftharpoons HO_2^- + OH^-$	–0.08

With reference to the electrode potential given, explain the difference in the observation for effervescence made when **FA4** is added in test **(ii)** and **(iii)**.

The effervescence is more vigorous for step **(iii)** as the H_2O_2 is in alkaline medium and exists as HO_2^-. HO_2^- is a stronger reducing agent as the $E^\ominus(O_2/HO_2^-)$ is more negative than that of H_2O_2. Hence the $E^\ominus$(cell) is more positive when hydrogen peroxide reacts with Fe^{3+} in alkaline medium.

[2]

(d) Write an equation to explain the colour of the Universal Indicator paper on addition of **FA1** before adding aqueous ammonia.

$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$

$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$

The presence of H^+ result in a pH of 1 or 2. [1]

3 (e) The pH of the resultant solution in test **(v)** is 7. Explain the chemistry behind the changes of pH in test **(v)** when aqueous ammonia is added dropwise followed by **FA1**.

When ammonia is added, the reddish brown ppt of $Fe(OH)_3$ was formed, and the pH was >7.

When more FA1 was added, the H^+ from FA1 neutralised the ammonia, hence the pH dropped to 7 and the ppt disappeared.

(neutralised by the H^+ from the **FA1**.

OR

The ppt disappeared as the OH^- in $Fe(OH)_3$ is removed by H^+.

There are no excess Fe^{3+} to make the solution acidic . Hence, the pH drops to 7.) [2]

(f) Predict what happen when the resultant solution in test **(v)** is added to phenol.

A purple/violet complex is formed. [1]

(g) **Planning**

Thermometry is sometimes used to determine the number of ligands attached to the central metal atom or ion. One of such monodentate ligand is X^- present in **FA5**.

A student performed an experiment to determine the structural formula of the hexa–coordinated complex.

$$[Fe(H_2O)_6]^{3+} + nX^- \rightarrow [Fe(H_2O)_{6-n}X_n]^{3-n} + nH_2O \qquad \Delta H < 0$$

He used varying volumes of **FA1** and **FA5** only, while keeping the total volume of the mixture at 80 cm^3. He recorded the change in temperature.

(i) Outline how you would:

- determine the effect of changing the volumes of **FA1** and **FA5** on the temperature change of the experiment and hence,
- vary the volumes of **FA1** and **FA5** to form the needed hexa–coordinated complex, $[Fe(H_2O)_{6-n}X_n]^{3-n}$.

You are provided with the same solutions, which were used in the test **(iv)** described. **There is no need to perform the experiment.**

No details regarding the use of specific apparatus are required.

[3]

For experiment **1**

A 10 cm^3 portion of **FA1** was added to 70 cm^3 of **FA5**. The mixture was mixed thoroughly and the highest temperature reached was noted down.

The procedure was repeated for experiments **2** to **7** (minimum 5), with the following changes in the volume of **FA1** and **FA5** as stated in the table below.

Experiment	Volume of **FA1** / cm^3	Volume of **FA5** / cm^3	ΔT / °C
1	10	70	
2	20	60	
3	30	50	
4	40	40	
5	50	30	
6	60	20	
7	70	10	

(ii) The student plotted a graph and concluded that n=1 in the structural formula of $[Fe(H_2O)_{6-n}X_n]^{3-n}$. On the axes of **Figure 3.1**, sketch a graph that the student would obtain from your experiment in **3(g)(i)** to draw this conclusion. Indicate the volume of **FA1** that the student would use to reach this conclusion on the x-axis of the graph.

3 (h)

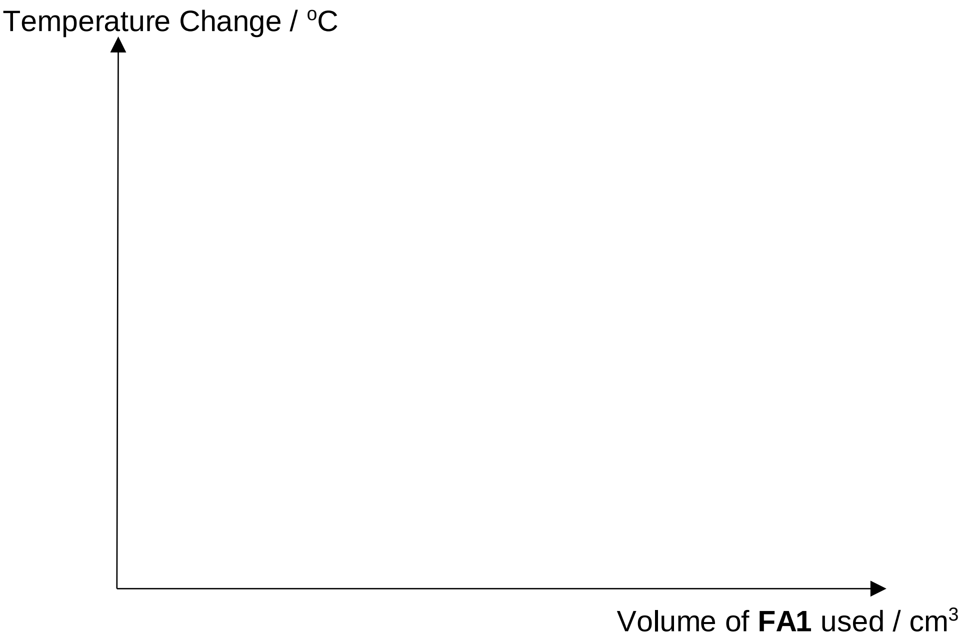
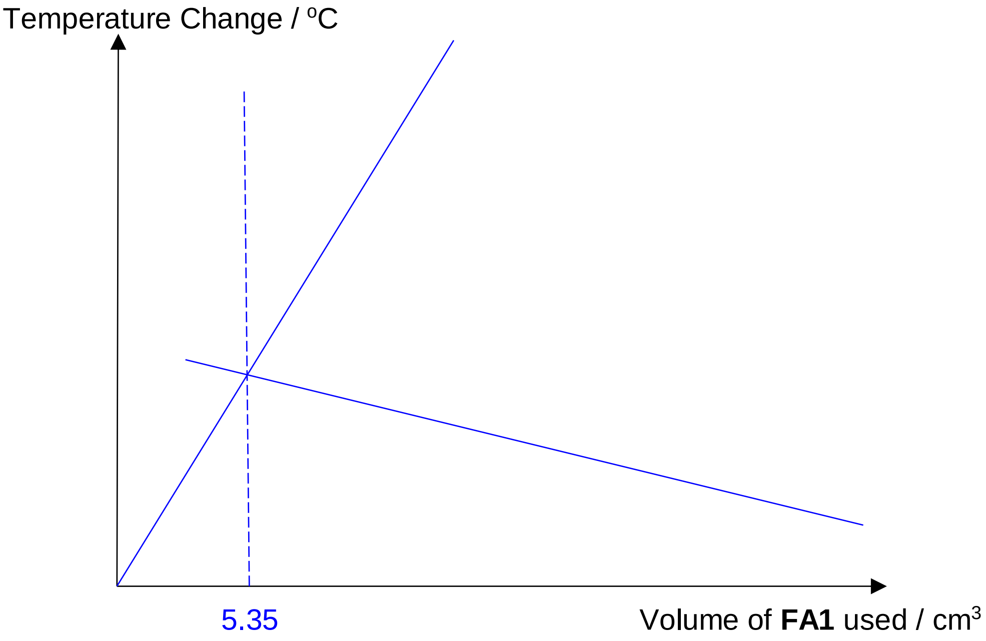


Figure 3.1



Two straight lines drawn

Concentration of **FA1** = 0.03 mol dm^{-3}

Concentration of X^- = 0.00215 mol dm^{-3}

Let the intersection occur at y cm^3 of **FA1**

Amount of **FA1** used $= \frac{y}{1000} \times 0.03 = 3 \times 10^{-5}\ y$ mol

Amount of X^- used $= \frac{80 - y}{1000} \times 0.00215 = (1.72 \times 10^{-4} - 2.15 \times 10^{-6}\ y)$ mol

Since ratio of Fe^{3+} : X^{-} is 1 : 1;

3×10^{-5} y = $1.72 \times 10^{-4} - 2.15 \times 10^{-6}$ y

Intersection occurred at 5.35 cm^3 of FA1

[2]

[Total: 19 marks]

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice

26 September 2019

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 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.

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.

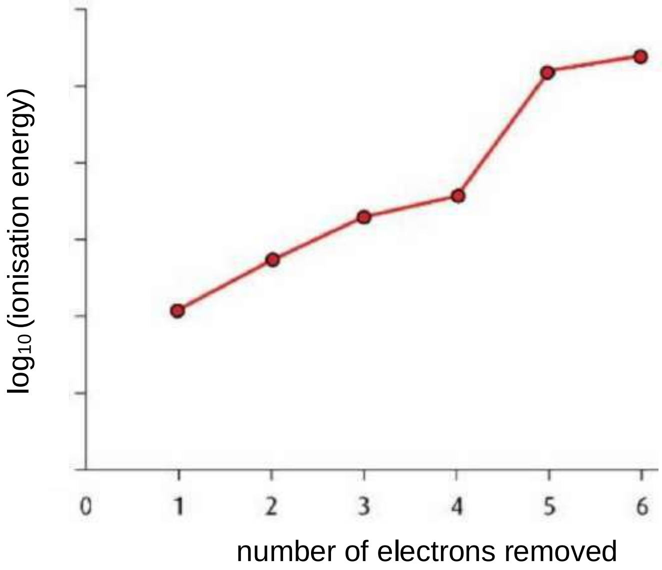
1 Some data of the ions of four unknown elements are given in the table below.

	A^+	B^-	D^{2-}	E^{3-}
mass number	21	20	20	21
number of protons	–	11	9	–
number of electrons	9	–	–	12

Which of the following correctly shows pairs of isotopic and isoelectronic species?

	isotopic	isoelectronic
A	D^{2-}, E^{3-}	B^-, E^{3-}
B	B^-, D^{2-}	A^+, B^-
C	B^-, D^{2-}	B^-, E^{3-}
D	D^{2-}, E^{3-}	A^+, B^-

2 The first six ionisation energies of element **G** are plotted in the graph below.



Which of the following can be deduced from the graph?

A There are 2 quantum shells in element **G**.

B Element **G** is from Group 2 in the Periodic Table.

C The fifth and sixth electrons are removed from the same subshell.

D The identity of element **G** is carbon.

3 For which of the following pairs does the first molecule have a higher polarity than the second molecule?

1 CH_3OH, CH_3I

2 CF_4, CCl_4

3 *cis*-CHF=CHF, *trans*-CHF=CHF

A 1 only

B 1 and 3

C 2 and 3

D 1, 2 and 3

4 Three substances **H**, **I** and **J** have physical properties shown in the table below.

substance	melting point/ °C	boiling point/ °C	electrical conductivity	
			of solid	of liquid
H	801	1413	poor	good
I	2852	3600	poor	good
J	3500 at very high pressure	unable to determine	poor	unable to determine

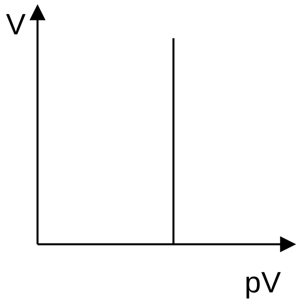
What are the possible identities for substances **H**, **I** and **J**?

	H	**I**	**J**
A	$NaCl$	$AlCl_3$	C (diamond)
B	MgO	$AlCl_3$	C (graphite)
C	$NaCl$	MgO	C (graphite)
D	$NaCl$	MgO	C (diamond)

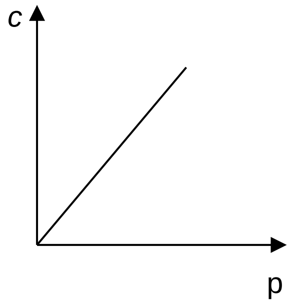
5 Which of the following diagrams correctly describe the behaviour of a fixed mass of an ideal gas at constant temperature?

[*c* is concentration]

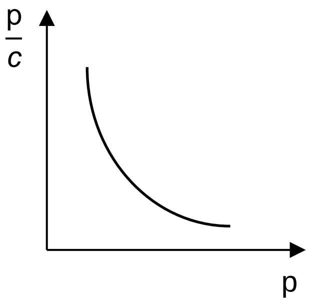
graph 1



graph 2



graph 3



A 2 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

6 In which of the following reactions is the underlined reactant acting as a Lewis acid?

A $\underline{BF_3} + F^- \longrightarrow BF_4^-$

B $AlCl_3 + \underline{Cl_2} \longrightarrow AlCl_4^- + Cl^+$

C $Ag^+ + 2\underline{NH_3} \longrightarrow [Ag(NH_3)_2]^+$

D $H_2O + \underline{HSO_3^-} \longrightarrow H_2SO_3 + OH^-$

7 Which of the following statements is true of the Period 3 chlorides, $NaCl$ to PCl_5?

A The melting points of the chlorides show a continuously decreasing trend.

B The pH of the solutions formed when the chlorides are added to water range from alkaline to acidic.

C Three of the chlorides have simple molecular structures.

D The only chlorides which undergo hydrolysis in water are $AlCl_3$ and $MgCl_2$.

8 The relative abundances of the isotopes of a sample of titanium are shown in the table below.

relative isotopic mass	46	47	48
relative abundance	11.2	10.1	*z*

Given that the relative atomic mass of the sample is 47.862, what is the value of *z*?

A 214.2 **B** 79.1 **C** 78.7 **D** 26.6

9 A metallic salt was found to react exactly with sulfite ions in a 2 : 1 ratio.

In this reaction, the sulfite ion is oxidised as follows.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

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

10 The enthalpy changes for the following reactions are given:

$2Cr(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s)$ $\Delta H_f(Cr_2O_3(s)) = -1120$ kJ mol^{-1}

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H_f(CO(g)) = -110$ kJ mol^{-1}

What is the enthalpy change of reaction for the following reaction, in terms of kJ mol^{-1}?

$$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$$

A – 940 **B** – 870 **C** + 590 **D** + 790

11 An experiment was conducted by reacting propyne with hydrogen gas in a shock tube.

$$CH_3C{\equiv}CH(g) \ + \ 2H_2(g) \ \rightarrow \ CH_3CH_2CH_3(g)$$

The value of ΔG for the reaction is found to be negative at low temperature.

What is the sign of ΔH and ΔS for the above reaction?

	ΔH	ΔS
A	–	–
B	+	–
C	–	+
D	+	+

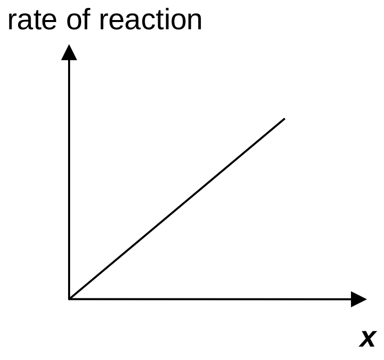
12 The kinetics of the reaction between hydrogen peroxide and acidified iodide ions were investigated.

$$H_2O_2(aq) \ + \ 2H^+(aq) \ + \ 2I^-(aq) \ \rightarrow \ I_2(aq) \ + \ 2H_2O(l)$$

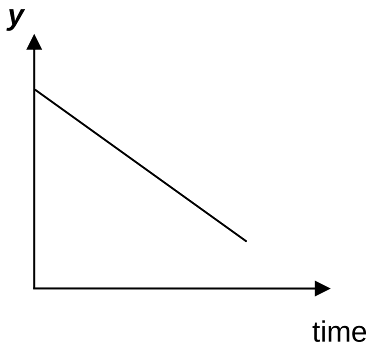
The rate equation was found to be: rate = $k[H_2O_2][I^-]$

Which of the following shows the correct labelling of the ***x***-axis for **Graph I** and ***y***-axis for **Graph II**?

Graph I



Graph II



	x-axis for **Graph I**	***y***-axis for **Graph II**
A	$[I^-]$	$[H_2O_2][I^-]$
B	$[H^+]$	$[I_2]$
C	$[H_2O_2][I^-]$	$[H^+]$
D	$[H_2O_2][H^+]$	$[I^-]$

13 The reaction between HBr and O_2 is thought to occur via a multi-step mechanism:

$HBr + O_2 \rightarrow HO_2Br$ (slow)

$HO_2Br + HBr \rightarrow 2HOBr$ (fast)

$HOBr + HBr \rightarrow Br_2 + H_2O$ (fast)

The overall reaction is given to be $4HBr + O_2 \rightarrow 2Br_2 + 2H_2O$.

Which of the following statements are true?

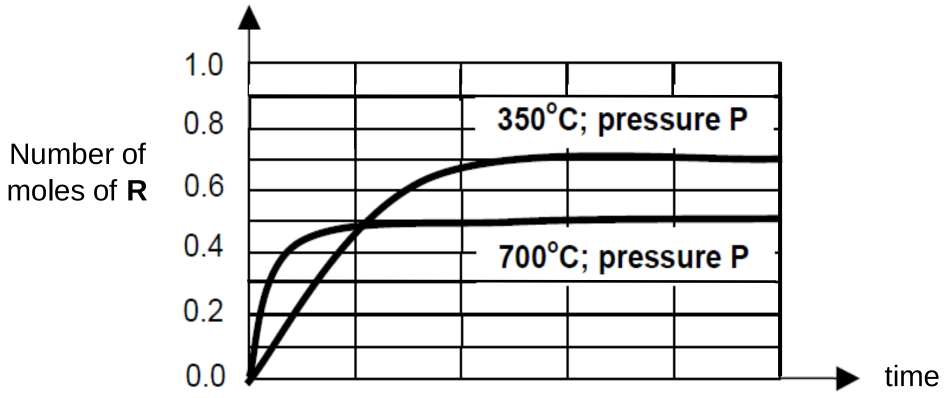
1 The overall order of reaction is 2.
2 HO_2Br is the only intermediate in the reaction.
3 HOBr acts as a catalyst in the reaction.

A 1 only **B** 3 only **C** 1 and 2 **D** 1, 2 and 3

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_c decreases with an increase in temperature.

B The equilibrium is achieved at a faster rate at higher temperatures.

C The enthalpy change for the forward reaction is negative.

D The activation energy of the forward reaction is high.

15 The dissociation constants, K_w, for the ionisation of water at different temperatures are given below.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

temperature / °C	K_w / mol^2 dm^{-6}
0	1.15 x 10^{-15}
25	1.00 x 10^{-14}
50	5.50 x 10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.

B K_w is not affected by changes in temperature.

C The forward reaction is exothermic.

D The pH of water decreases as temperature increases.

16 The following tests were performed on an aqueous solution containing chloride and iodide ions.

step	test	observations
1	Add excess $AgNO_3$(aq).	Mixture of white and yellow precipitates is formed.
2	To the mixture from step 1, add excess NH_3(aq).	White precipitate dissolves to form a colourless solution. Yellow precipitate is insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.

Which of the following statements are correct?

1 The K_{sp} for AgC*l* is lower than that for AgI.

2 There are no Ag^+(aq) and C*l*$^-$(aq) present in the filtrate formed in Step 3.

3 In step 2, the addition of NH_3(aq) results in the formation of $[Ag(NH_3)]_2^+$ that momentarily decreases the ionic product of AgC*l*.

A 3 only

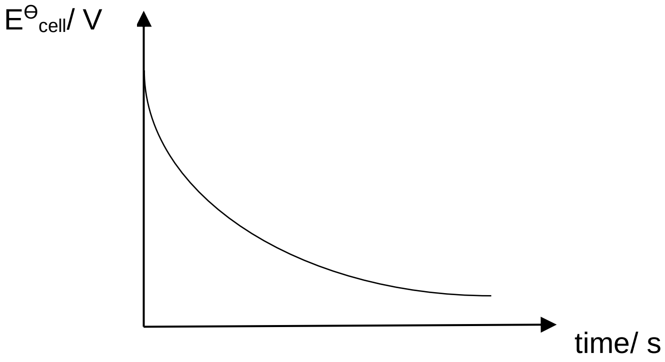
B 1 and 2

C 2 and 3

D 1, 2 and 3

17 An experiment is carried out between the Fe^{2+}/Fe and Co^{2+}/Co half cells.

The following graph of cell potential against time was obtained when a change was continuously made to the half-cell.



What continuous change could produce this graph?

A add aqueous cobalt(II) ions to the cobalt half-cell

B add aqueous ammonia to the cobalt half-cell

C add water to the iron half-cell

D increase the mass of solid iron immersed in the solution

18 Which of the following statements about octahedral complexes is correct?

A The ratio of hexadentate ligands to the central metal ion is 6:1.

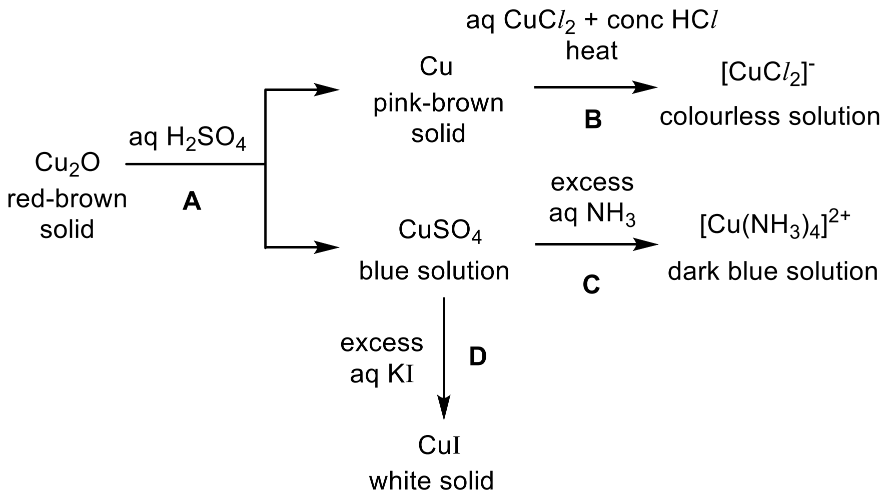
B The d_{xz}, d_{yz} and d_{xy} orbitals are higher in energy than the $d_{x^2-y^2}$ and d_{z^2} orbitals.

C The d orbitals are split into different energy levels due to different orientation of the orbitals to the ligands.

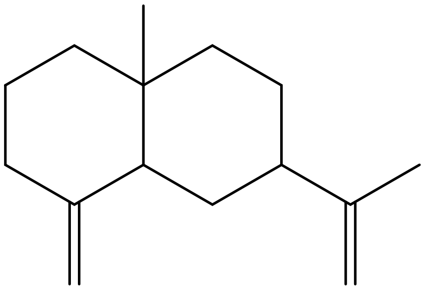
D The same transition metal with different oxidation states displays the same colour with the same ligands.

19 The diagram below shows some reactions involving copper and its compounds.

Which reaction involves ligand exchange only?



20 β-selinene is a molecule that can be isolated from plants. It has the following structural formula.



β-selinene

Which of the following statements about this molecule is correct?

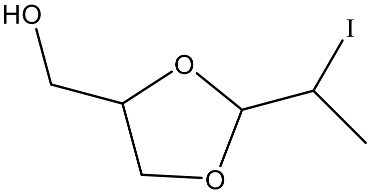
A It has a plane of symmetry.

B It does not contain any sp hybridised carbon.

C It has one chiral centre.

D It exhibits cis-trans isomerism.

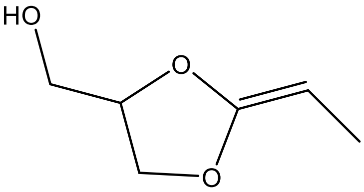
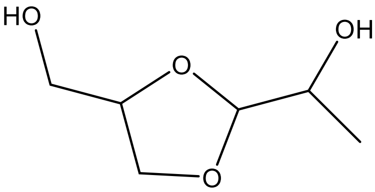
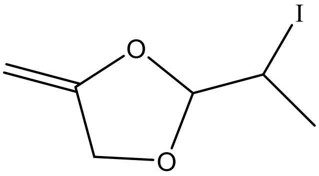
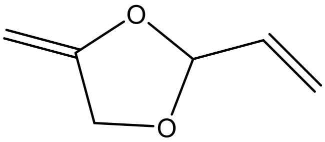
21 Iodinated glycerol is used in the symptomatic treatment of patients with chronic obstructive pulmonary disease.



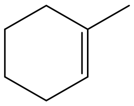
iodinated glycerol

Which of the following correctly shows the product formed when iodinated glycerol is reacted with the given reagents and conditions?

[The C–O–C bond in the structure is inert to the reagents.]

	reagent & conditions	*product*
A	alcoholic KOH, heat	
B	alcoholic KOH, heat	
C	aqueous KOH, heat	
D	concentrated H_2SO_4, heat	

22 Which of the following compounds react with HBr in an addition reaction to give a major chiral product?

1 

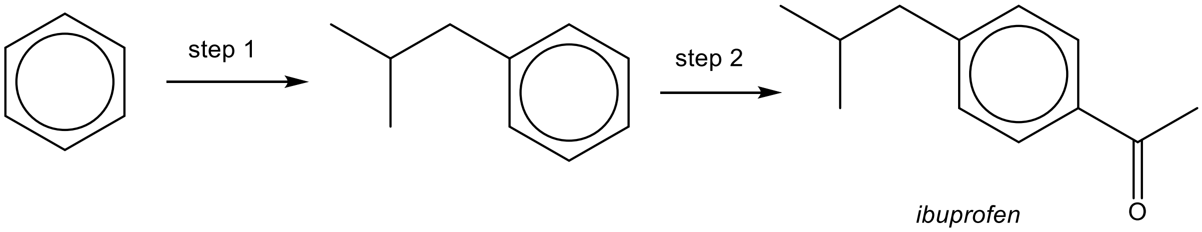
2 CH(Br)=CH_2

3 $CH_3CH=C(CH_3)CH_2CH_3$

4 $CH_2=CHCH_2CH_3$

A 1 and 3 **B** 1 and 4 **C** 2 and 3 **D** 4 only

23 Two of the steps in the manufacture of the pain-relief drug, *ibuprofen* are shown below.



ibuprofen

Which statement is correct?

A Both steps involve the use of catalyst.

B The sequence of the steps are interchangeable.

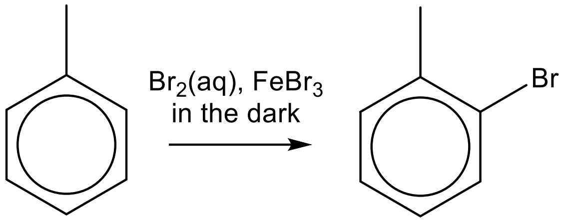
C Both steps involve different types of reaction.

D Only step 2 involves the use of a halogen-containing reagent.

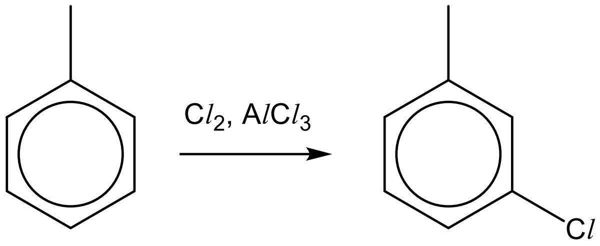
24 The reaction conditions for four electrophilic substitution reactions are given below.

Which reaction would yield the product stated?

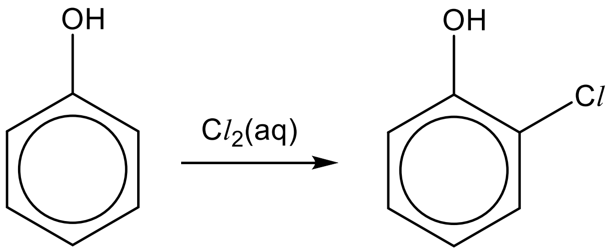
A



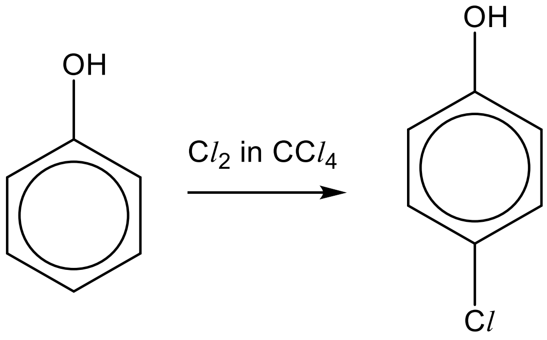
B



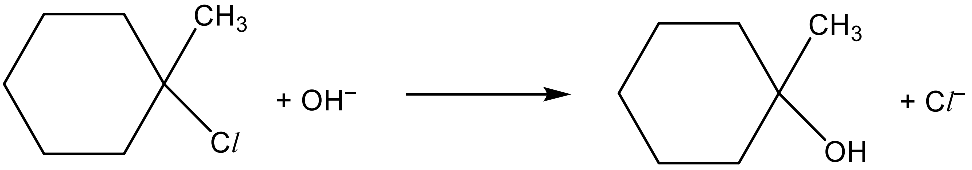
C



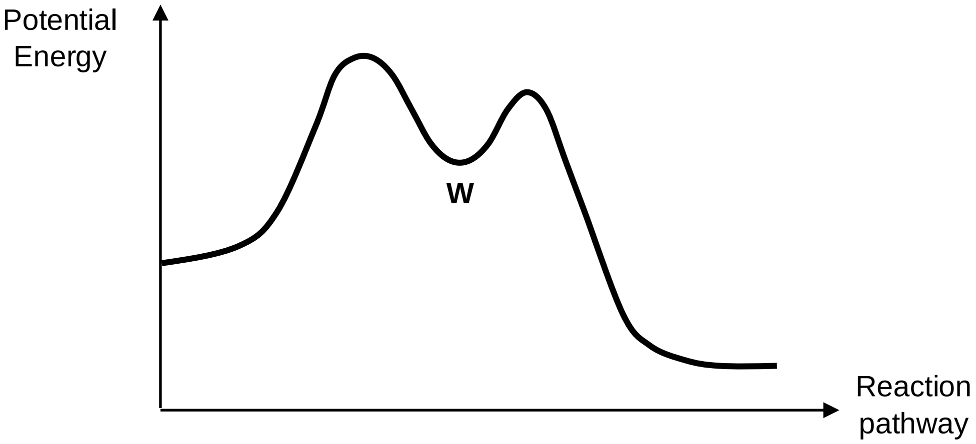
D



25 1-chloro-1-methylcyclohexane is hydrolysed by heating with NaOH(aq).



The energy profile diagram for this reaction is shown below.



Which statements regarding this reaction are correct?

1 The species at point **W** bears a positive charge.

2 The reaction proceeds via S_N2 mechanism since it is a two-step mechanism.

3 The same energy profile diagram would be obtained if chloromethane undergoes the same reaction.

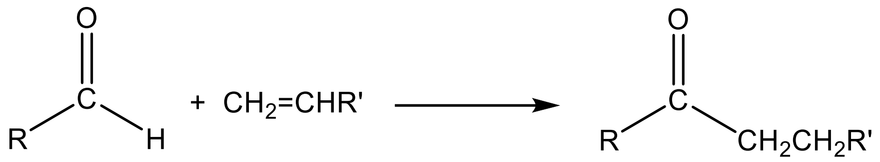
A 1 only

B 1 and 2

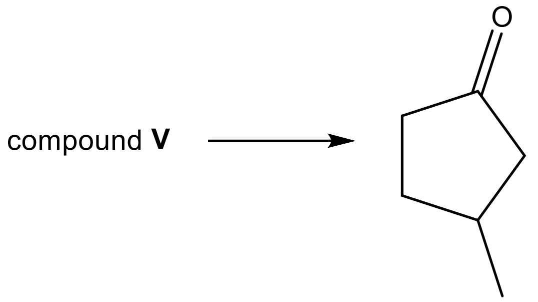
C 2 and 3

D 1, 2 and 3

26 Hydroacylation is a reaction in which an alkene is ‘inserted’ into the C–H bond of an aldehyde to form a ketone.



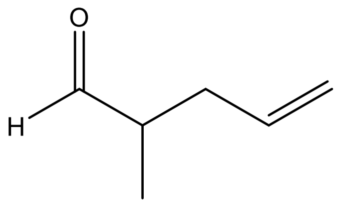
Compound **V** could be converted to 3-methylcyclopentanone using the above reaction.



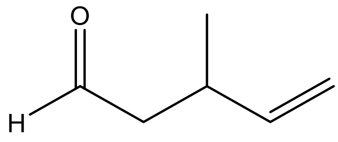
3-methylcyclopentanone

What could compound **V** be?

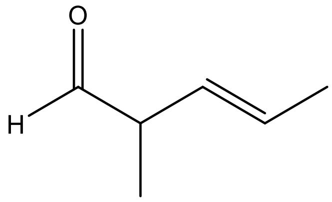
A



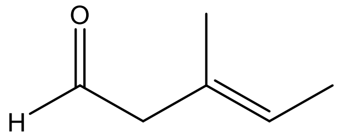
C



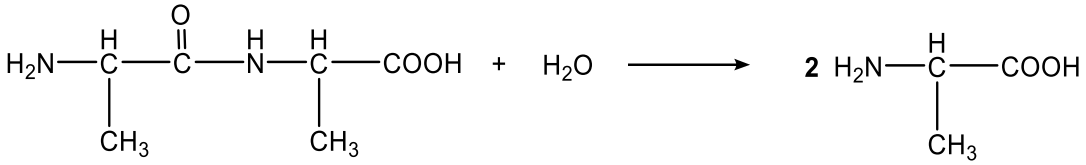
B



D

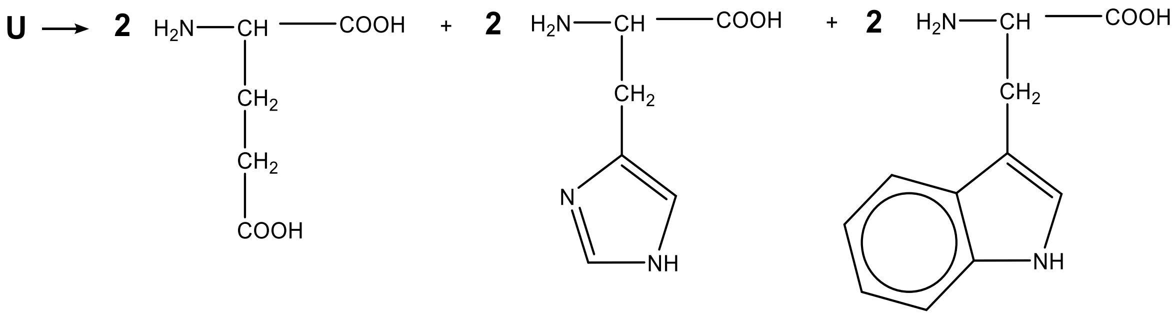


27 Peptidases are enzymes that hydrolyse the peptide bonds that bind amino acids together in the polypeptide chain of a protein.



$$H_2N-CH(CH_3)-CO-NH-CH(CH_3)-COOH + H_2O \longrightarrow 2\ H_2N-CH(CH_3)-COOH$$

Partial hydrolysis of a small peptide, **U**, by a peptidase, produces the following amino acids.



glutamic acid
$M_r = 147$

histidine
$M_r = 155$

tryptophan
$M_r = 204$

What is the M_r of the peptide **U**?

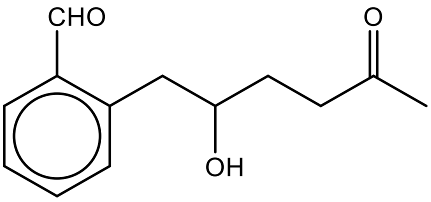
A 904

B 922

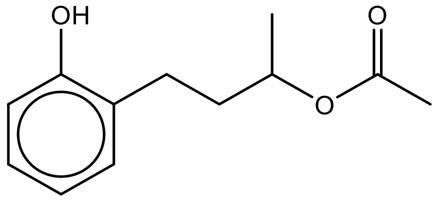
C 1012

D 1102

28 Which of the following reagents could be used to distinguish between compounds **S** and **T**?



Compound **S**



Compound **T**

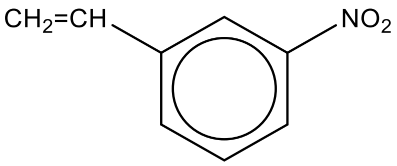
A I_2 in aqueous NaOH

B Cu^{2+} in alkaline solution

C aqueous NH_3 with $AgNO_3$

D acidified potassium dichromate

29 3-nitrostyrene is an aromatic organic compound.



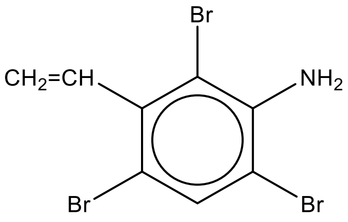
3-nitrostyrene

It is subjected to the following reactions:

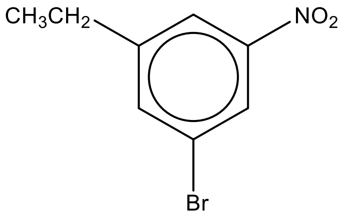
- heat with Sn in concentrated HC*l* followed by careful addition of cold NaOH(aq)
- then the addition of Br_2(aq)

What is the product obtained after the above reactions?

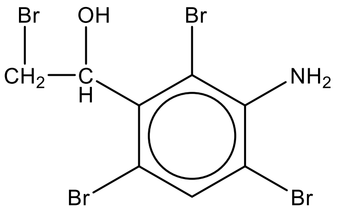
A



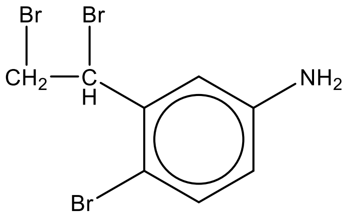
B



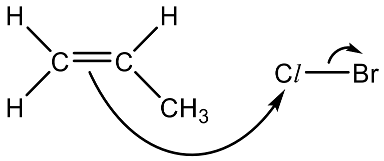
C

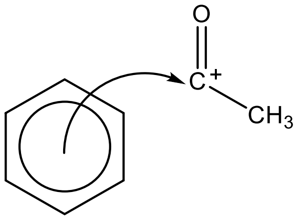


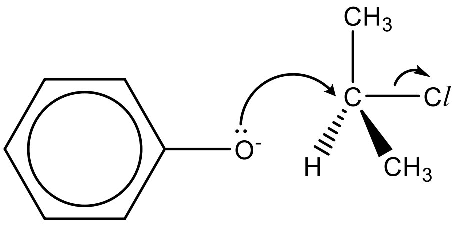
D



30 Which of the following show a correct mechanistic step in the reaction between the reagents?

1


2


3


A 3 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

End of Paper 1

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CIVICS GROUP	

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions

19 September 2019

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and civics group in the spaces at the top of this page.

Write in dark blue or black pen on both sides of the paper.

You may use an HB pencil for any diagrams, graphs or rough working.

Do not use 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.

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

Examiner's Use		
Paper 1	**MCQ**	**/ 30**
Paper 2	**Q1**	**/ 14**
	Q2	**/ 9**
	Q3	**/ 13**
	Q4	**/ 12**
	Q5	**/ 11**
	Q6	**/ 16**
		/ 75
Paper 3		**/ 80**
Paper 4		**/ 55**
Total		**/ 100**
Grade		

This document consists of **19** printed pages.

1 **(a)** Carbon forms compounds with Group 16 elements such as oxygen, sulfur and selenium. The properties of some of these compounds are given below.

compound	structure	net dipole moment	boiling point / °C
CO_2	O=C=O	0	sublimes
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	0.73	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling points of CS_2 and COS.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(ii) Explain why

- CO_2 has no net dipole moment.
- COSe has a greater net dipole moment than COS.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

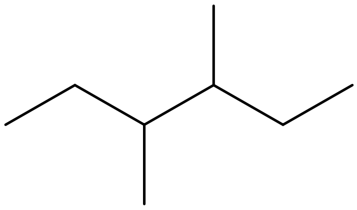
……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

Carbon forms the backbone of organic compounds. Hydrocarbons are the simplest organic compounds that contain carbon and hydrogen.

(b) Compound **A** is an isomer of the hydrocarbon octane, C_8H_{18}.



A

Controlled chlorination of compound **A** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

(i) Suggest the total number of constitutional isomers which can be formed from the possible mono-chlorination of compound **A**. Draw the structural formulae of any **two** of these products.

Total number of possible mono-chlorinated products = ...

[3]

(ii) Draw the **skeletal** formula of the isomer of octane which could produce **only one** possible mono-chlorinated product if it undergoes free radical substitution.

[1]

(c) Besides reaction of alkanes with halogens, the process of thermal cracking, in which large alkane molecules are broken down into smaller alkanes and alkenes, proceeds via free radical mechanism.

The following are reactions involved when propane undergoes thermal cracking.

$CH_3CH_2CH_3 \longrightarrow \bullet CH_3 + \bullet CH_2CH_3$ -- (1)

$CH_3CH_2CH_3 \longrightarrow \bullet H + \bullet CH_2CH_2CH_3$ -- (2)

$\bullet CH_3 + CH_3CH_2CH_3 \longrightarrow CH_4 + \bullet CH_2CH_2CH_3$ -- (3)

$\bullet CH_2CH_3 \longrightarrow \bullet H + CH_2{=}CH_2$ -- (4)

$\bullet CH_3 + CH_2{=}CH_2 \longrightarrow \bullet CH_2CH_2CH_3$ -- (5)

$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$ -- (6)

$2\ \bullet CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$ -- (7)

(i) Reactions (1) and (2) are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

……………………………………………………………………………………

……………………………………………………………………………………[1]

(ii) From reactions (3) to (7), identify those which may be termed propagation steps in the mechanism.

……………………………………………………………………………………[1]

(iii) Which gas, if detected in the product mixture, would support the occurrence of both reactions (2) and (4)?

……………………………………………………………………………………[1]

(iv) Suggest why reaction (7) may be termed a *disproportionation* reaction.

……………………………………………………………………………………

……………………………………………………………………………………[1]

(d) Methanoic acid, H_2CO_2, is the simplest carboxylic acid.

Draw a dot-and-cross diagram of methanoic acid. Suggest the shape around the carbon atom in methanoic acid.

Shape around C atom …………………………………………..

[2]

[Total: 14]

2 Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

In investigations of this reaction, the following results were obtained by varying the volumes of hydrogen peroxide and iodide ions.

experiment	volume of H_2O_2 / cm^3	volume of I^- / cm^3	volume of H_2O / cm^3	initial rate / mol dm^{-3} s^{-1}
1	20.0	20.0	20.0	1.2×10^{-2}
2	20.0	30.0	10.0	1.8×10^{-2}
3	50.0	10.0	0.0	1.5×10^{-2}

(a) Explain why water was added to experiments 1 and 2.

………………………………………………………………………………………………..

……………………………………………………………………………………………..[1]

(b) The reaction was determined to be **zero order** with respect to hydrogen ions.

(i) Sketch the rate-concentration graph for H^+ ions.

[1]

(ii) Determine the order of reaction with respect to the other two reactants.

Hence, write down the rate equation.

[3]

(c) In order to further investigate the kinetics of the reaction, experiments 4 and 5 were conducted. The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

experiment	initial [H_2O_2(aq)] / mol dm^{-3}	initial [I^-(aq)] / mol dm^{-3}
4	0.020	0.500
5	0.050	1.000

The half-life of hydrogen peroxide was 9.6 min in experiment 4. Explain and predict the half-life of hydrogen peroxide in experiment 5.

…………………………………………………………………………………………………...

…………………………………………………………………………………………………

…………………………………………………………………………………………………...

………………………………………………………………………………………..……[2]

(d) An alternative method of investigating the rate of the above reaction is by withdrawing aliquots at specified time intervals and titrating the iodine formed in each aliquot with sodium thiosulfate solution.

Suggest how the reaction can be quenched at specified time intervals.

……………………………………………………………………………………………….

……………………………………………………………………………………………….[1]

(e) Hydrogen peroxide decomposes easily. Suggest a method whereby the shelf-life of the hydrogen peroxide solution could be increased.

……………………………………………………………………………………………….

……………………………………………………………………………………………….[1]

[Total: 9]

3 Lithium forms various compounds used for a wide range of purposes. For example, Li_2CO_3 is used as a mood-stabilising drug and LiF is used to record ionising radiation exposure from gamma rays, beta particles and neutrons.

(a) Numerical values of the solubility products of some lithium salts at 298 K are given in the table below.

salt	solubility product
LiF	2.68×10^{-3}
Li_2CO_3	2.14×10^{-2}
Li_3PO_4	3.20×10^{-9}

(i) Write an expression for the solubility product, K_{sp}, of lithium phosphate, including its units.

[2]

(ii) Using the data above, calculate a value for the solubility of lithium phosphate.

[2]

(iii) LiF was precipitated when equal volumes of a solution of 0.050 mol dm^{-3} $LiNO_3$ and a solution of KF were mixed.

Calculate the minimum concentration of the KF solution required for precipitation to occur.

[2]

(iv) Describe and explain how the solubility of Li_2CO_3 is affected by adding solid Na_2CO_3 into the solution.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(b) When a precipitate is formed, $\Delta G^\ominus_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^\ominus_{ppt} = 2.303\,RT \log K_{sp}$$

For lithium sulfate, Li_2SO_4, K_{sp} = 128 mol^3 dm^{-9} at 298 K.

Using the above expression, determine whether lithium sulfate is soluble in water at 298 K. Explain your answer.

[2]

(c) Another use of Li_2CO_3 is in the processing of metal oxides. When Li_2CO_3 decomposes, it forms Li_2O solid and CO_2 gas according to the following equation.

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$$

(i) Calculate the standard enthalpy change of reaction for the decomposition of Li_2CO_3 using the following standard enthalpy changes of formation, $\Delta H_f^\ominus$.

compound	Li_2CO_3	Li_2O	CO_2
$\Delta H_f^\ominus$ / kJ mol^{-1}	−1216	−596	−394

[1]

(ii) The entropy change for the decomposition reaction is positive. Explain the effect on spontaneity of this decomposition reaction as temperature increases.

[2]

[Total: 13]

4 *Use of the Data Booklet is relevant to this question.*

(a) Chemical companies manufacture containers filled with liquid butane for use by campers. The complete combustion of butane produces carbon dioxide and water. The enthalpy change of combustion of butane is –3000 kJ mol^{-1}.

A camper estimates that the liquid butane left in a container would give 1.2 dm^3 of butane gas (measured at room temperature of 20 °C and pressure of 1 atm).

(i) Calculate the mass of water at room temperature that could be brought to boiling point at 100 °C by completely burning this mass of butane, given that the process is only 80% efficient.

[3]

(ii) Suggest a reason why the combustion process is only 80% efficient.

…………………………………………………………………………………………

…………………………………………………………………………………………[1]

(b) When burnt in a limited supply of air, butane forms carbon and water. The enthalpy change of this reaction is –1400 kJ mol^{-1}.

(i) Construct a balanced equation for this reaction.

…………………………………………………………………………………………[1]

(ii) Explain why the enthalpy changes of the two combustion reactions in **(a)** and **(b)** are different.

…………………………………………………………………………………………[1]

(iii) State the quantitative information that can be obtained from this difference in enthalpy changes.

…………………………………………………………………………………………[1]

(c) The carbon-oxygen *bond energy* in carbon monoxide, CO, is 1077 kJ mol^{-1}.

Carbon monoxide can be formed by the following reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \qquad \Delta H^\ominus = +172.5 \text{ kJ mol}^{-1}$$

(i) Explain, with the aid of a suitable equation, what is meant by the term *bond energy* of carbon monoxide.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………[2]

(ii) Determine the enthalpy change of atomisation of carbon by using relevant bond energy data from the *Data Booklet* to complete the energy cycle below. Include relevant information in your cycle.

$$C(s) \quad + \quad CO_2(g) \xrightarrow{\Delta H = +172.5 \text{ kJ mol}^{-1}} 2CO(g)$$

[3]

[Total: 12]

5 *Use of the Data Booklet is relevant to this question.*

A student wanted to study the following reaction.

$$2Au^{3+} + 3Zn \rightleftharpoons 2Au + 3Zn^{2+}$$

He first sets up an electrochemical cell which comprises of Au^{3+}/Au and Zn^{2+}/Zn half-cells prepared under standard conditions.

(a) **(i)** Draw a fully labelled diagram of the electrochemical cell under standard conditions.

[2]

(ii) Given that $E^\ominus_{Au^{3+}/Au}$ is +1.50 V, calculate the $E^\ominus_{cell}$ of this cell.

[1]

(iii) Suggest a replacement transition element ion-ion half-cell for the Zn^{2+}/Zn half-cell so that the direction of electron flow is reversed.

……………………………………………………………………………………….[1]

(b) When the reaction in **(a)** begins, $[Au^{3+}]$ starts to decrease while $[Zn^{2+}]$ increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non-standard conditions.

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n}\log_{10} Q$$

where n is the number of moles of electrons transferred and Q is the reaction quotient given by $\frac{[Zn^{2+}]}{[Au^{3+}]}$.

(i) Using your answer in **(a)(ii)**, calculate the new E_{cell} using the Nernst equation, when $[Au^{3+}]$ and $[Zn^{2+}]$ are 0.02 mol dm^{-3} and 2.47 mol dm^{-3} respectively.

[1]

(ii) Suggest the value of E_{cell} when the reaction goes to completion.

[1]

(c) The redox reaction in **(a)** is an example of a spontaneous reaction which proceeds as predicted by the cell potential. However, not every chemical reaction agrees with the theoretical prediction. One example is the reaction between acidified $K_2Cr_2O_7$ and water.

(i) Using information from the *Data Booklet*, calculate $\Delta G^{\ominus}$ for the reaction between acidified $K_2Cr_2O_7$ and water. Based on your value for $\Delta G^{\ominus}$, comment on the spontaneity of the reaction.

[3]

(ii) The reaction between water and acidified $K_2Cr_2O_7$ has an $E^\ominus_{cell}$ greater than 0 V under standard conditions, yet the reaction does not proceed. Suggest a reason for this observation.

……………………………………………………………………………………………

……………………………………………………………………………………………[1]

(iii) Another example of a reaction that does not agree with the theoretical prediction is the reaction between Cu^{2+} and I^- according to the equation below.

$$2Cu^{2+}(aq) + 4I^-(aq) \rightleftharpoons 2CuI(s) + I_2(aq) \qquad E^\ominus_{cell} = -0.39\ V$$

White precipitate of CuI is formed during the reaction. Suggest a reason why the reaction proceeds despite the $E^\ominus_{cell}$ being less than 0 V.

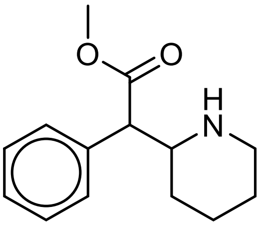
……………………………………………………………………………………………

……………………………………………………………………………………………[1]

[Total: 11]

6 Adrenaline is a naturally occurring hormone and stimulant released in the body during times of danger or stress. Stimulant drugs that can mimic the effect of adrenaline have been developed for treatment of various conditions.

(a) Methylphenidate is a stimulant drug commonly used in the treatment of Attention Deficit Hyperactive Disorder (ADHD).

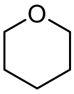


methylphenidate

(i) Draw the structures of the organic products formed when methylphenidate is heated with dilute hydrochloric acid.

[2]

(ii) An isomer of methylphenidate, compound **X**, is neutral and has the following structural properties:

- contains one aromatic six-membered ring
- contains 

Suggest a structure for compound **X** and state its isomeric relationship to methylphenidate.

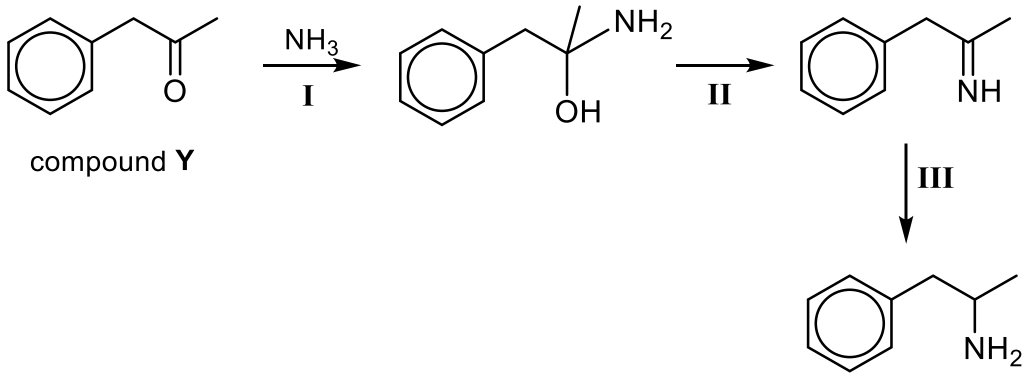
X

isomeric relationship to methylphenidate:

…………………………………………..……………………………………….……..

[2]

(b) Another stimulant, amphetamine, is prepared commercially from compound **Y** as shown below.



compound **Y**

amphetamine

(i) Suggest the type of reaction occurring in:

Step **II** ……………………………………….

Step **III** ………………………………………. [2]

(ii) Suggest suitable reagents and conditions for the conversion in step **III**. You may assume the R=NH group reacts in a similar manner to the carbonyl group.

reagents and conditions …………………………………………………… [1]

(iii) Reaction **I** which occurs between compound **Y** and NH_3 is a nucleophilic addition reaction.

Draw the mechanism for this reaction, given that in the rate-determining step, the nucleophilic attack by NH_3, results in an intermediate species containing both a positive and negative charge.

[3]

(iv) With reference to the mechanism you have drawn in **(iii)**, explain why the product from step **I** is expected to be optically inactive.

…………………………………………………………………………………………

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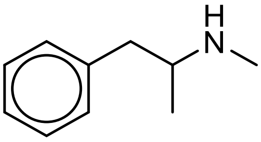
…………………………………………………………………………………………[2]

(c) Methamphetamine is a stimulant which has a structure similar to amphetamine.



methamphetamine

(i) The hydrochloride salt of methamphetamine exists as colourless crystals.

Methamphetamine is immiscible with water whereas the salt is soluble in water.

With reference to the interactions formed between each of the compounds and water, explain the difference in the solubility of methamphetamine and its salt in water.

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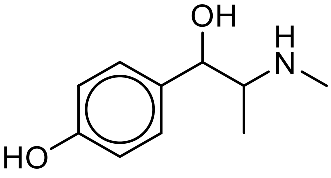
…………………………………………………………………………………………[2]

(ii) In the human body, methamphetamine can be converted to compound **Z**.



Z

Describe a simple chemical test which could be used to distinguish between methamphetamine and compound **Z**.

You should state the reagents and conditions required, together with the expected observations for each compound.

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…………………………………………………………………………………………

…………………………………………………………………………………………[2]

[Total: 16]

End of Paper 2

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

H2 CHEMISTRY **9729/03**

Paper 3 Free Response

23 September 2019

2 hours

Candidates answer on Answer Booklet.

Additional Materials:	Answer Booklet Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and civics group on all your work you hand in.

Write in dark blue or black pen on both pages in the answer booklet.
You may use an HB pencil for any diagrams, graphs or rough working.
Do not use 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.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **14** printed pages.

Section A

Answer **all** the questions from this section.

1 Hydrocarbons, C_xH_y, are used extensively as sources of fuel in our modern day civilisation.

(a) 10 cm^3 of a gaseous hydrocarbon C_5H_y was allowed to burn in an excess of oxygen at 300 ºC and 1 atm. In the reaction, there was an expansion of volume by 20 cm^3.

(i) Write a balanced equation, with state symbols, for the reaction at 300 ºC and 1 atm. [2]

(ii) Determine the value of **y**. [2]

Methane, CH_4, is sometimes used in the production of hydrogen via a process known as steam reforming.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(b) The steam reforming process is an endothermic reaction.

(i) Using data from the *Data Booklet*, calculate a value for the enthalpy change of the forward reaction. [2]

(ii) The actual value of the enthalpy change of reaction is found to be +206 kJ mol^{-1}. Suggest a reason why your calculated answer in **(i)** differs from this value. [1]

(c) At 600 K, the value of the equilibrium constant, K_p, for the steam reforming reaction is 7.20×10^{-4}.

(i) Write the K_p expression for this reaction, giving its units. [2]

(ii) Gaseous CH_4, H_2O and CO are introduced into a closed container at 600 K and their initial partial pressures are 1.20 atm, 2.10 atm and 1.80 atm respectively.

Determine the partial pressure of H_2 when equilibrium is reached.

(You may assume that the extent of the forward reaction is small.) [3]

(iii) Using information from **(b)**, suggest how the temperature of the reaction can be changed so as to increase the yield of H_2. Explain your answer. [2]

(d) Additional hydrogen can be recovered using the carbon monoxide produced in another reaction known as the water-gas shift reaction.

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

(i) Name the type of hybridisation in the carbon atom in CO. Draw the hybrid orbitals around the carbon atom. [2]

(ii) Given that the above reaction was conducted at 300 °C and 1 atm, calculate the volume of H_2 that can be recovered from 5 kg of CO. [3]

(iii) The volume of CO_2 collected in the water-shift reaction should be the same as that of H_2. However, the actual volume of CO_2 collected was smaller. Suggest a reason why this is so. [1]

[Total: 20]

2 Propanoic acid, CH_3CH_2COOH was initially known as propionic acid based on the Greek words, *protos*, meaning ‘first’ and *pion*, meaning ‘fat’.

The pK_a values of CH_3CH_2COOH and $CH_3CH(Cl)COOH$ are listed below.

acid	structural formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CH(Cl)COOH$	2.8
3	$CH_2(Cl)CH_2COOH$	[redacted]

(a) **(i)** Explain why acid 2 has a lower pK_a than acid 1. [2]

(ii) Suggest a pK_a value for acid 3. [1]

(b) A 25.0 cm^3 solution of 0.10 mol dm^{-3} CH_3CH_2COOH was titrated against 0.20 mol dm^{-3} sodium hydroxide, NaOH.

(i) Calculate the pH of the 0.10 mol dm^{-3} CH_3CH_2COOH. [1]

(ii) Calculate the volume of NaOH required for complete neutralisation. [1]

(iii) Write a suitable equation to explain why the pH at equivalence point is greater than 7. [1]

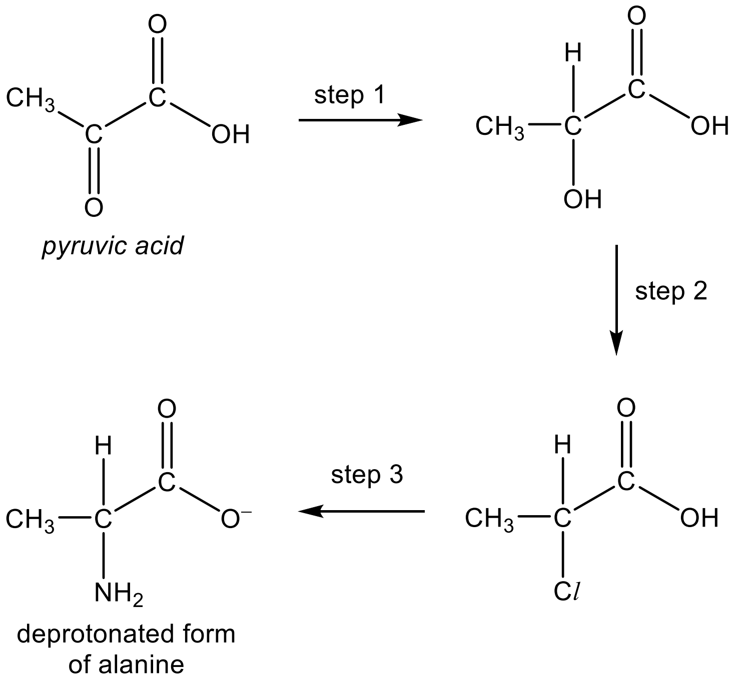
(iv) Sketch the expected titration curve for this titration given that a total volume of 25.0 cm^3 of NaOH was added. On the titration curve, indicate the initial pH value and the equivalence volume. [2]

(v) A buffer involving CH_3CH_2COOH and its salt was formed during the progress of the titration. Circle the buffer region on the sketched curve in **(iv)** and indicate the corresponding pH value and volume at the maximum buffering capacity. [2]

There are many organic compounds such as amino acids and drug molecules that are derivatives of propanoic acid.

(c) The starting material to synthesise 2-aminopropanoic acid, also known as alanine can be either *pyruvic acid* or ethanal.

(i) The proposed synthesis for the deprotonated form of alanine from *pyruvic acid* is shown below.

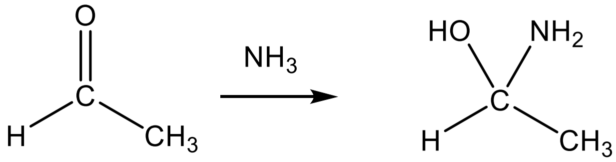


Suggest the reagents and conditions for steps 1, 2 and 3. [3]

(ii) State the **two** types of reaction that had occurred in step 3 of the above proposed synthesis. [2]

(iii) Write an equation to show how the zwitterion form of *alanine* can act as a buffer when a small amount of base is added. [1]

(iv) The first step to synthesise alanine from ethanal is shown below.

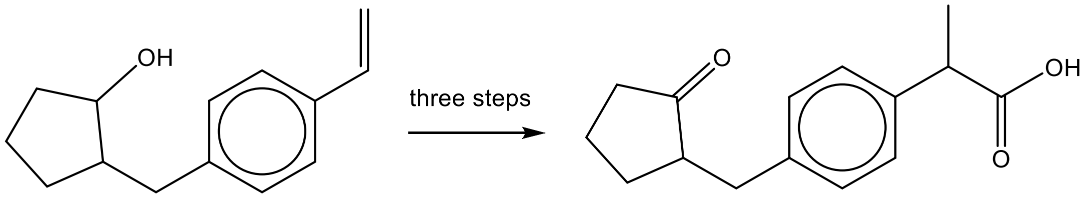


ethanal

Explain whether ammonia can be considered as a Lewis base in the context of this synthesis. [1]

(d) Non-steroidal anti-inflammatory drugs are used for the relief of pain. One example is *loxoprofen* that is considered as a propanoic acid derivative based on its chemical structure.

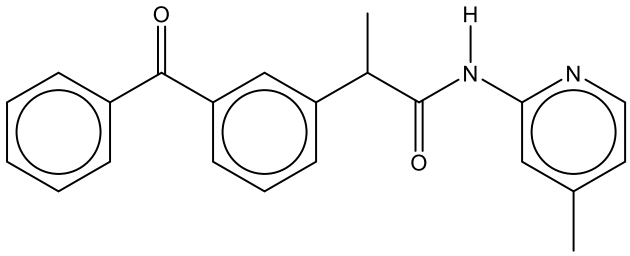
(i) Suggest a three-step synthesis of *loxoprofen* starting from compound **E**.



compound **E** *loxoprofen*

[4]

(ii) *Piketoprofen* is produced by the reaction between an acyl chloride and a suitable organic compound. Suggest the structures of the acyl chloride and the organic compound.



piketoprofen

[1]

(iii) The use of acyl chloride requires anhydrous conditions. Explain why acyl chloride undergoes hydrolysis more readily than chloroalkane. [2]

[Total: 24]

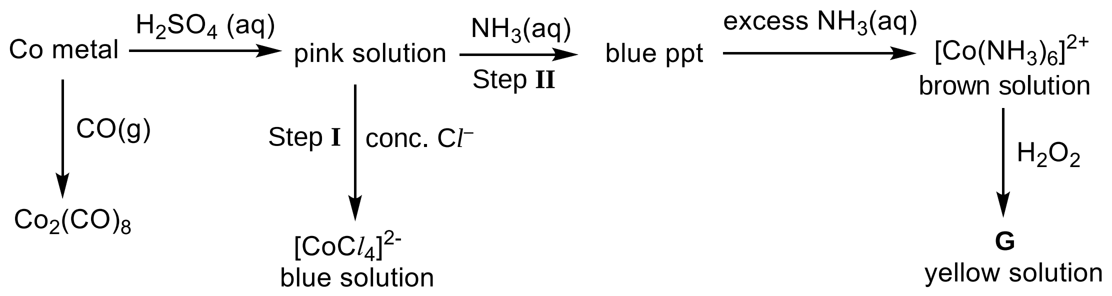
3 Cobalt is a transition element that plays an important role in hybrid electric vehicles and is also an essential part of vitamin B12. The common oxidation states of cobalt are +2 and +3.

(a) Define *transition element*. [1]

(b) Write the electronic configuration of cobalt(II) ion. [1]

(c) State one **physical** characteristic property of transition elements that is different from the main group metals. Briefly explain why transition elements exhibit this property. [2]

(d) The following sequence of reactions involving cobalt illustrates many of the characteristic properties of transition elements.

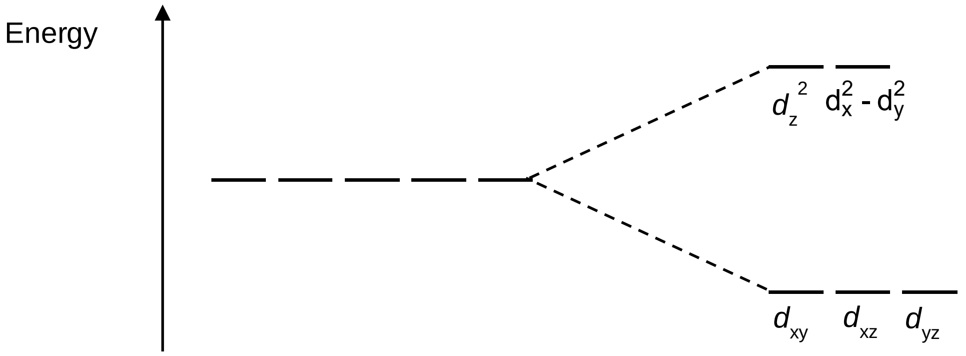


(i) State the types of reaction occurring in steps **I** and **II**. [2]

(ii) Suggest the formula of the cobalt-containing species **G**. [1]

(iii) Cobalt is said to be a d-block element.

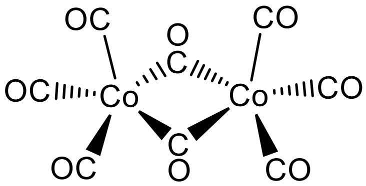
The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment as shown.



Explain why the splitting occurs. [2]

(iv) Given the fact in **(iii)** that d orbitals split into 2 energy levels in the presence of ligands, explain why $[CoCl_4]^{2-}$ solution is blue. [2]

(v) Cobalt can react with carbon monoxide to form $Co_2(CO)_8$, a commonly used reagent and catalyst in organic synthesis.



Suggest the co-ordination number and the oxidation state of cobalt in the complex, $Co_2(CO)_8$. [1]

(vi) With the aid of *Data Booklet* and given that $E^{\ominus}_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}}$ is +0.10 V, predict the stability of an alkaline solution of $[Co(NH_3)_6]^{2+}$ when left exposed to air. [2]

(e) A radioactive form of cobalt, ^{60}Co, is used in the inspection of materials to reveal internal structure, flaws, or foreign objects.

(i) State the number of protons, neutrons and electrons present in the isotopic species, ^{60}Co. [1]

(ii) The radioactive decay of ^{60}Co produces beta (β) particles. A simplified balanced decay equation is provided below.

$$^{60}Co \rightarrow \mathbf{L} + \beta$$

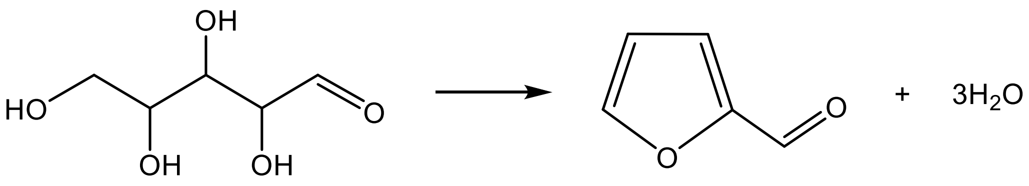
Given that β is $_{-1}^{0}e$, deduce the identity of the element **L**. [1]

[Total: 16]

Section B

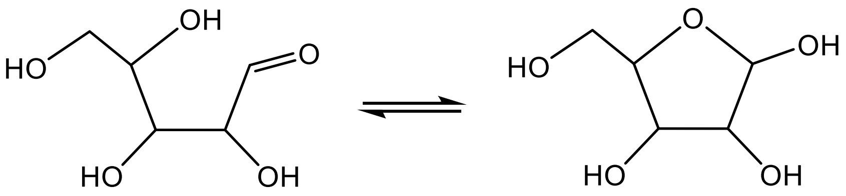
Answer **one** question from this section.

4 Furfural is an aromatic compound with all its carbon atoms lying on the same plane. Today, one of the ways to manufacture furfural is by the acid catalysed dehydration of xylose.



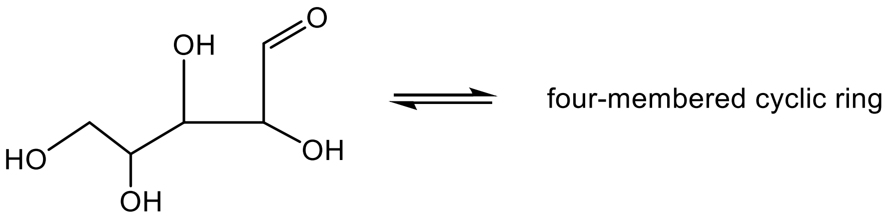
xylose furfural

(a) Xylose exists in more than one form, one of which is the non-cyclic form shown below (i.e. form 1). Form 2 is a five-membered cyclic ring produced as follows.



form 1 of xylose form 2 of xylose

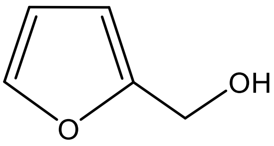
It is theoretically possible to produce a four-membered cyclic ring by following a similar pattern of reaction.



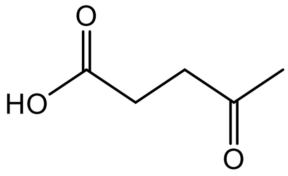
(i) Draw the structure of the theoretical four-membered cyclic ring. [1]

(ii) The four-membered cyclic ring is **not** actually produced because it is unstable. Suggest why it is unstable. [1]

(b) Furfural can be reduced into furfuryl alcohol. Furfuryl alcohol can then be used to synthesise levulinic acid.



furfuryl alcohol

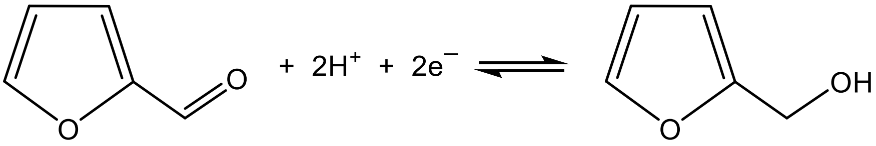


levulinic acid

(i) Using the **molecular** formulae of furfuryl alcohol and levulinic acid, write a balanced equation for the synthesis of furfuryl alcohol into levulinic acid. [2]

(ii) Using your answer in **(i)**, state the type of reaction that has taken place. [1]

(c) The standard reduction potential involving furfural, $C_5H_4O_2$ measured against the standard hydrogen electrode (S.H.E.) is shown below.

electrode reaction	$E^\ominus$ / V
 furfural furfuryl alcohol	–0.80

A neutral aqueous solution of furfural is prepared. Electrolysis of this solution is performed using copper at both electrodes to increase the percentage yield of the reaction.

When 0.030 A was passed through the cell for 2.0 hours, the *actual* mass of the product formed at the cathode was found to be 0.060 g. Copper is reacted at the anode but not the cathode.

(i) Using the $E^\ominus$ values given above as well as that from the *Data Booklet*, deduce the products formed at the anode and the cathode.
(In your deduction, you may use name or molecular formula to represent the structures of the respective organic compounds.) [3]

(ii) Write the overall balanced equation for the reaction. [1]

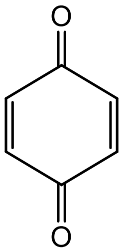
(iii) Calculate the *expected* mass of the product formed at the cathode. [2]

(iv) Calculate the percentage yield of the product formed at the cathode. [1]

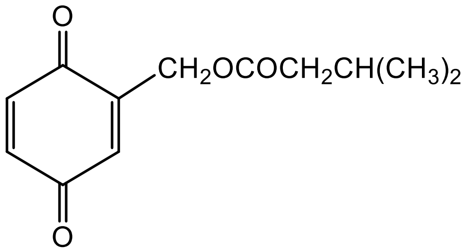
(v) Besides the S.H.E., another standard electrode that can be used is the standard calomel electrode (S.C.E.). When the S.C.E. is compared against the S.H.E., the $E^\ominus$ of the S.C.E. is +0.24 V.

Calculate the $E^\ominus$ of the furfural / furfuryl alcohol half-cell when measured against the S.C.E. [1]

Another compound with all its carbon atoms lying on the same plane is paraquinone, with a characteristic irritating odour of hot plastic. One derivative of paraquinone is blattellaquinone which is a pheromone in cockroaches.

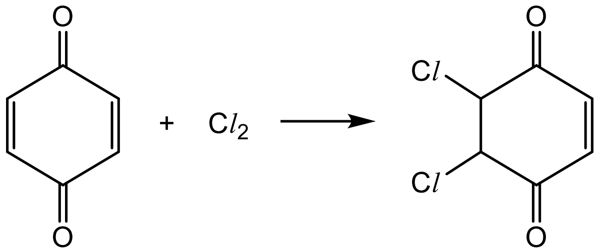


paraquinone



blattellaquinone

(d) Paraquinone and limited chlorine react as follows.



Name and draw the mechanism of this reaction. [3]

(e) Draw the major products formed when **blattellaquinone** is separately reacted under suitable conditions with each of the following:

(i) hydrogen gas [1]

(ii) gaseous hydrogen bromide [1]

(iii) hot acidified potassium manganate(VII) [2]

[Total: 20]

5 This question concerns the compounds of Period 3 elements.

(a) Properties of the oxides of some Period 3 elements, **P**, **Q** and **R**, are given below.

oxide	physical state at room conditions	electrical conductivity when molten
P	gas	nil
Q	solid	high
R	solid	low

These three oxides, in no particular order, are Al_2O_3, SiO_2 and SO_3.

(i) Identify **P**, **Q** and **R**. [1]

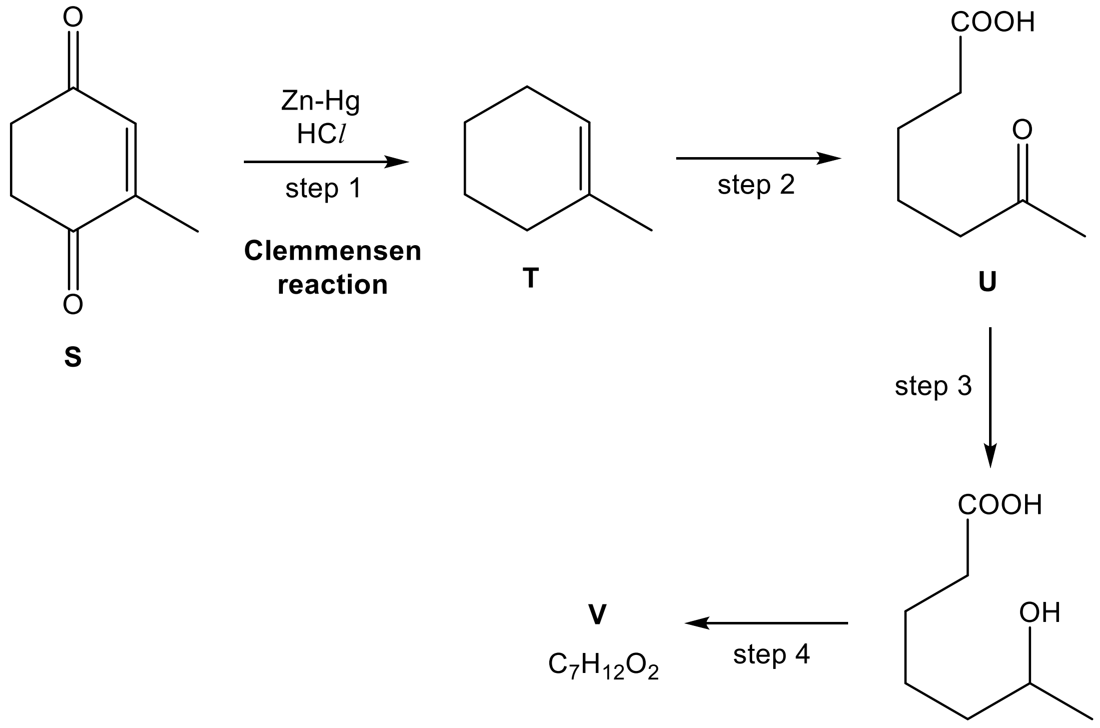
(ii) Account for your answer, in terms of their structure and bonding. [4]

(iii) Al_2O_3 is described as an amphoteric oxide.
Write two equations to show the amphoteric nature of Al_2O_3. [2]

(b) Hydrogen chloride is a colourless gas commonly used in organic synthesis.

In the Clemmensen reaction, carbonyl compounds are reduced to alkanes using zinc-mercury and hydrogen chloride dissolved in an organic solvent.

A reaction scheme involving the Clemmensen reaction is shown below.



(i) Write the balanced equation for the reduction of compound **S** to **T**. Use [H] to represent the formula of the reducing agent. [1]

(ii) Suggest a reagent which can determine if the reaction in step 3 is complete. [1]

(iii) Given that compound **V** is neutral, state the type of reaction occurring in step 4 and suggest the structure of compound **V**. [2]

(iv) Compound **U** is more soluble in water than compound **S**.

1. Suggest a reason why this is so. [1]

2. Draw a labelled diagram to show how compound **U** dissolves in water. [1]

(c) HC*l* is stable to heat while HBr and HI, can undergo thermal decomposition. At 700 K, HBr is approximately 10% decomposed but HI, is approximately 20% decomposed.

Explain these differences with reference to relevant data in the *Data Booklet* and the factors that affect them. [3]

(d) Compound **W**, $C_6H_{10}O_2$ is an ester which decolourises Br_2 in CCl_4 to form $C_6H_{10}Br_2O_2$.

Upon prolonged heating with excess acidified $KMnO_4$, 1 mol of **W** produces 1 mol of **X**, $C_4H_6O_3$ and 2 mol of CO_2.

X gives a yellow precipitate **Y** when warmed with aqueous alkaline iodine. **X** also undergoes the Clemmensen reaction to give **Z**, $C_4H_8O_2$. Both **X** and **Z** produce effervescence when reacted with aqueous sodium carbonate.

Suggest structures for the identity of **W**, **X**, **Y** and **Z**. [4]

[Total: 20]

End of Paper 3

TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME	
CIVICS GROUP	

H2 CHEMISTRY **9729/04**

Paper 4 Practical **4 September 2019**

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 and Civics Group in the spaces at the top of the 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 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	
Total	

This document consists of **18** printed pages.

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

1 Determination of the concentration of a base and the enthalpy change of the neutralisation reaction

FA 1 is 2.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 2 is aqueous sodium hydroxide, NaOH.

The reaction of sulfuric acid and sodium hydroxide is exothermic.
In separate experiments, you will add increasing volumes of **FA 2** to a fixed volume of **FA 1**. In each experiment you will measure the maximum temperature rise, ΔT. As the volume of **FA 2** is increased, this maximum temperature rise, ΔT, will increase and then decrease.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following:

- the concentration of sodium hydroxide, NaOH, in **FA 2**
- the enthalpy change when 1 mol of H_2SO_4 is neutralised by NaOH

(a) Method

- Fill the labelled burette with **FA 1**.
- Support a styrofoam cup in the 250 cm^3 beaker.
- Run 10.00 cm^3 of **FA 1** from the burette into the styrofoam cup.
- Measure 20.0 cm^3 of **FA 2** using a measuring cylinder.
- Place the thermometer in the **FA 2** in the measuring cylinder and record the steady temperature of the solution.
- Pour the **FA 2** into the styrofoam cup, stir and record the maximum temperature obtained in the reaction.
- Empty and rinse the styrofoam cup; shake dry the styrofoam cup. Rinse the thermometer.
- Carry out the experiment three more times. Each time use 10.00 cm^3 of **FA 1**.
- Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 2** in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 2** which will allow you to investigate more precisely the volume of **FA 2** that produces the highest temperature rise when added to 10.00 cm^3 of **FA 1**.

Results
Record your results below in an appropriate form showing, for each experiment, the volumes of solutions used, temperature measurements and the temperature rise, ΔT.

[4]

(b) Plot a graph of temperature rise, ΔT, on the y-axis against the volume of **FA 2** added on the x-axis.

Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

The intersection of these lines represents the temperature rise for the volume of **FA 2** that exactly neutralises the sulfuric acid present in 10.00 cm^3 of **FA 1**.

[3]

(c) Read from the graph the volume of **FA 2** that gives the maximum temperature rise.

Volume of **FA 2** giving the maximum temperature rise = ... cm^3 [1]

(d) **(i)** Calculate the amount of NaOH required to neutralise the amount of H_2SO_4 at the maximum temperature rise.

Amount of NaOH required = ... mol
[1]

(ii) Hence, calculate the concentration of NaOH in **FA 2**.

Concentration of NaOH in **FA 2** = ... mol dm^{-3}
[1]

(e) Read the maximum temperature rise from the graph and use this to calculate the enthalpy change when 1 mol of H_2SO_4 is neutralised by NaOH. Give your answer in kJ mol^{-1}.

[4.18 J are absorbed or released when the temperature of 1 cm^3 of solution changes by 1 °C.]

Enthalpy change = ... kJ mol^{-1}
[2]

(f) The enthalpy change of neutralisation, ΔH_{neut}, between a strong acid and a strong base is –57 kJ mol^{-1}.

Explain why the enthalpy change calculated in **(e)** is significantly more exothermic than ΔH_{neut}.

....

....

....[1]

(g) A student suggested that the experiments carried out in **(a)** would be more accurate if volumes of 20.00 cm^3 of 1.0 mol dm^{-3} H_2SO_4 were used instead.

State and explain whether you agree or disagree with the student's suggestion.

evaluation of student's suggestion ....

explanation ....

....

[1]

[Total: 14]

2 **Determination of the percentage by mass of sodium carbonate in a mixture of sodium hydroxide and sodium carbonate**

Sodium carbonate is neutralised by hydrochloric acid in two steps:

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$
$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

This step-wise neutralisation can be observed when the acid is added slowly to the sodium carbonate.

The percentage by mass of sodium carbonate in a mixture of sodium hydroxide and sodium carbonate can be determined by carrying out titrations using two different indicators. Since both sodium hydroxide and sodium carbonate react with acids, through careful selection of the indicators used for the titration, the volume of acid required to react with only the sodium carbonate can be found.

FA 3 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 4 is an aqueous solution containing sodium hydroxide, $NaOH$, and sodium carbonate, Na_2CO_3.

You are also provided with bromophenol blue indicator.

In this question, you will carry out titrations to determine the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in solution **FA 4**.

(a) (i) **Titration of FA 4 against FA 3 using bromophenol blue**

1. Fill a burette with **FA 3**.
2. Pipette 25.0 cm^3 of **FA 4** into a conical flask.
3. Add four to five drops of bromophenol blue indicator.
4. Titrate the mixture in the flask with **FA 3** until the blue-violet colour of the solution changes to yellow.
5. Record your titration results, to an appropriate level of precision, in the space provided.

Repeat steps 2 to 5 to obtain consistent results.

Titration results

[6]

(ii) From your titration results, obtain a suitable volume of **FA 3**, $V_{\textbf{FA 3}}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{\textbf{FA 3}}$ = ...

[1]

(b) When the titrations in **(a)** were repeated using **phenolphthalein** as the indicator, 25.0 cm^3 of **FA 4** required 15.00 cm^3 of **FA 3**.

The following explains why different results are obtained using two different indicators.

- When phenolphthalein is used as the indicator, the following reactions have taken place at the end-point of the titration.

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

- When bromophenol blue is used as the indicator in **(a)**, the following reactions have taken place at the end-point of the titration.

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

Reaction 3 $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

For the titration using **bromophenol blue**, the amount of Na_2CO_3 reacted in *Reaction 2* is equal to the amount of sodium bicarbonate, $NaHCO_3$, reacted in *Reaction 3*. Both the amounts of Na_2CO_3 reacted in *Reaction 2* using **phenolphthalein or bromophenol blue** are the **same**.

Show your working and use appropriate significant figures in the final answers to all steps of your calculations.

(i) Calculate the amount of HC*l* in the volume of **FA 3**, $V_{\textbf{FA 3}}$, determined in **(a)(ii)**.

Amount of HC*l* in $V_{\textbf{FA 3}}$ = ...

(ii) Calculate the amount of HC*l*, in 15.00 cm^3 of **FA 3**.

Amount of HC*l* in 15.00 cm^3 of **FA 3** = ...

[1]

(iii) With reference to the information given in **(b)** and your answers to **(b)(i)** and **(b)(ii)**, calculate the amount of HC*l* that reacted with Na_2CO_3 in *Reaction 2* using **phenolphthalein** indicator.

Amount of HC*l* reacted with Na_2CO_3 in *Reaction 2* using phenolphthalein = ...

[1]

(iv) Use your answer to **(b)(iii)** to calculate the mass of Na_2CO_3 present in 25.0 cm^3 of **FA 4**.
[A_r : C, 12.0; O, 16.0; Na, 23.0]

Mass of Na_2CO_3 in 25.0 cm^3 of **FA 4** = ...

[1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HC*l* when **bromophenol blue** is used as indicator is given below.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

Calculate the amount of HC*l* that reacted with Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 4**.

Amount of HC*l* reacted with Na_2CO_3 using bromophenol blue = ...

[1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of NaOH in 25.0 cm^3 of **FA 4**.
[A_r : H, 1.0; O, 16.0; Na, 23.0]

Mass of NaOH in 25.0 cm^3 of **FA 4** = ...

[1]

(vii) Calculate the percentage by mass of Na_2CO_3 in the mixture of NaOH and Na_2CO_3 in **FA 4**.

FA 4 contains .... % by mass of Na_2CO_3

[2]

(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:	±0.06 cm^3

Calculate the percentage error (uncertainty) when a
- 50.00 cm^3 burette
- 25.0 cm^3 pipette

is used to measure 25 cm^3 of **FA 4** into the conical flask.

Hence explain whether the 50.00 cm^3 burette or the 25.0 cm^3 pipette will be a more precise apparatus to measure 25 cm^3 of **FA 4**.

percentage error (uncertainty) of burette = ... %

of pipette = ... %

explanation ....

....

[2]

(d) Planning

You are to plan an experiment to determine the percentage by mass of sodium carbonate in an unknown solid sample by measuring the volume of carbon dioxide gas evolved on reaction with excess acid at room temperature and pressure.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

You may assume that you are provided with:
- 0.5 mol dm^{-3} hydrochloric acid, HC*l*;
- 0.5 g impure solid sample containing sodium carbonate, Na_2CO_3. Other impurities present are assumed to have no reaction with acid;
- 100 cm^3 gas syringe for gas collection;
- apparatus normally found in a school laboratory.

Your plan should include:
- calculations of suitable mass of impure sample and volume of excess hydrochloric acid to be used, based on a 100 cm^3 gas syringe;
- a fully-labelled diagram of the experimental set-up;
- practical details of how you would
  - ensure a known mass of solid sample and volume of acid are measured;
  - determine the volume of carbon dioxide evolved, including the measurements to be made;
  - ensure that an **accurate** and **reliable** volume of gas is obtained.

  [M_r : Na_2CO_3, 106.0]

Diagram

[7]

[Total: 23]

3 Qualitative Analysis

Where reagents are selected for use in a test, the **name** or **correct formula** of the element or compound must be given.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You should indicate clearly at what stage in a test a change occurs.
If there is no observable change, write **no observable change**.

Rinse and reuse test-tubes and boiling tubes where possible.

(a) **FA 5** contains **two** cations and **two** anions from the lists on pages 17 and 18.

- To approximately half a boiling tube of distilled water, add all the **FA 5**.
- Stopper and shake the boiling tube thoroughly for one minute to make sure that no more of the solid will dissolve.
- Filter the mixture into a clean boiling tube.
- Place the filter funnel in a conical flask and wash the residue well with distilled water.
- **Keep both filtrate and residue for (a)(i) and (a)(ii) respectively.**

While you are waiting for the mixture to filter, continue with (b) or (c).

(i) **Tests on the filtrate**

Carry out the following tests and record your observations in Table 3.1 below.

Table 3.1

	test	observations
1.	To a 1 cm depth of the filtrate in a test-tube, add aqueous ammonia, slowly with shaking until no further change is seen;	[1]
	then add aqueous hydrogen peroxide.	[1]

(ii) **Tests on the residue**

Carry out the following tests and record your observations in Table 3.2 below.

Table 3.2

	test	observations
2.	Place the funnel containing the residue into a clean test-tube. Pour approximately 5 cm^3 of dilute nitric acid onto the residue. Collect the resultant filtrate. Discard the first 1 cm depth of this resultant filtrate and collect the remaining filtrate in another clean test-tube for test 3.	[1]
3.	To 1 cm depth of the solution in a test-tube, add aqueous sodium hydroxide, slowly with shaking until no further change is seen.	[1]

(iii) Identify the **two** cations present in **FA 5**. Use evidence from your observations in **(a)(i)** and **(a)(ii)** to support your deduction.

cations present .... and ....

evidence ....

....

....

.... [2]

(iv) The tests you have carried out in **(i)** and **(ii)** would have enabled you to identify only one of the two anions present in **FA 5**. Identify this anion.

anion present .... [1]

(v) Suggest what type of reaction is happening when hydrogen peroxide is added in test **(a)(i)**.

.... [1]

(vi) In test 1 of **(a)(i)**, aqueous ammonia behaved as an Arrhenius base:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In a separate experiment, an equal volume of aqueous ammonium chloride, NH_4Cl was added to a second portion of the filtrate that was used in **(a)(i)**. When aqueous ammonia was then added to this resultant solution, no precipitate formed.

Suggest an explanation for the results of this experiment.

....

....

....

.... [2]

(b) **FA 6** is an aqueous solution containing nickel(II) ion.

Carry out the following tests on **FA 6** and record your observations in Table 3.3 below.

Table 3.3

	test	*observations*
(i)	To a 1 cm depth of **FA 6** in a test-tube, add aqueous ammonia, slowly with shaking, until no further change is seen.	[1]
(ii)	To a 1 cm depth of **FA 6** in a test-tube, add aqueous sodium hydroxide, slowly with shaking, until no further change is seen.	[1]

(iii) Nickel(II) ions form complexes with ligands such as ammonia and ethylenediamine as shown:

$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$ $K_c = 4.8 \times 10^7\ mol^{-6}\ dm^{18}$

$[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons \underset{\text{purple}}{[Ni(en)_3]^{2+}(aq)} + 6H_2O(l)$ $K_c = 2.0 \times 10^{18}\ mol^{-3}\ dm^9$

[en ≡ ethylenediamine]

The observation in **(b)(i)** is due to the formation of the nickel-ammonia complex.

Suggest, with reason, what might be observed if aqueous ammonia were added to a solution containing $[Ni(en)_3]^{2+}$ ions instead of $Ni^{2+}(aq)$.

....

....

....

....[2]

(c) **FA 7**, **FA 8** and **FA 9** are 1.0 mol dm^{-3} sulfuric acid, 0.1 mol dm^{-3} sulfuric acid and 1.0 mol dm^{-3} hydrochloric acid, but not necessarily in that order.

You are to plan and carry out **two** simple tests, using only the bench reagents provided, which will enable you to determine the identities of **FA 7**, **FA 8** and **FA 9**.

You should record, in a suitable form in the space below, your tests and observations. You should show clearly the observations for each of **FA 7**, **FA 8** and **FA 9** with all test reagents.

FA 7 is ....

FA 8 is ....

FA 9 is ....

[4]

[Total: 18]

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) 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) 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

TAMPINES MERIDIAN JUNIOR COLLEGE

2019 JC2 H2 Chemistry Prelim Exam Paper 1

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1 Some data of the ions of four unknown elements are given in the table below.

	A^+	$B^–$	$D^{2–}$	$E^{3–}$
mass number	21	20	20	21
number of protons	–	11	9	–
number of electrons	9	–	–	12

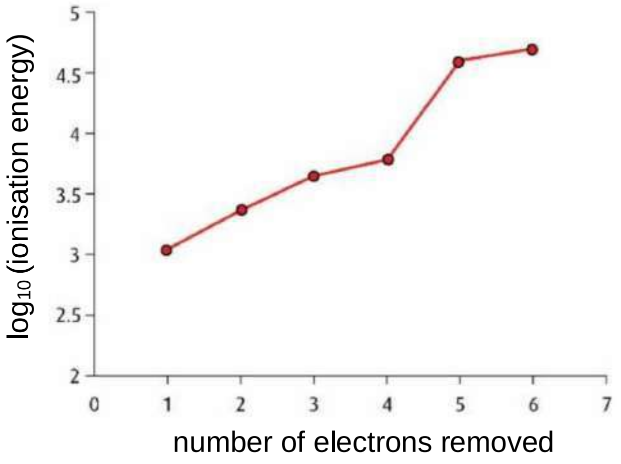
Which of the following correctly shows pairs of isotopic and isoelectronic species?

	isotopic	isoelectronic
A	$D^{2–}$, $E^{3–}$	$B^–$, $E^{3–}$
B	$B^–$, $D^{2–}$	A^+, $B^–$
C	$B^–$, $D^{2–}$	$B^–$, $E^{3–}$
D	$D^{2–}$, $E^{3–}$	A^+, $B^–$

Answer: A

<table>
<tr><th></th><th>A^+</th><th>$B^–$</th><th>$D^{2–}$</th><th>$E^{3–}$</th></tr>
<tr><td>mass number</td><td>21</td><td>20</td><td>20</td><td>21</td></tr>
<tr><td rowspan="2">number of protons</td><td rowspan="2">10</td><td rowspan="2">11</td><td>9</td><td>9</td></tr>
<tr><td colspan="2">D^{2-} and E^{3-} are isotopic</td></tr>
<tr><td rowspan="2">number of electrons</td><td rowspan="2">9</td><td>12</td><td>11</td><td>12</td></tr>
<tr><td colspan="3">B^- and E^{3-} are isoelectronic</td></tr>
</table>

2 The first six ionisation energies of element **G** are plotted in the graph below.



Which of the following can be deduced from the graph?

A There are 2 quantum shells in element **G**.

B Element **G** is from Group 2 in the Periodic Table.

C The fifth and sixth electrons are removed from the same subshell.

D The identity of element **G** is carbon.

Answer: C

With limited information from the graph, it is unclear if the jump from the 4th to the 5th I.E. is a change in subshell or quantum shell. Hence, options A, B and D cannot be concluded using the graph. Then only conclusion which can be made is that the 5th and 6th electrons are in the same subshell.

3 For which of the following pairs does the first molecule have a higher polarity than the second molecule?

1 CH_3OH, CH_3I

2 CF_4, CCl_4

3 *cis*-CHF=CHF, *trans*-CHF=CHF

A 1 only

B 1 and 3

C 2 and 3

D 1, 2 and 3

Answer: B

1 Although both CH_3OH and CH_3I are polar, CH_3OH has higher polarity because O is more electronegative than I, hence the C–O bond is more polar than the C–I bond.

2 Both CF_4 and CCl_4 are non-polar as both have net zero dipole moment.

3 *trans*-CHF=CHF is non-polar as both C–F dipole moment cancels out, hence net zero dipole moment. *cis*-CHF=CHF is polar.

4 Three substances **H**, **I** and **J** have physical properties shown in the table below.

substance	melting point/ °C	boiling point/ °C	electrical conductivity	
			of solid	of liquid
H	801	1413	poor	good
I	2852	3600	poor	good
J	3500 at very high pressure	unable to determine	poor	unable to determine

What are the possible identities for substances **H**, **I** and **J**?

	H	**I**	**J**
A	$NaCl$	$AlCl_3$	C (diamond)
B	MgO	$AlCl_3$	C (graphite)
C	$NaCl$	MgO	C (graphite)
D	$NaCl$	MgO	C (diamond)

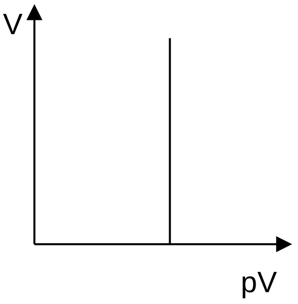
Answer: D

- Substance **H** should have a **giant ionic structure**, where NaCl or MgO are possible identities.
- Substance **I** should also have a **giant ionic structure but with larger lattice energy** compared to substance **H**. $AlCl_3$ cannot be substance **H** because it is a simple molecule. Hence, **H** must be MgO.
- Substance **J** should have a **giant molecular structure, which does not conduct electricity**. Hence, **J** must be diamond.

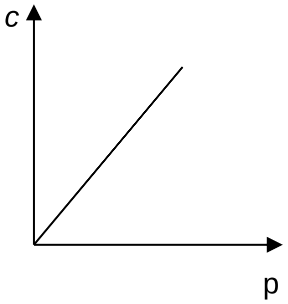
5 Which of the following diagrams correctly describe the behaviour of a fixed mass of an ideal gas at constant temperature?

[*c* is concentration]

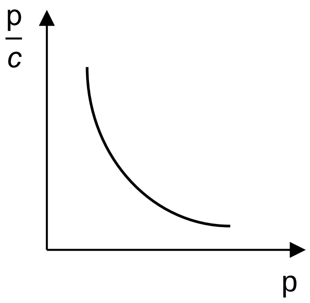
graph 1



graph 2



graph 3



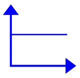
A 2 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

Answer: B

✓	1	pV = nRT pV = constant (T is constant) pV plotted on horizontal axis ⇒ graph resembles "x = constant" graph.
✓	2	pV = nRT pV = $\frac{m}{M}$RT (where m is mass and M is molar mass) p = $\frac{m}{V}$ × constant (T and M are constant) p = *c* × constant ⇒ *c* = p × constant ⇒ graph resembles "y = constant × x" graph.
✗	3	p = *c* × constant $\frac{p}{c}$ = constant ⇒ graph resembles "y = constant" graph. 

6 In which of the following reactions is the underlined reactant acting as a Lewis acid?

A $\underline{BF_3} + F^- \longrightarrow BF_4^-$

B $AlCl_3 + \underline{Cl_2} \longrightarrow AlCl_4^- + Cl^+$

C $Ag^+ + 2\underline{NH_3} \longrightarrow [Ag(NH_3)_2]^+$

D $H_2O + \underline{HSO_3^-} \longrightarrow H_2SO_3 + OH^-$

Answer: A

Lewis acid: species (molecule or ion) that can **accept** a pair of electrons

✓	A	In the formation of BF_4^-, F^- donates a pair of electrons for dative bond formation to B in BF_3 (B here is electron-deficient, with only 6 electrons around it).
×	B	Cl in Cl_2 donates a pair of electrons for dative bond formation to Al in $AlCl_3$ (Al here is electron-deficient, with only 6 electrons around it) ⇒ $AlCl_3$ is the Lewis acid.
×	C	NH_3 donates a pair of electrons for dative bond formation to Ag^+.
×	D	HSO_3^- donates a pair of electrons for dative bond formation to H^+ (from H_2O) ⇒ H^+ is the Lewis acid.

7 Which of the following statements is true of the Period 3 chlorides, $NaCl$ to PCl_5?

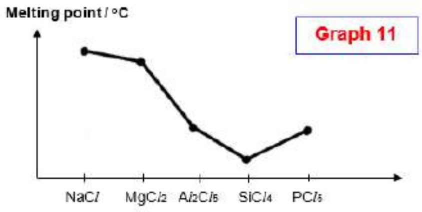
A The melting points of the chlorides show a continuously decreasing trend.

B The pH of the solutions formed when the chlorides are added to water range from alkaline to acidic.

C Three of the chlorides have simple molecular structures.

D The only chlorides which undergo hydrolysis in water are $AlCl_3$ and $MgCl_2$.

Answer: C

×	A	 *(pg 15 of Periodic Table lecture notes)*
×	B	The pH of aqueous $NaCl$ is 7, not alkaline.
✓	C	$NaCl$ and $MgCl_2$ are both ionic while the other 3 chlorides are covalent. The covalent chlorides have simple molecular structure.
×	D	All the chlorides, except for $NaCl$ undergo slight or complete hydrolysis.

8 The relative abundances of the isotopes of a sample of titanium are shown in the table below.

relative isotopic mass	46	47	48
relative abundance	11.2	10.1	*z*

Given that the relative atomic mass of the sample is 47.862, what is the value of *z*?

A 214.2 **B** 79.1 **C** 78.7 **D** 26.6

Answer: A

$$\frac{(46 \times 11.2) + (47 \times 10.1) + (48 \times z)}{11.2 + 10.1 + z} = 47.862 \qquad \Rightarrow z = \underline{\mathbf{214.2}}$$

9 A metallic salt was found to react exactly with sulfite ions in a 2 : 1 ratio.

In this reaction, the sulfite ion is oxidised as follows.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e^-$$

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

Since SO_3^{2-} lost e^-, the metallic salt gained e^-.

Let the moles of e^- gained by 1 mole of metallic salt be y

Total moles of e^- gained = Total moles of e^- lost

$2 \times y = 1 \times 2$

$\Rightarrow y = 1$

$\Rightarrow$ new ox. state is $\underline{\mathbf{+2}}$

10 The enthalpy changes for the following reactions are given:

$2Cr(s) + \frac{3}{2}O_2(g) \rightarrow Cr_2O_3(s)$ $\Delta H_f(Cr_2O_3(s)) = -1120$ kJ mol^{-1}

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ $\Delta H_f(CO(g)) = -110$ kJ mol^{-1}

What is the enthalpy change of reaction for the following reaction, in terms of kJ mol^{-1}?

$$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g)$$

A – 940 **B** – 870 **C** + 590 **D** + 790

Answer: D

$\Delta H_{rxn} = 3(-110) - (-1120) = \underline{\mathbf{+790\ kJ\ mol^{-1}}}$

11 An experiment was conducted by reacting propyne with hydrogen gas in a shock tube.

$$CH_3C{\equiv}CH(g) + 2H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

The value of ΔG for the reaction is found to be negative at low temperature.

What is the sign of ΔH and ΔS for the above reaction?

	ΔH	ΔS
A	–	–
B	+	–
C	–	+
D	+	+

Answer: A

There is a decrease in number of moles of gaseous particles (from 3 moles to 1 mole) after the reaction, thus ΔS is negative.

$\Delta G = \Delta H - T\Delta S$

Since ΔG is negative and $-T\Delta S$ is positive, ΔH should be negative.

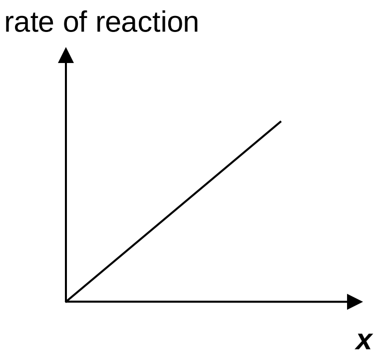
12 The kinetics of the reaction between hydrogen peroxide and acidified iodide ions were investigated.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

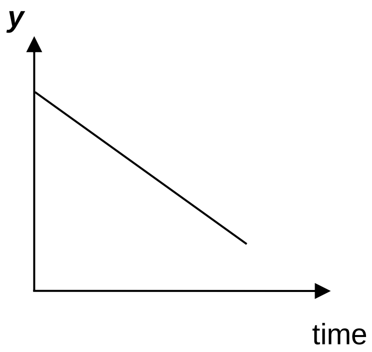
The rate equation was found to be: rate = $k[H_2O_2][I^-]$

Which of the following shows the correct labelling of the ***x***-axis for **Graph I** and ***y***-axis for **Graph II**?

Graph I



Graph II



	***x*-axis for Graph I**	***y*-axis for Graph II**
A	$[I^-]$	$[H_2O_2][I^-]$
B	$[H^+]$	$[I_2]$
C	$[H_2O_2][I^-]$	$[H^+]$
D	$[H_2O_2][H^+]$	$[I^-]$

Answer: C

Graph I : $\underbrace{\text{Rate}}_{y} = k\underbrace{[H_2O_2][I^-]}_{x}$ (similar to y=mx graph)

Graph II : gradient of the graph shows that rate is independent [reactant]

13 The reaction between HBr and O_2 is thought to occur via a multi-step mechanism:

$HBr + O_2 \rightarrow HO_2Br$ (slow)

$HO_2Br + HBr \rightarrow 2HOBr$ (fast)

$HOBr + HBr \rightarrow Br_2 + H_2O$ (fast)

The overall reaction is given to be $4HBr + O_2 \rightarrow 2Br_2 + 2H_2O$.

Which of the following statements are true?

1 The overall order of reaction is 2.

2 HO_2Br is the only intermediate in the reaction.

3 HOBr acts as a catalyst in the reaction.

A 1 only

B 3 only

C 1 and 2

D 1, 2 and 3

Answer: A

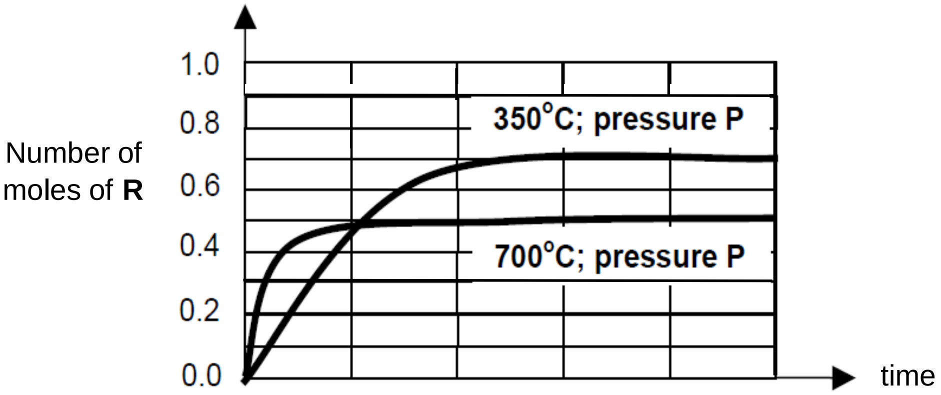
Rate = k[HBr][O_2] ⇒ overall order of reaction is 2

HO_2Br and HOBr are the intermediates in the reaction (they do not appear in the overall equation).

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_c decreases with an increase in temperature.

B The equilibrium is achieved at a faster rate at higher temperatures.

C The enthalpy change for the forward reaction is negative.

D The activation energy of the forward reaction is high.

Answer: D

From the graph,
Amount of product R decreases when temperature is increased from 350°C to 700°C
=> $\boldsymbol{K_c}$ decreases.
Rate of reaction increases with increase in temperature.

By Le Chatelier's Principle, when temperature increases, equilibrium position shifts towards the endothermic reaction to absorb heat. From graph, equilibrium position shifts to the left.

⇨ Backward reaction is endothermic
⇨ Forward reaction is exothermic.
⇨ Enthalpy change for the forward reaction is negative.

The graph does not provide any information about the activation energy for the reaction.

15 The dissociation constants, K_w, for the ionisation of water at different temperatures are given below.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

temperature / °C	K_w / mol^2 dm^{-6}
0	1.15×10^{-15}
25	1.00×10^{-14}
50	5.50×10^{-14}

What can be deduced from this information?

A Only at 25 °C are $[H^+]$ and $[OH^-]$ equal.
B K_w is not affected by changes in temperature.
C The forward reaction is exothermic.
D The pH of water decreases as temperature increases.

Answer: D

- Option **A** is incorrect. $[H^+]$ and $[OH^-]$ are equal at all temperature for pure water.
- Option **B** is incorrect. K_w is an equilibrium constant thus it is affected by changes in temperature as shown in the different K_w values at various temperatures.
- Option **C** is incorrect. When temperature increases, K_w increases. This shows that position of equilibrium shifts to the right towards the forward reaction which is endothermic.
- Option **D** is correct. $K_w = [H^+][OH^-]$. By inspection, when temperature rises, $[H^+]$ increases. Hence, pH of water decreases.

16 The following tests were performed on an aqueous solution containing chloride and iodide ions.

step	test	observations
1	Add excess $AgNO_3$(aq).	Mixture of white and yellow precipitates is formed.
2	To the mixture from step 1, add excess NH_3(aq).	White precipitate dissolves to form a colourless solution. Yellow precipitate is insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.

Which of the following statements are correct?

1 The K_{sp} for Ag*Cl* is lower than that for AgI.

2 There are no Ag^+(aq) and Cl^-(aq) present in the filtrate formed in Step 3.

3 In step 2, the addition of NH_3(aq) results in the formation of $[Ag(NH_3)]_2^+$ that momentarily decreases the ionic product of Ag*Cl*.

A 3 only
B 1 and 2
C 2 and 3
D 1, 2 and 3

Answer: A

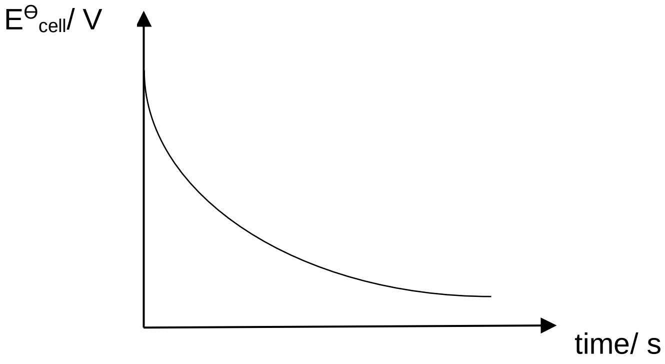
Statement 1 is incorrect as K_{sp} for Ag*Cl* is higher than that for AgI.

Statement 2 is incorrect. The filtrate contains saturated solution of Ag^+(aq) and Cl^-(aq) as well as I^-(aq) that is not precipitated.

Statement 3 is correct. The complex formation $[Ag(NH_3)]^{2+}$ reduces the concentration of Ag^+(aq) which decreases ionic product of Ag*Cl*.

17 An experiment is carried out between the Fe^{2+}/Fe and Co^{2+}/Co half cells.

The following graph of cell potential against time was obtained when a change was continuously made to the half-cell.



What continuous change could produce this graph?

A add aqueous cobalt(II) ions to the cobalt half-cell

B add aqueous ammonia to the cobalt half-cell

C add water to the iron half-cell

D increase the mass of solid iron immersed in the solution

Answer: **B**

$E_{cell} = E_{red} - E_{oxd} = E_{Co^{2+}/Co} - E_{Fe/Fe^{2+}}$

Option **A** is incorrect.

$Co^{2+} + 2e \rightleftharpoons Co$ $E^{\theta} = -0.28V$

When cobalt (II) ions is added to the cobalt half-cell, $[Co^{2+}]$ increases. Position of eqm shifts right which causes $E_{Co^{2+}/Co}$ (E_{red}) to be more positive. Thus, E_{cell} increases.

Option **B** is correct.

When aqueous ammonia is added to the cobalt half-cell, complex $[Co(CN)_6]^{2+}$ is formed. This complex formation decreases the concentration of aqueous Co^{2+} which causes the position of eqm to shift left leading to $E_{Co^{2+}/Co}$ (E_{red}) becoming less positive. Thus, E_{cell} decreases.

Option **C** is incorrect.

$Fe^{2+} + 2e \rightleftharpoons Fe$ $E^{\theta} = -0.44V$

When water is added to the iron half-cell, $[Fe^{2+}]$ decreases. Position of eqm shift left causing $E_{Fe^{2+}/Fe}$ (E_{oxd}) to be less positive. Thus, E_{cell} increases.

Option **D** is incorrect as an increase in the mass of solid iron does not affect E values.

18 Which of the following statements about octahedral complexes is correct?

A The ratio of hexadentate ligands to the central metal ion is 6:1.

B The d_{xz}, d_{yz} and d_{xy} orbitals are higher in energy than the $d_{x^2-y^2}$ and d_{z^2} orbitals.

C The d orbitals are split into different energy levels due to different orientation of the orbitals to the ligands.

D The same transition metal with different oxidation states displays the same colour with the same ligands.

Answer: C

A is not correct as the coordination number of octahedral complexes is 6; as each hexadentate ligands can form 6 dative bonds per ligand, the ratio of hexadentate ligands to complex should thus be 1:1 (not 6:1).

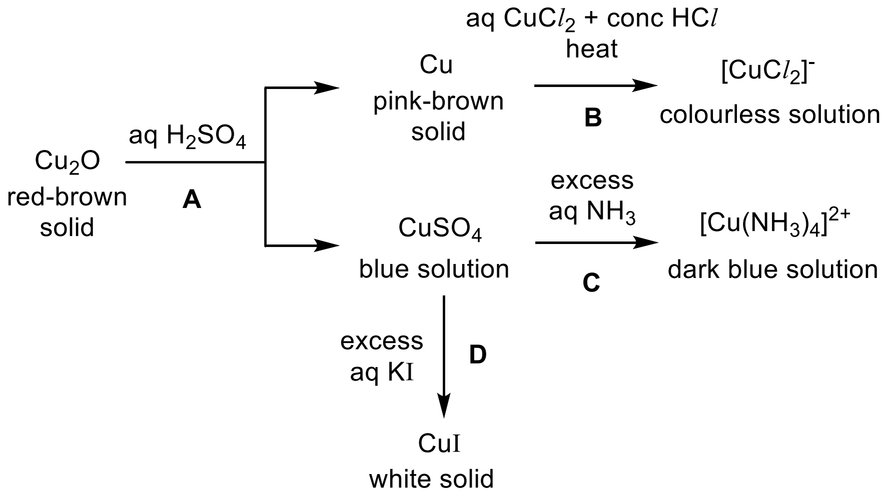
B is not correct as electrons in the d orbitals lying along the bonding axes (ie. x, y and z axes) would experience greater repulsion with the ligands, the $d_{x^2-y^2}$ and d_{z^2} orbitals are higher in energy in octahedral complex.

C is correct as the ligand field splitting arises from the repulsion of the electrons in the d orbitals with the ligands and this would be influenced by the orientation of the orbitals and the ligands.

D is not correct as different complexes with the same metal but different oxidation states will have with different d electronic configurations, hence even though the ligands may be same, the colours will be different.

19 The diagram below shows some reactions involving copper and its compounds.

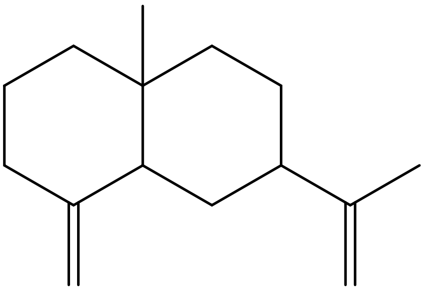
Which reaction involves ligand exchange only?



Answer: C

- **A** is a disproportionation (redox) reaction where Cu_2O (O.S.= +1) forms Cu metal (O.S. = 0) and $CuSO_4$ (O.S. = +2).
- **B** is a redox (comproportionation) reaction where Cu metal (O.S. = 0) and $CuCl_2$ (O.S. = +2) forms $[CuCl_2]^-$ (O.S. = +1).
- **C** is a **ligand exchange** where H_2O ligands in $[Cu(H_2O)_6]^{2+}$ complex is replaced with NH_3 ligands to form a new complex $[Cu(NH_3)_4]^{2+}$.
- **D** is a redox reaction involving Cu^{2+} (O.S. = +2) reducing to form CuI in the presence of excess I^-; $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

20 β-selinene is a molecule that can be isolated from plants. It has the following structural formula.



β-selinene

Which of the following statements about this molecule is correct?

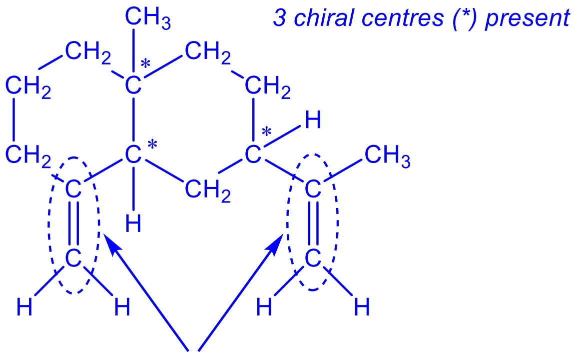
A It has a plane of symmetry.

B It does not contain any sp hybridised carbon.

C It has one chiral centre.

D It exhibits cis-trans isomerism.

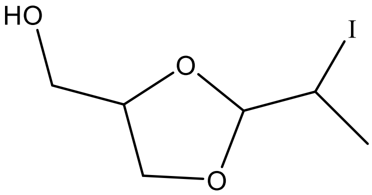
Answer: B



do not exibit cis-trans isomerism

Based on the options, only constitutional isomers possible.

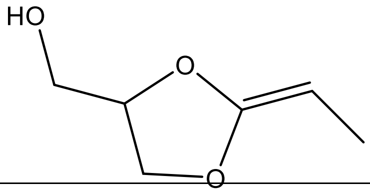
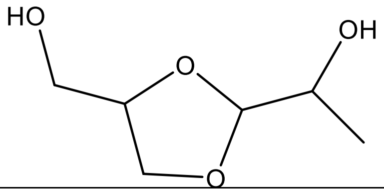
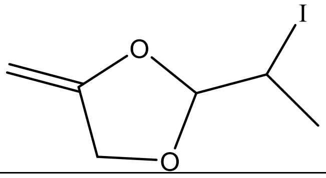
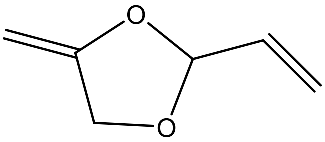
21 Iodinated glycerol is used in the symptomatic treatment of patients with chronic obstructive pulmonary disease.



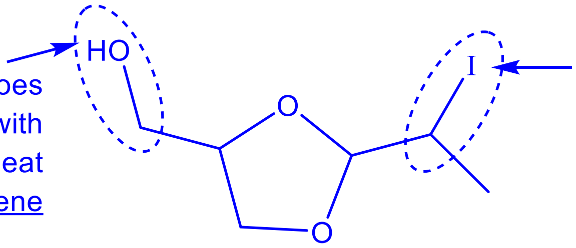
iodinated glycerol

Which of the following correctly shows the product formed when iodinated glycerol is reacted with the given reagents and conditions?

[The C–O–C bond in the structure is inert to the reagents.]

	reagent & conditions	*product*
A	alcoholic KOH, heat	
B	alcoholic KOH, heat	
C	aqueous KOH, heat	
D	concentrated H_2SO_4, heat	

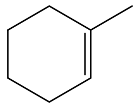
Answer: A



alcohol, undergoes elimination with conc H_2SO_4, heat to form alkene

halogenoalkane, undergoes elimination with alcoholic base, heat to form alkene / *nucleophilic substitution* with *aqueous* base, heat to *form alcohol*

22 Which of the following compounds react with HBr in an addition reaction to give a major chiral product?

1 

2 CH(Br)=CH_2

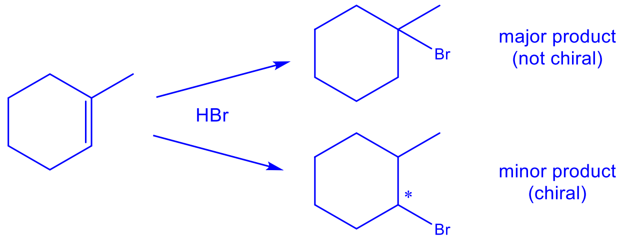
3 $CH_3CH=C(CH_3)CH_2CH_3$

4 $CH_2=CHCH_2CH_3$

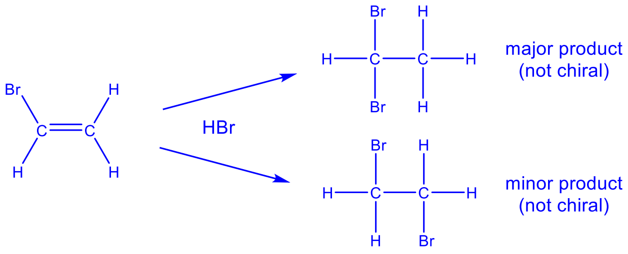
A 1 and 3 **B** 1 and 4 **C** 2 and 3 **D** 4 only

Answer: D

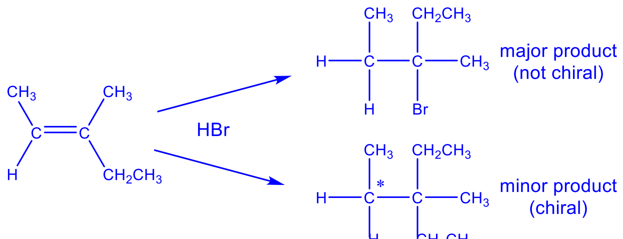
Compound 1



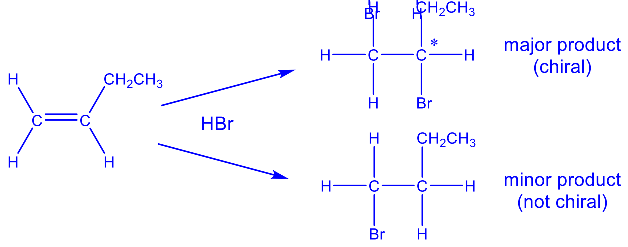
Compound 2



Compound 3

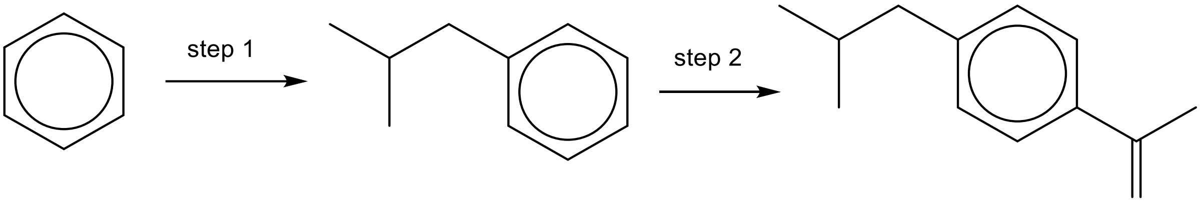


Compound 4



Only Compound 4 gives a major product upon electrophilic addition that is chiral.

23 Two of the steps in the manufacture of the pain-relief drug, ibuprofen are shown below.



ibuprofen

Which statement is correct?

A Both steps involve the use of catalyst.

B The sequence of the steps are interchangeable.

C Both steps involve different types of reaction.

D Only step 2 involves the use of a halogen-containing reagent.

Answer: A

Both reactions are electrophilic substitution (Friedel-Crafts Alkylation and Friedel-Crafts Acylation respectively) and both require the use of $AlCl_3$ catalyst.

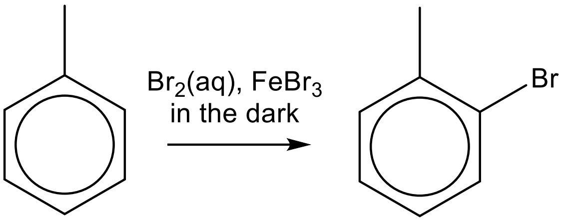
The reagents required for alkylation and acylation are halogenalkane, $CH_3CH(CH_2Cl)CH_3$ and acyl chloride, CH_3COCl respectively and both contain halogen.

As the desired product contains a benzene ring that is 1,4-disubstituted, it is necessary to carry out alkylation first followed by acylation as alkyl group is 2,4-directing whereas $–COCH_3$ group is 3-directing.

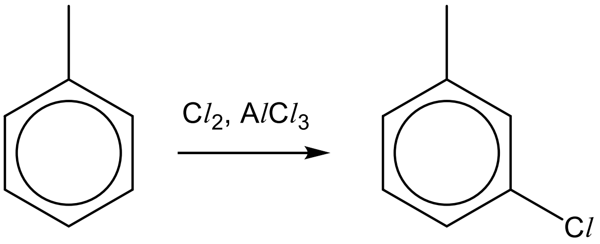
24 The reaction conditions for four electrophilic substitution reactions are given below.

Which reaction would yield the product stated?

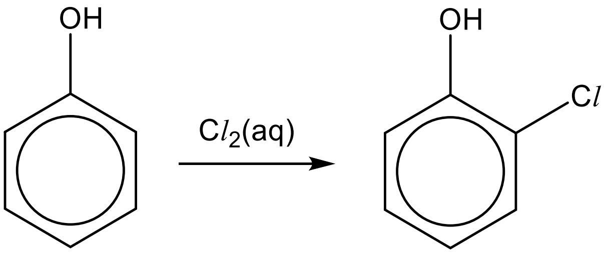
A



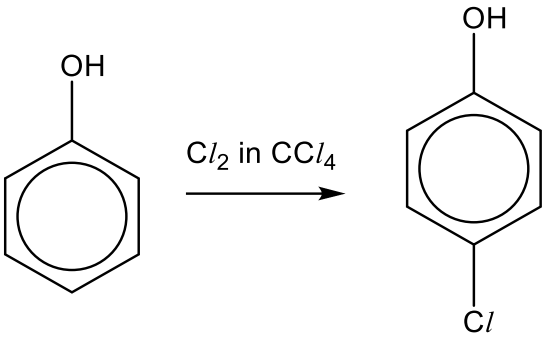
B



C



D



Answer: D

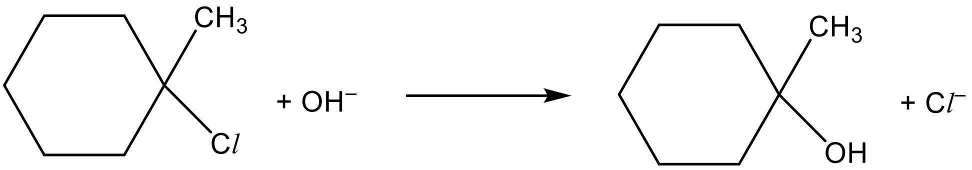
A: As aqueous Br_2 is used, $FeBr_3$ may not be formed.

B: as $–CH_3$ is 2,4-directing thus 3-chloromethylbenzene formed is a minor product

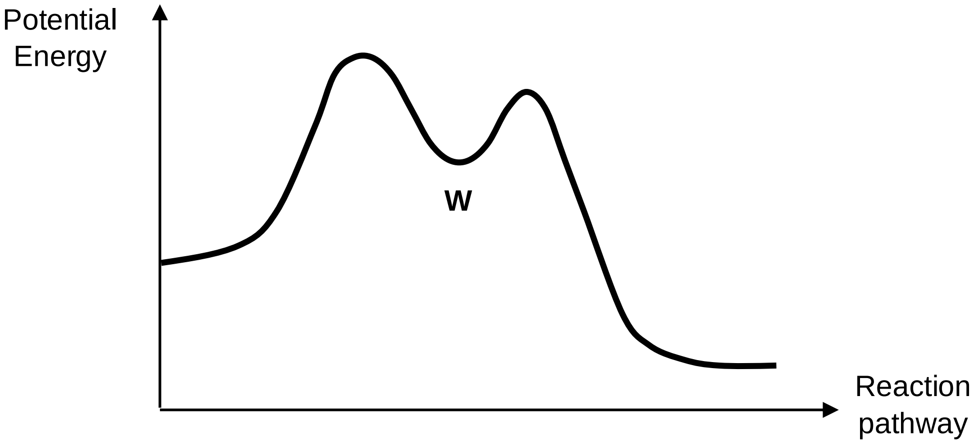
C: use of aqueous chlorine should result in a multi-substituted product for phenol

D: use of chlorine in organic solvent will result in a mono-substituted product for phenol

25 1-chloro-1-methylcyclohexane is hydrolysed by heating with NaOH(aq).



The energy profile diagram for this reaction is shown below.



Which statements regarding this reaction are correct?

1 The species at point **W** bears a positive charge.

2 The reaction proceeds via S_N2 mechanism since it is a two-step mechanism.

3 The same energy profile diagram would be obtained if chloromethane undergoes the same reaction.

A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

Answer: A

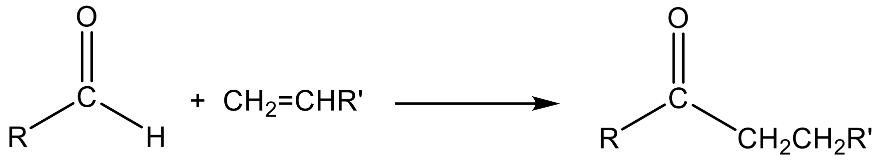
The mechanism shown is S_N1

1 **W** is an intermediate which is a carbocation.

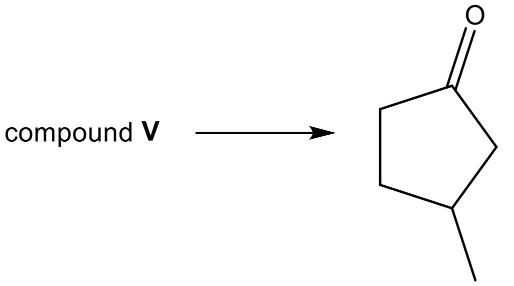
2 The energy profile diagram depicts the S_N1 mechanism which is two-step

3 Chloromethane is a primary halogenoalkane and should undergo S_N2 mechanism.

26 Hydroacylation is a reaction in which an alkene is 'inserted' into the C–H bond of an aldehyde to form a ketone.



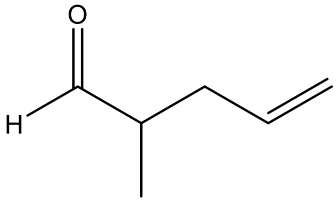
Compound **V** could be converted to 3-methylcyclopentanone using the above reaction.



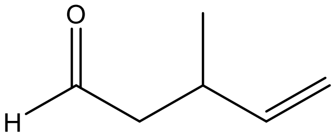
3-methylcyclopentanone

What could compound **V** be?

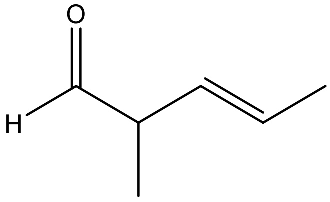
A



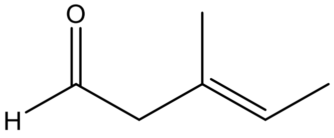
C



B

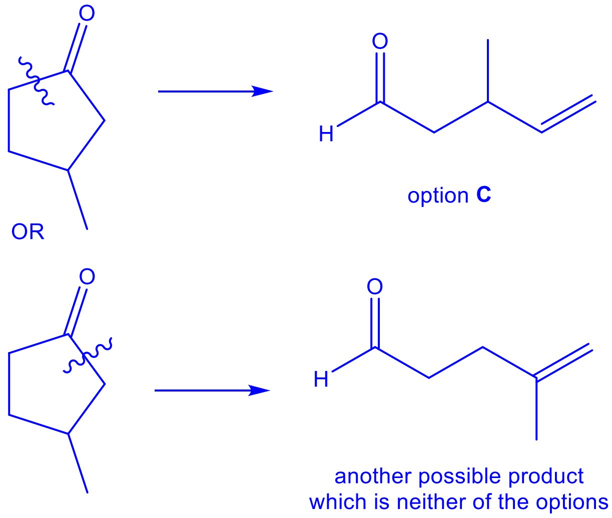


D



Answer: C

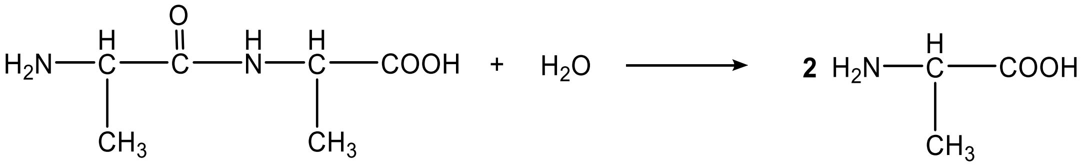
working backwards,



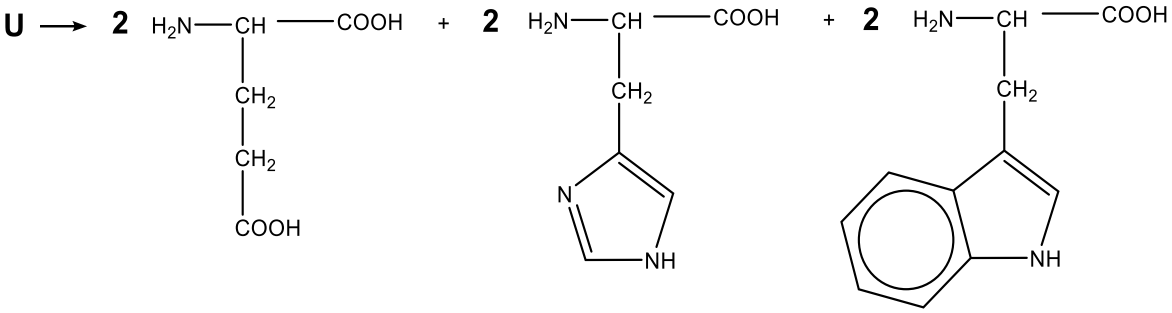
option **C**

another possible product
which is neither of the options

27 Peptidases are enzymes that hydrolyse the peptide bonds that bind amino acids together in the polypeptide chain of a protein.



Partial hydrolysis of a small peptide, **U**, by a peptidase, produces the following amino acids.



glutamic acid
M_r = 147

histidine
M_r = 155

tryptophan
M_r = 204

What is the M_r of the peptide **U**?

A 904

B 922

C 1012

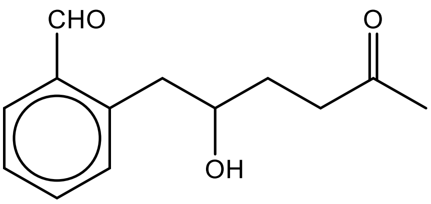
D 1102

Answer: B

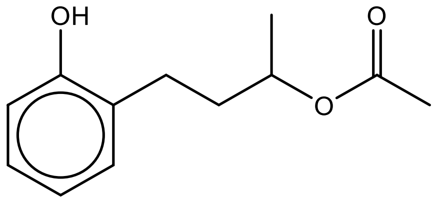
Since there are 6 amino acids, there are 6 –1 = 5 amide bonds

M_r of the peptide **U** = (147 x 2) + (155 x 2) + (204 x 2) – ({6–1} x 18) = **922**

28 Which of the following reagents could be used to distinguish between compounds **S** and **T**?



Compound **S**



Compound **T**

A I_2 in aqueous NaOH

B Cu^{2+} in alkaline solution

C aqueous NH_3 with $AgNO_3$

D acidified potassium dichromate

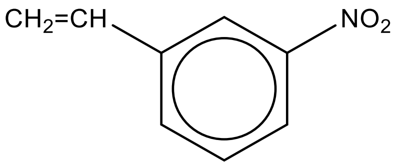
Answer: C

Aromatic aldehyde on compound **S** – positive test for Tollens' Reagent. (aqueous NH_3 with $AgNO_3$)

Both will give a positive test for iodoform test and oxidation reaction.

Both will give a negative test Fehling's solution.

29 3-nitrostyrene is an aromatic organic compound.



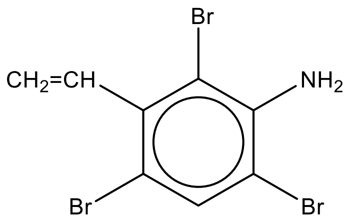
3-nitrostyrene

It is subjected to the following reactions:

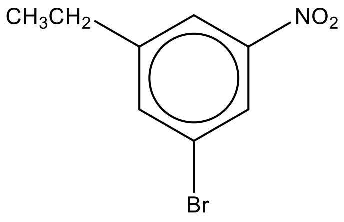
- heat with Sn in concentrated HC*l* followed by careful addition of cold NaOH(aq)
- then the addition of Br_2(aq)

What is the product obtained after the above reactions?

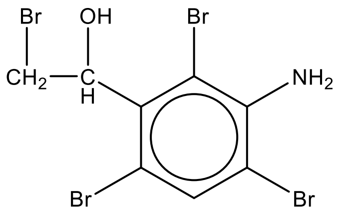
A



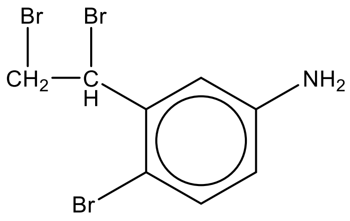
B



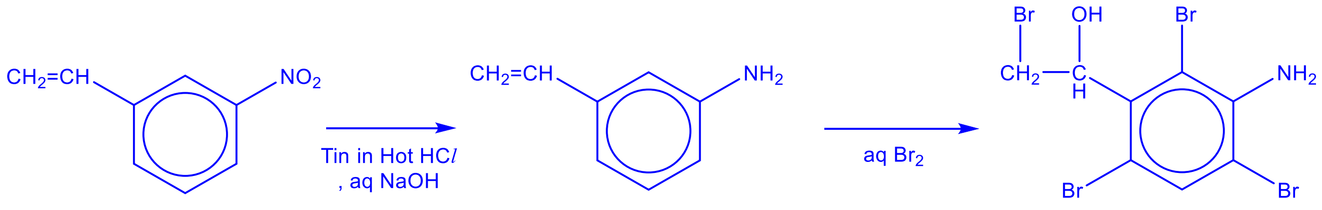
C



D

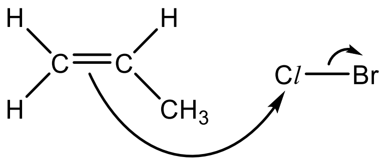


Answer: C

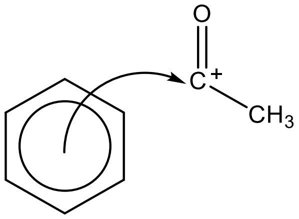


30 Which of the following show a correct mechanistic step in the reaction between the reagents?

1



2



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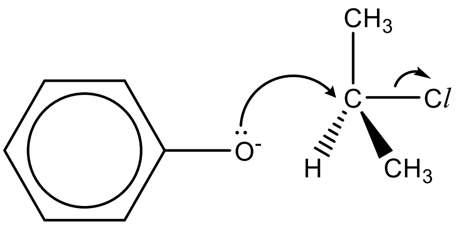

A 3 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

Answer: C

Option 1 is wrong as the alkene should attack the electron poor bromine atom instead.

Answers

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

TAMPINES MERIDIAN JUNIOR COLLEGE

2019 JC2 H2 Chemistry Prelim Exam Paper 2

(Suggested Answers)

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1 **(a)** Carbon forms compounds with Group 16 elements such as oxygen, sulfur and selenium. The properties of some of these compounds are given below.

compound	structure	net dipole moment	boiling point / °C
CO_2	O=C=O	0	sublimes
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	0.73	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling points of CS_2 and COS.

CS_2 has a **higher boiling point**. Both CS_2 and COS have **simple molecular structures.**
CS_2 has a **larger electron** cloud (or larger number of electrons) than COS. More energy is required to overcome the **stronger** **instantaneous dipole-induced dipole interactions (or IMF/Dispersion forces) between CS_2 molecules** than the **instantaneous dipole-induced dipole interactions between COS molecules**.

[2]

(ii) Explain why

- CO_2 has no net dipole moment.
- COSe has a greater net dipole moment than COS.

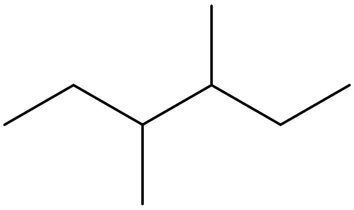
CO_2 has not net dipole moment because it is **linear** and the **dipole moments cancel out**.

COSe has a greater net dipole moment than COS.
There is a **smaller difference between the dipole moment of C=O and C=S in COS than that between C=O and C=Se in COSe**
since **S is more electronegative than Se**.
OR polarity of C=S is greater than that of C=Se.

[2]

Carbon forms the backbone of organic compounds. Hydrocarbons are the simplest organic compounds that contain carbon and hydrogen.

(b) Compound **A** is an isomer of the hydrocarbon octane, C_8H_{18}.

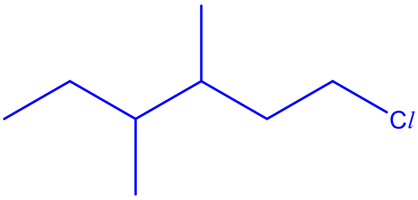


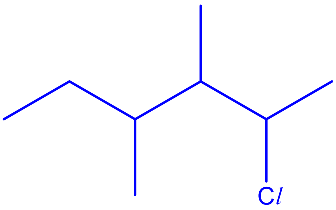
A

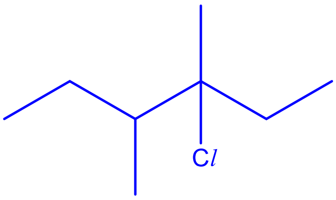
Controlled chlorination of compound **A** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

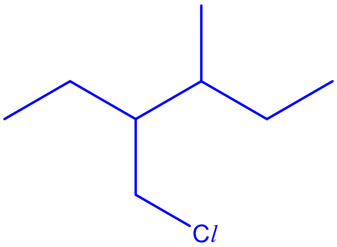
(i) Suggest the total number of constitutional isomers which can be formed from the possible mono-chlorination of compound **A**. Draw the structural formulae of any **two** of these products.

Total number of possible mono-chlorinated products = **4**



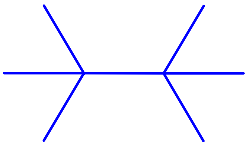






[3]

(ii) Draw the **skeletal** formula of the isomer of octane which could produce **only one** possible mono-chlorinated product if it undergoes free radical substitution.



[1]

(c) Besides reaction of alkanes with halogens, the process of thermal cracking, in which large alkane molecules are broken down into smaller alkanes and alkenes, proceeds via free radical mechanism.

The following are reactions involved when propane undergoes thermal cracking.

$CH_3CH_2CH_3 \longrightarrow \bullet CH_3 + \bullet CH_2CH_3$ -- (1)
$CH_3CH_2CH_3 \longrightarrow \bullet H + \bullet CH_2CH_2CH_3$ -- (2)
$\bullet CH_3 + CH_3CH_2CH_3 \longrightarrow CH_4 + \bullet CH_2CH_2CH_3$ -- (3)
$\bullet CH_2CH_3 \longrightarrow \bullet H + CH_2{=}CH_2$ -- (4)
$\bullet CH_3 + CH_2{=}CH_2 \longrightarrow \bullet CH_2CH_2CH_3$ -- (5)
$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$ -- (6)
$2\ \bullet CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$ -- (7)

(i) Reactions (1) and (2) are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

Reaction (1) is more likely to occur as it is easier to break a C-C bond (350 kJ mol^{-1}) compared to a C-H bond (410 kJ mol^{-1}).

[1]

(ii) From reactions (3) to (7), identify those which may be termed propagation steps in the mechanism.

Reactions (3), (4) and (5)

[1]

(iii) Which gas, if detected in the product mixture, would support the occurrence of both reactions (2) and (4)?

Hydrogen

[1]

(iv) Suggest why reaction (7) may be termed a *disproportionation* reaction.

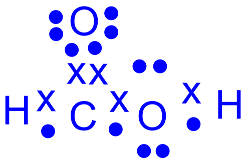
The $\bullet CH_2CH_3$ radical loses a hydrogen (is oxidised) to form ethene and gains a hydrogen (is reduced) to form ethane.

OR
The oxidation number of carbon in $\bullet CH_2CH_3$ increases –3 from to –2 in ethane and decreases from to –3 to form ethane.

[1]

(d) Methanoic acid, H_2CO_2, is the simplest carboxylic acid.

Draw a dot-and-cross diagram of methanoic acid. Suggest the shape around the carbon atom in methanoic acid.



Shape around C atom: **Trigonal planar**

[2]

[Total: 14]

2 Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

In investigations of this reaction, the following results were obtained by varying the volumes of hydrogen peroxide and iodide ions.

experiment	volume of H_2O_2 / cm^3	volume of I^- / cm^3	volume of H_2O / cm^3	initial rate / mol dm^{-3} s^{-1}
1	20.0	20.0	20.0	1.2×10^{-2}
2	20.0	30.0	10.0	1.8×10^{-2}
3	50.0	10.0	0.0	1.5×10^{-2}

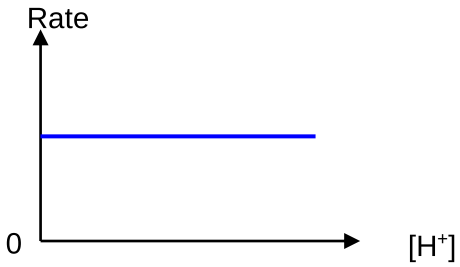
(a) Explain why water was added to experiments 1 and 2.

To ensure the **total volume of the mixture remains constant**, so that **volume of reactant is directly proportional to [reactant]** in the mixture .

[1]

(b) The reaction was determined to be **zero order** with respect to hydrogen ions.

(i) Sketch the rate-concentration graph for H^+ ions.



[1]

(ii) Determine the order of reaction with respect to the other two reactants.

Hence, write down the rate equation.

Let rate= $k[H_2O_2(aq)]^m[I^-(aq)]^n$

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ and total volume constant

$\frac{1.2x10^{-2}}{1.8x10^{-2}} = \frac{k(20.0)^m(20.0)^n}{k(20.0)^m(30.0)^n}$ (or use inspection method)

n = 1

Rate of reaction is **1st order with respect to $I^-(aq)$** .

Or

Compare experiments 1 & 2, keeping $[H_2O_2(aq)]$ and total volume constant

when $[I^-]$ x 3/2, rate of reaction x 3/2

Order of reaction **w.r.t. I^-** = **1**

Compare experiments 1 & 3, keeping total volume constant

$\frac{1.2x10^{-2}}{1.5x10^{-2}} = \frac{k(20.0)^m(20.0)^1}{k(50.0)^m(10.0)^1}$

m = 1

Rate of reaction is **1st order with respect to $H_2O_2(aq)$** .

Or

Compare experiments 1 & 3, keeping total volume constant

When **$[I^-]$ x 1/2 and $[H_2O_2]$ x 5/2, rate x 5/4 (1/2 x 5/2)**

Since the order wrt. I^- is 1, order wrt to H_2O_2 is 1.

rate= $k[H_2O_2(aq)][I^-(aq)]$

[3]

(c) In order to further investigate the kinetics of the reaction, experiments 4 and 5 were conducted. The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

experiment	initial $[H_2O_2(aq)]$ / mol dm^{-3}	initial $[I^-(aq)]$ / mol dm^{-3}
4	0.020	0.500
5	0.050	1.000

The half-life of hydrogen peroxide was 9.6 min in experiment 4. Explain and predict the half-life of hydrogen peroxide in experiment 5.

For experiment 4 and 5, since $[I^-(aq)] >> [H_2O_2(aq)]$, $[I^-(aq)]$ is approximately constant.

Thus, rate = $k'[H_2O_2(aq)]$ (a pseudo first order reaction)

where **$k' = k[I^-(aq)]$**

$t_{1/2} = = \frac{ln\,2}{k'} = \frac{ln\,2}{k[I^-]}$

$t_{1/2}$ of H_2O_2 in experiment 4 = 9.6 min (for $[I^-(aq)]$ = 0.500 mol dm^{-3})

$t_{1/2}$ of H_2O_2 in experiment 5 = **4.8 min** (for $[I^-(aq)]$ = 1.00 mol dm^{-3})

[2]

(d) An alternative method of investigating the rate of the above reaction is by withdrawing aliquots at specified time intervals and titrating the iodine formed in each aliquot with sodium thiosulfate solution.

Suggest how the reaction can be quenched at specified time intervals.

Sudden **cooling** of the reaction mixture or sudden **dilution** through the addition of large volume of water.

[1]

(e) Hydrogen peroxide decomposes easily. Suggest a method whereby the shelf-life of the hydrogen peroxide solution could be increased.

Keep away from light by storing it in a **dark-coloured bottle**.
or
Ensure purity of the solutions, i.e. no contaminants, especially **those that hasten the decomposition of peroxide**.

[1]

[Total: 9]

3 Lithium forms various compounds used for a wide range of purposes. For example, Li_2CO_3 is used as a mood-stabilising drug and LiF is used to record ionising radiation exposure from gamma rays, beta particles and neutrons.

(a) Numerical values of the solubility products of some lithium salts at 298 K are given in the table below.

salt	solubility product
LiF	2.68×10^{-3}
Li_2CO_3	2.14×10^{-2}
Li_3PO_4	3.20×10^{-9}

(i) Write an expression for the solubility product, K_{sp}, of lithium phosphate, including its units.

$K_{sp} = [Li^+]^3 [PO_4^{3-}]$ $mol^4\,dm^{-12}$

[2]

(ii) Using the data above, calculate a value for the solubility of lithium phosphate.

Let solubility of Li_3PO_4 be **s** mol dm^{-3}

$Li_3PO_4(s) \rightleftharpoons 3Li^+(aq) + PO_4^{3-}(aq)$ ----- (1)

s **3s** **s**

K_{sp} **= $[Li^+]^3[PO_4^{3-}]$**

= $(3s)^3(s)$

= $27s^4$

3.20×10^{-9} **= $27s^4$**

Solubility of Li_3PO_4 = **s** = **<u>3.30×10^{-3}</u>** mol dm^{-3}

[2]

(iii) LiF was precipitated when equal volumes of a solution of 0.050 mol dm^{-3} $LiNO_3$ and a solution of KF were mixed.

Calculate the minimum concentration of the KF solution required for precipitation to occur.

Since equal volumes are mixed, new $[Li^+] = 0.050 / 2 = 0.025$ mol dm^{-3}

Precipitation occurs when Ionic Product $\geq K_{sp}$

$[Li^+][F^-] \geq 2.68 \times 10^{-3}$

$0.025 \times [F^-] \geq 2.68 \times 10^{-3}$

$[F^-] \geq 0.1072$ mol dm^{-3}

$KF \rightarrow K^+ + F^-$

Original concentration of KF= 0.1072 x 2 = **<u>0.214 mol dm^{-3}</u>**

[2]

(iv) Describe and explain how the solubility of Li_2CO_3 is affected by adding solid Na_2CO_3 into the solution.

$Li^+(aq) + CO_3^{2-}(aq) \rightleftharpoons LiCO_3(s)$ ----- (1)

Due to **<u>common ion CO_3^{2-}</u>**, when Na_2CO_3 is added into the solution, **<u>$[CO_3^{2-}]$ increases</u>**. By Le Chatelier's Principle, **<u>equilibrium position</u>** (1) shifts to the **<u>right</u>** to **<u>decrease</u>** $[CO_3^{2-}]$ Hence, **<u>solubility</u>** of **<u>Li_2CO_3 decreases.</u>** .

[2]

(b) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

For lithium sulfate, Li_2SO_4, K_{sp} = 128 mol^3 dm^{-9} at 298 K.

Using the above expression, determine whether lithium sulfate is soluble in water at 298 K. Explain your answer.

For Li_2SO_4, $\Delta G^{\ominus}_{ppt}$ $= 2.303RT \log K_{sp}$
$= 2.303 \times 8.31 \times 298 \times \log (128)$
$= \underline{\mathbf{+1.20 \times 10^4\ J\ mol^{-1}}}$

Since $\underline{\mathbf{\Delta G^{\ominus}_{ppt} > 0}}$, it implies that the **precipitation** of Li_2SO_4, is **not feasible.** Hence, Li_2SO_4, is **soluble in water at 298K**.

[2]

(c) Another use of Li_2CO_3 is in the processing of metal oxides. When Li_2CO_3 decomposes, it forms Li_2O solid and CO_2 gas according to the following equation.

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$$

(i) Calculate the standard enthalpy change of reaction for the decomposition of Li_2CO_3 using the following standard enthalpy changes of formation, $\Delta H_f^{\ominus}$.

compound	Li_2CO_3	Li_2O	CO_2
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−1216	−596	−394

$\Delta H_r^{\ominus}$ $= \Sigma\ \Delta H_f^{\ominus}(\text{products}) - \Sigma\ \Delta H_f^{\ominus}(\text{reactants})$
$= \Delta H_f^{\ominus}(CO_2) + \Delta H_f^{\ominus}(Li_2O) - \Delta H_f^{\ominus}(Li_2CO_3)$
$= -394 - 596 - (-1216)$
$= \underline{\mathbf{+226\ kJ\ mol^{-1}}}$

[1]

(ii) The entropy change for the decomposition reaction is positive. Explain the effect on spontaneity of this decomposition reaction as temperature increases.

$\Delta H^\ominus$ is positive while **$\Delta S^\ominus$ is positive. So $-T\Delta S$ is negative.**

As temperature increases, **$-T\Delta S$** becomes **more negative** so **ΔG** becomes **more negative.** Thus the decomposition becomes **more spontaneous** as temperature increases.

OR

At low T,
$|T\Delta S| < |\Delta H|$
$\Rightarrow$ Hence, **ΔG** **> 0 (+ve)** at **low** temperatures.

At high T,
$|T\Delta S| > |\Delta H|$
$\Rightarrow$ Hence, **ΔG** **< 0 (–ve)** at **high** temperatures.

Thus the decomposition becomes **more spontaneous** as temperature increases.

[2]

[Total: 13]

4 *Use of the Data Booklet is relevant to this question.*

(a) Chemical companies manufacture containers filled with liquid butane for use by campers. The complete combustion of butane produces carbon dioxide and water. The enthalpy change of combustion of butane is –3000 kJ mol^{-1}.

A camper estimates that the liquid butane left in a container would give 1.2 dm^{3} of butane gas (measured at room temperature of 20 °C and pressure of 1 atm).

(i) Calculate the mass of water at room temperature that could be brought to boiling point at 100 °C by completely burning this mass of butane, given that the process is only 80% efficient.

No. of moles of butane present = $\frac{1.2}{24}$ = 0.0500 mol

Quantity of heat released by combustion, q' = 3000 × 0.0500 = 150 kJ

Quantity of heat absorbed by water, q = 80% × q' = 80% × 150 = 120 kJ
$q = m\,c\,\Delta T \Rightarrow q = m \times 4.18 \times (100 - 20)$

Mass of water, m = $\frac{120}{334.4}$ = **<u>0.359 kg</u>** **<u>(or 359 g)</u>** (3 s.f.)

[3]

(ii) Suggest a reason why the combustion process is only 80% efficient.

- **<u>Heat is lost to surroundings</u>** during combustion.
- Some of the **<u>heat is used to vapourise the liquid butane</u>**.

[1]

(b) When burnt in a limited supply of air, butane forms carbon and water. The enthalpy change of this reaction is –1400 kJ mol^{-1}.

(i) Construct a balanced equation for this reaction.

$$\mathbf{C_4H_{10} + \frac{5}{2}O_2 \rightarrow 4C + 5H_2O}$$

[1]

(ii) Explain why the enthalpy changes of the two combustion reactions in **(a)** and **(b)** are different.

Due to **<u>complete combustion in (a)</u>**, **more energy is released** due to the **formation of CO_2** (bond formation), compared with **only C formed** in the **<u>incomplete combustion in (b)</u>**. *(or reverse discussion)*

[1]

(iii) State the quantitative information that can be obtained from this difference in enthalpy changes.

(Standard) **<u>Enthalpy change of combustion of carbon</u>** / **ΔH_c (C)**

[1]

(c) The carbon-oxygen *bond energy* in carbon monoxide, CO, is 1077 kJ mol^{-1}.

Carbon monoxide can be formed by the following reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \qquad \Delta H^{\ominus} = +172.5 \text{ kJ mol}^{-1}$$

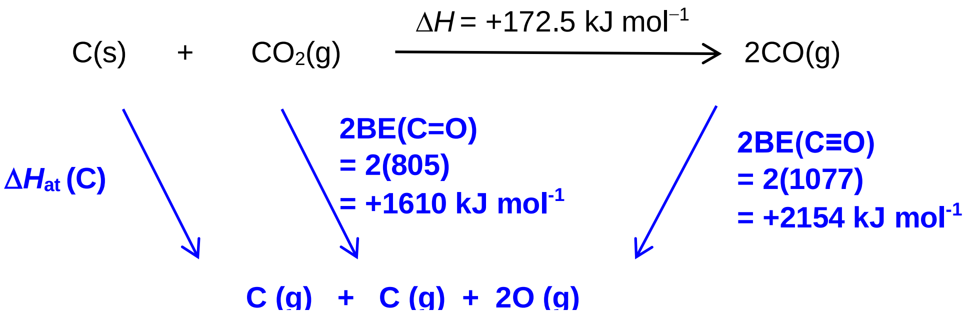
(i) Explain, with the aid of a suitable equation, what is meant by the term *bond energy* of carbon monoxide.

$$\mathbf{C{\equiv}O\ (g) \rightarrow C\ (g) + O\ (g)}$$

Bond energy of CO is the **energy required** to **break 1 mole of gaseous CO** (triple) **bond** to form **gaseous** (C and O) **atoms**.

[2]

(ii) Determine the enthalpy change of atomisation of carbon by using relevant bond energy data from the *Data Booklet* to complete the energy cycle below. Include relevant information in your cycle.



By Hess' Law,

ΔH_{at} **(C) + 2BE(C=O) =** ΔH **+ 2BE(C≡O)**

ΔH_{at} **(C) + 2(805) = 172.5 + 2(1077)**

ΔH_{at} **(C) =** 172.5 + 2154 – 1610

= **+716.5 kJ mol^{-1}**

[3]

[Total: 12]

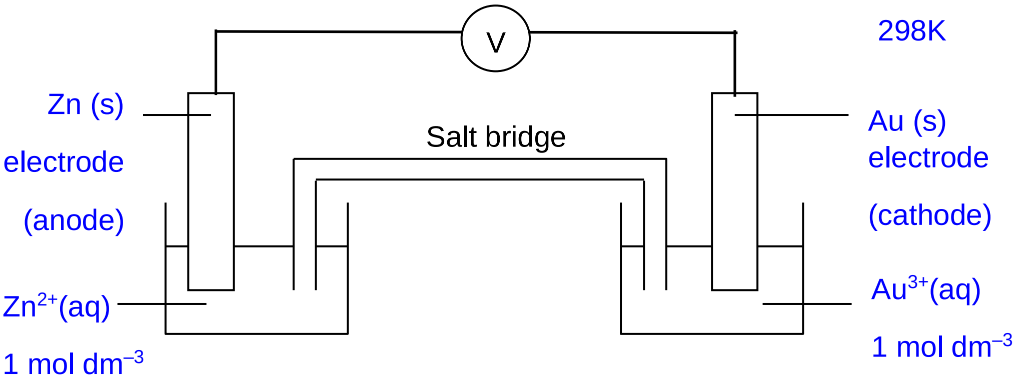
5 *Use of the Data Booklet is relevant to this question.*

A student wanted to study the following reaction.

$$2Au^{3+} + 3Zn \rightleftharpoons 2Au + 3Zn^{2+}$$

He first sets up an electrochemical cell which comprises of Au^{3+}/Au and Zn^{2+}/Zn half-cells prepared under standard conditions.

(a) **(i)** Draw a fully labelled diagram of the electrochemical cell under standard conditions.



[2]

(ii) Given that $E^\ominus_{Au^{3+}/Au}$ is +1.50 V, calculate the $E^\ominus_{cell}$ of this cell.

$E^\ominus_{cell}$ = +1.50 – (–0.76) = **+2.26 V**

[1]

(iii) Suggest a replacement transition element ion-ion half-cell for the Zn^{2+}/Zn half-cell so that the direction of electron flow is reversed.

Co^{3+}/Co^{2+}, Mn^{3+}/Mn^{2+}, MnO_4^-/Mn^{2+}

[1]

(b) When the reaction in **(a)** begins, $[Au^{3+}]$ starts to decrease while $[Zn^{2+}]$ increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non-standard conditions.

$$E_{cell} = E^\ominus_{cell} - \frac{0.0592}{n}\log_{10} Q$$

where n is the number of moles of electrons transferred and Q is the reaction quotient given by $\dfrac{[Zn^{2+}]}{[Au^{3+}]}$.

(i) Using your answer in **(a)(ii)**, calculate the new E_{cell} using the Nernst equation, when $[Au^{3+}]$ and $[Zn^{2+}]$ are 0.02 mol dm^{-3} and 2.47 mol dm^{-3} respectively.

$$E_{cell} = +2.26 - \frac{0.0592}{6} \log_{10} \frac{[2.47]}{[0.02]} = \underline{\mathbf{+2.24\ V}}$$

[1]

(ii) Suggest the value of E_{cell} when the reaction goes to completion.

<u>0 V</u>

[1]

(c) The redox reaction in **(a)** is an example of a spontaneous reaction which proceeds as predicted by the cell potential. However, not every chemical reaction agrees with the theoretical prediction. One example is the reaction between acidified $K_2Cr_2O_7$ and water.

(i) Using information from the *Data Booklet*, calculate $\Delta G^\ominus$ for the reaction between acidified $K_2Cr_2O_7$ and water. Based on your value for $\Delta G^\ominus$, comment on the spontaneity of the reaction.

$$\begin{aligned}\Delta G^\ominus &= -nFE^\ominus \\ &= -12 \times 96500 \times (1.33 - 1.23) \\ &= \underline{\mathbf{-1.16 \times 10^5\ kJ\ mol^{-1}}}\end{aligned}$$

$\Delta G^\ominus < 0$, the **<u>reaction is spontaneous</u>**.

[3]

(ii) The reaction between water and acidified $K_2Cr_2O_7$ has an $E^\ominus_{cell}$ greater than 0 V under standard conditions, yet the reaction does not proceed. Suggest a reason for this observation.

<u>The reaction has high activation energy</u> so it cannot take place under standard condition.

[1]

(iii) Another example of a reaction that does not agree with the theoretical prediction is the reaction between Cu^{2+} and I^- according to the equation below.

$$2Cu^{2+}(aq) + 4I^-(aq) \rightleftharpoons 2CuI(s) + I_2(aq) \qquad E^\ominus_{cell} = -0.39\ V$$

White precipitate of CuI is formed during the reaction. Suggest a reason why the reaction proceeds despite the $E^\ominus_{cell}$ being less than 0 V.

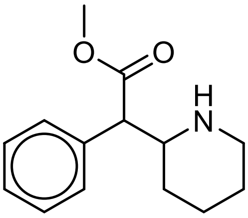
The continuous **<u>precipitation of CuI</u>** from the solution will **<u>shift the equilibrium position to the right</u>** and drive the reaction forward.

[1]

[Total: 11]

6 Adrenaline is a naturally occurring hormone and stimulant released in the body during times of danger or stress. Stimulant drugs that can mimic the effect of adrenaline have been developed for treatment of various conditions.

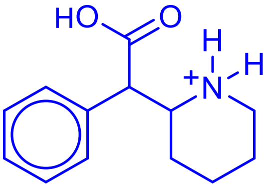
(a) Methylphenidate is a stimulant drug commonly used in the treatment of Attention Deficit Hyperactive Disorder (ADHD).



methylphenidate

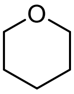
(i) Draw the structures of the organic products formed when methylphenidate is heated with dilute hydrochloric acid.

$H_3C—OH$

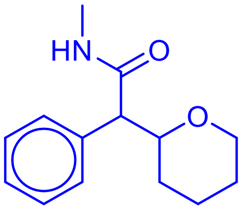


[2]

(ii) An isomer of methylphenidate, compound **X**, is neutral and has the following structural properties:

- contains one aromatic six-membered ring
- contains 

Suggest a structure for compound **X** and state its isomeric relationship to methylphenidate.



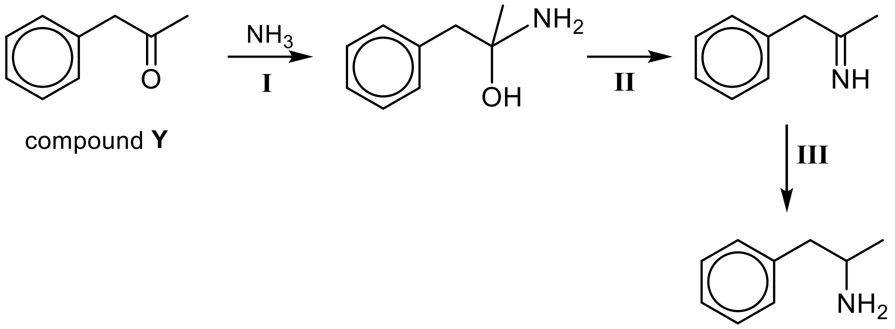
X

isomeric relationship to methylphenidate:

constitutional isomer (OR structural isomer)

[2]

(b) Another stimulant, amphetamine, is prepared commercially from compound **Y** as shown below.



compound **Y**

amphetamine

(i) Suggest the type of reaction occurring in:

[2]

Step **II** **elimination**
Step **III** **addition / reduction**

(ii) Suggest suitable reagents and conditions for the conversion in step **III**. You may assume the R=NH group reacts in a similar manner to the carbonyl group.

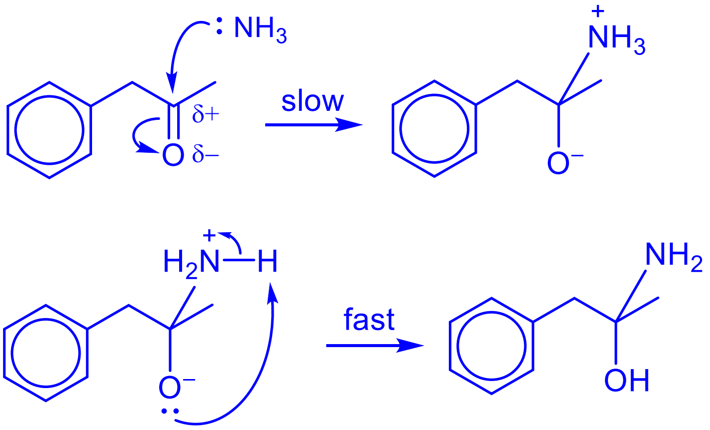
[1]

reagents and conditions: **$NaBH_4$ in ethanol** or **H_2(g) with Ni heat / Pt / Pd**

(iii) Reaction **I** which occurs between compound **Y** and NH_3 is a nucleophilic addition reaction.

Draw the mechanism for this reaction, given that in the rate-determining step, the nucleophilic attack by NH_3, results in an intermediate species containing both a positive and negative charge.

[3]

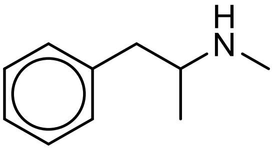


(iv) With reference to the mechanism you have drawn in **(iii)**, explain why the product from step **I** is expected to be optically inactive.

In the slow step, the nucleophile attacks the **trigonal planar carbonyl C** atom with **equal probability from above and below the plane** . This results in the formation of a **racemic mixture** which is optically inactive.

[2]

(c) Methamphetamine is a stimulant which has a structure similar to amphetamine.



methamphetamine

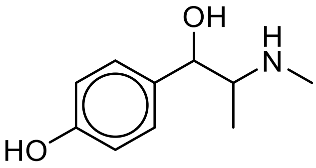
(i) The hydrochloride salt of methamphetamine exists as colourless crystals. Methamphetamine is immiscible with water whereas the salt is soluble in water. With reference to the interactions formed between each of the compounds and water, explain the difference in the solubility of methamphetamine and its salt in water.

Methamphetamine forms instantaneous dipole-induced dipole interactions with water whereas the **salt is able to form ion-dipole interactions with water** .

The **strong interactions formed between the salt and water release sufficient energy to overcome hydrogen bonding between water molecules OR to cause detachment of ions from the crystal lattice** . (OR **weak i.d.-i.d. attraction of methamphetamine are not compatible with strong hydrogen bonding between water**)

[2]

(ii) In the human body, methamphetamine can be converted to compound **Z**.



Z

Describe a simple chemical test which could be used to distinguish between methamphetamine and compound **Z**.

You should state the reagents and conditions required, together with the expected observations for each compound.

Add aqueous Br_2 to each compound

Compound Z will decolourise Br_2 with the formation of a white ppt whereas **methamphetamine will give no visible observation** .

Other possible test reagents: neutral $FeCl_3$ / Na / PCl_5 / hot acidified $K_2Cr_2O_7$ (not $KMnO_4$)

[2]

[Total: 16]

End of Paper 2

TAMPINES MERIDIAN JUNIOR COLLEGE

2019 JC2 H2 Chemistry Prelim Exam Paper 3
(Suggested Answers)

Section A

Answer **all** the questions from this section.

1 Hydrocarbons, C_xH_y, are used extensively as sources of fuel in our modern day civilisation.

(a) 10 cm^3 of a gaseous hydrocarbon C_5H_y was allowed to burn in an excess of oxygen at 300 °C and 1 atm. In the reaction, there was an expansion of volume by 20 cm^3.

(i) Write a balanced equation, with state symbols, for the reaction at 300 °C and 1 atm. [2]

$$C_5H_y\,(g) + \left(5+\frac{y}{4}\right)O_2\,(g) \longrightarrow 5\,CO_2\,(g) + \frac{y}{2}\,H_2O\,(g)$$

(ii) Determine the value of **y**. [2]

Using Avogadro's Law, mole ratio ≡ volume ratio

Equation:	$C_5H_y\,(g)$ +	$\left(5+\frac{y}{4}\right)O_2\,(g)$ $\longrightarrow$	$5\,CO_2\,(g)$ +	$\frac{y}{2}\,H_2O\,(g)$
Vol of gases:	10 cm^3	$(\left(5+\frac{y}{4}\right) \times 10)\ cm^3$	50 cm^3	$(\frac{y}{2} \times 10)\ cm^3$

Volume of gases used up in the reaction = $10 + (50+\frac{10y}{4}) = \left(60+\frac{10y}{4}\right)\ cm^3$

Volume of gases produced in the reaction = $50 + \left(\frac{y}{2}\right) \times 10 = (50+5y)\ cm^3$

Volume of gas produced – Volume of gas used up = 10 cm^3

$$(50+5y) - \left(60+\frac{10y}{4}\right) = 20$$

y = **12**

Methane, CH_4, is sometimes used in the production of hydrogen via a process known as steam reforming.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(b) The steam reforming process is an endothermic reaction.

(i) Using data from the *Data Booklet*, calculate a value for the enthalpy change of the forward reaction. [2]

$$\begin{aligned}\Delta H_r &= \Sigma BE\text{ (reactants)} - \Sigma BE\text{ (products)}\\ &= 410 \times 4 + 460 \times 2 - (1077 + 436 \times 3)\\ &= \underline{\mathbf{+175\ kJ\ mol^{-1}}}\end{aligned}$$

(ii) The actual value of the enthalpy change of reaction is found to be $+206$ kJ mol^{-1}. Suggest a reason why your calculated answer in **(i)** differs from this value. [1]

The bond energy calculation is an approximation method as the **bond energy values given** in the ***Data Booklet*** are **average values** .

(c) At 600 K, the value of the equilibrium constant, K_p, for the steam reforming reaction is 7.20×10^{-4}.

(i) Write the K_p expression for this reaction, giving its units. [2]

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})} \quad \mathbf{atm^2}\ \mathbf{(accept\ Pa^2)}$$

(ii) Gaseous CH_4, H_2O and CO are introduced into a closed container at 600 K and their initial partial pressures are 1.20 atm, 2.10 atm and 1.80 atm respectively.

Determine the partial pressure of H_2 when equilibrium is reached.

(You may assume that the extent of the forward reaction is small.) [3]

	$CH_4(g)$	$+ H_2O(g)$	$\rightleftharpoons$	$CO(g)$	$+ 3H_2(g)$
Initial pp/atm	1.20	2.10		1.80	0
Change pp/atm	$-x$	$-x$		$+x$	$+3x$
Eqm pp/atm	$1.20 - x$	$2.10 - x$		$1.80 + x$	$3x$

$$K_p = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$$

$$7.20 \times 10^{-4} = \frac{(1.80 + x)(3x)^3}{(1.20 - x)(2.10 - x)}$$

Assuming x is small,

$$7.20 \times 10^{-4} = \frac{(1.80)(3x)^3}{(1.20)(2.10)}$$

Solving for x,
x = **0.0334**

Partial pressure of H_2 at equilibrium = 3 x 0.0334
= **0.100 atm**

(iii) Using information from **(b)**, suggest how the temperature of the reaction can be changed so as to increase the yield of H_2. Explain your answer. [2]

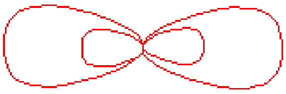
The **temperature should be raised** to increase the yield of H_2.

When the temperature is raised, by Le Chartelier's Principle, the **equilibrium position shifts to the right towards the endothermic reaction to absorb heat**, increasing the yield of H_2.

(d) Additional hydrogen can be recovered using the carbon monoxide produced in another reaction known as the water–gas shift reaction.

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

(i) Name the type of hybridisation in the carbon atom in CO. Draw the hybrid orbitals around the carbon atom. [2]



sp hybridisation

(ii) Given that the above reaction was conducted at 300 °C and 1 atm, calculate the volume of H_2 that can be recovered from 5 kg of CO. [3]

Amount of H_2 that can be recovered = 5000/28 = **178.6 mol**

pV = nRT

$$V = \frac{nRT}{p}$$

$$V = \frac{178.6 \times 8.31 \times (300 + 273)}{101325}$$

= **8.39 m^3**

(iii) The volume of CO_2 collected in the water-shift reaction should be the same as that of H_2. However, the actual volume of CO_2 collected was smaller. Suggest a reason why this is so. [1]

CO_2 deviates more from ideal gas behaviour as it has **more significant intermolecular instantaneous dipole–induced dipole interaction** . Hence it will occupy a smaller volume than H_2.

[Total: 20]

2 Propanoic acid, CH_3CH_2COOH was initially known as propionic acid based on the Greek words, *protos*, meaning ‘first’ and *pion*, meaning ‘fat’.

The pK_a values of CH_3CH_2COOH and $CH_3CH(Cl)COOH$ are listed below.

acid	structural formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CH(Cl)COOH$	2.8
3	$CH_2(Cl)CH_2COOH$	[redacted]

(a) **(i)** Explain why acid 2 has a lower pK_a than acid 1. [2]

The **electron-withdrawing C*l* group** in **acid 2** (OR **$CH_3CH(Cl)COOH$**) further **reduces the intensity of the negative charge** on **$CH_3CH(Cl)COO^-$** to a **greater extent** .

$CH_3CH(Cl)COO^-$ is **more stable** and **$CH_3CH(Cl)COOH$** has a **greater tendency** to **dissociate** and therefore a **stronger acid**. .

(ii) Suggest a pK_a value for acid 3. [1]

Accept value **between 2.8 to 4.9**

(b) A 25.0 cm^3 solution of 0.10 mol dm^{-3} CH_3CH_2COOH was titrated against 0.20 mol dm^{-3} sodium hydroxide, NaOH.

(i) Calculate the pH of the 0.10 mol dm^{-3} CH_3CH_2COOH. [1]

$[H^+] = \sqrt{\mathbf{0.10 \times 10^{-4.9}}} = \mathbf{0.00112}$ mol dm^{-3}

pH = $-\log_{10}(0.00112)$ = 2.95

(ii) Calculate the volume of NaOH required for complete neutralisation. [1]

Amount of CH_3CH_2COOH = (25 ÷ 1000) x 0.1 = 2.50 x 10^{-3} mol

$CH_3CH_2COOH \equiv NaOH$

Amount of NaOH required = **2.50 x 10^{-3} mol**

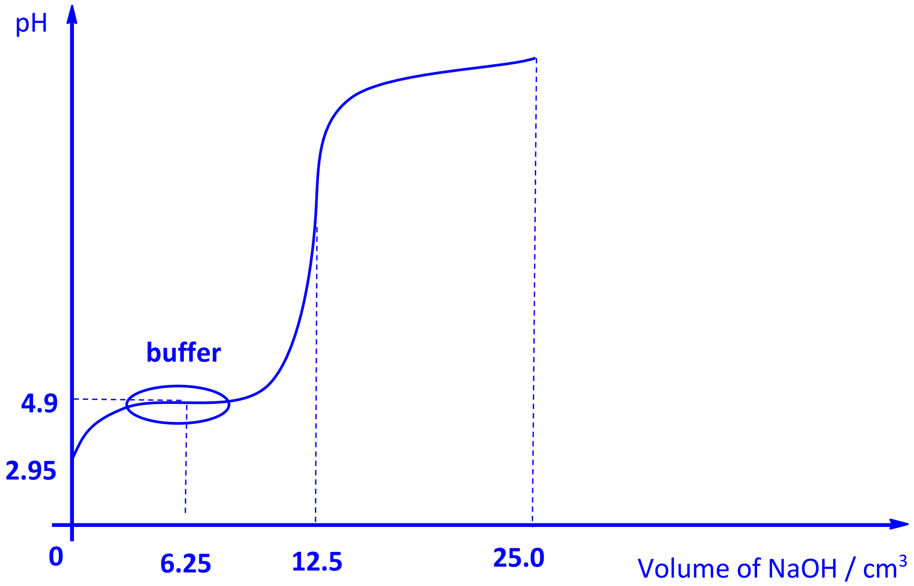
Volume of NaOH required = **2.50 x 10^{-3} ÷ 0.20**
= **0.0125 dm^3** OR **12.5 cm^3**

(iii) Write a suitable equation to explain why the pH at equivalence point is greater than 7. [1]

$CH_3CH_2COO^- + H_2O \rightleftharpoons CH_3CH_2COOH + OH^-$

Concept:
$CH_3CH_2COO^-$ undergoes hydrolysis to form OH^-. At equilibrium, $[OH^-] > [H^+]$
pH at equivalence point is basic (> 7).

(iv) Sketch the expected titration curve for this titration given that a total volume of 25.0 cm^3 of NaOH was added. On the titration curve, indicate the initial pH value and the equivalence volume. [2]

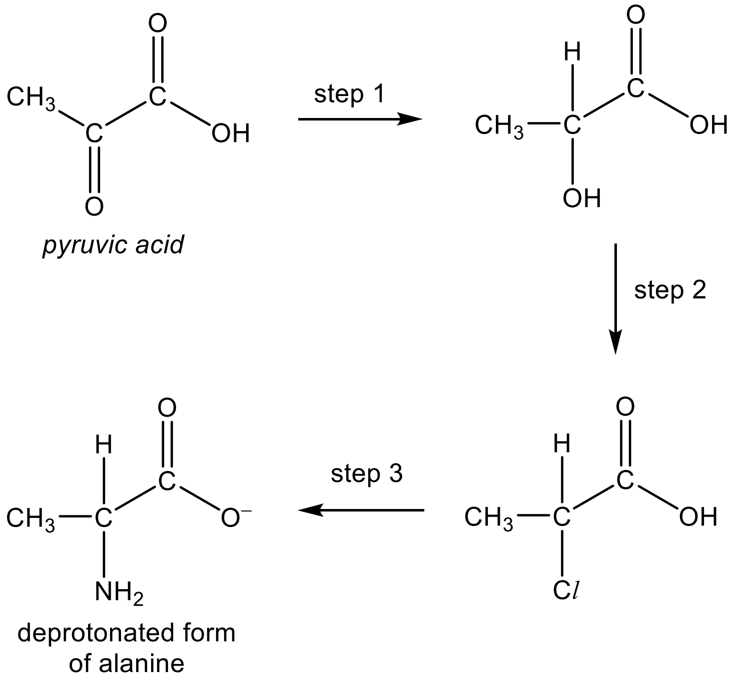


(v) A buffer involving CH_3CH_2COOH and its salt was formed during the progress of the titration. Circle the buffer region on the sketched curve in **(iv)** and indicate the corresponding pH value and volume at the maximum buffering capacity. [2]

There are many organic compounds such as amino acids and drug molecules that are derivatives of propanoic acid.

(c) The starting material to synthesise 2-aminopropanoic acid, also known as alanine can be either *pyruvic acid* or ethanal.

(i) The proposed synthesis for the deprotonated form of alanine from *pyruvic acid* is shown below.



Suggest the reagents and conditions for steps 1, 2 and 3. [3]

Step **1**: **$NaBH_4$ in ethanol**

Step **2**: **HC*l* (g)**, **heat**

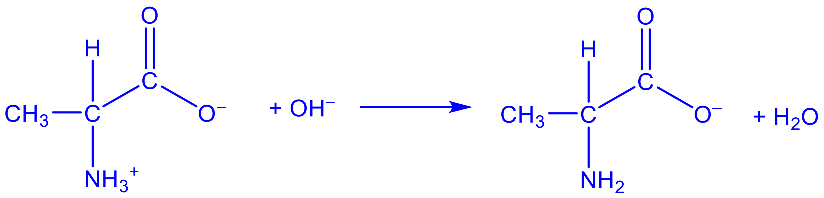
Step **3**: excess **conc. NH_3 in ethanol**, **heat in sealed tube**

(ii) State the **two** types of reaction that had occurred in step 3 of the above proposed synthesis. [2]

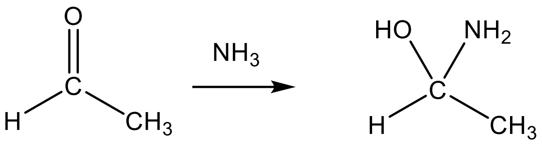
Nucleophilic substitution

Acid-base reaction (OR **neutralisation**)

(iii) Write an equation to show how the zwitterion form of *alanine* can act as a buffer when a small amount of base is added. [1]



(iv) The first step to synthesise alanine from ethanal is shown below.



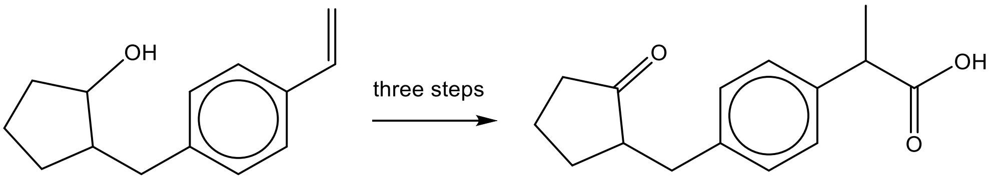
ethanal

Explain whether ammonia can be considered as a Lewis base in the context of this synthesis. [1]

NH_3 uses its **lone pair to form a** dative **bond with the carbonyl carbon** therefore it **is considered** as a Lewis base.

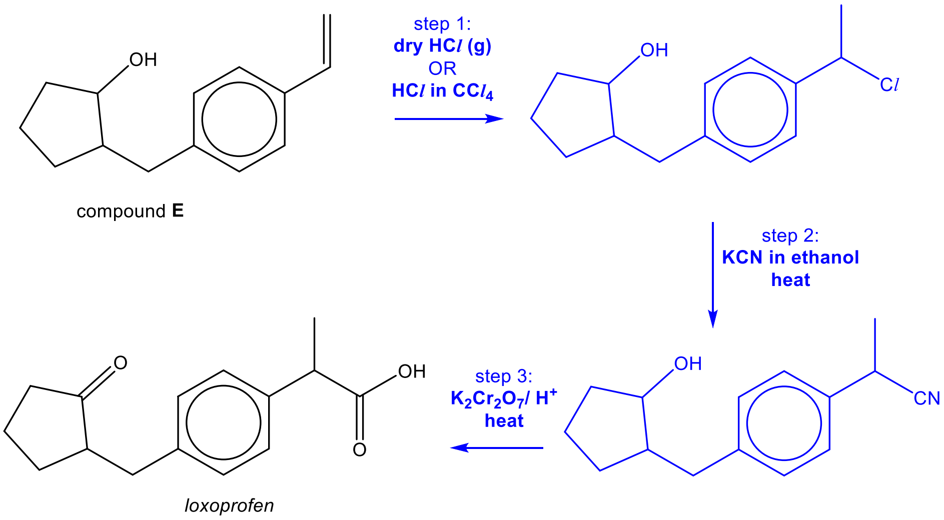
(d) Non-steroidal anti-inflammatory drugs are used for the relief of pain. One example is *loxoprofen* that is considered as a propanoic acid derivative based on its chemical structure.

(i) Suggest a three-step synthesis of *loxoprofen* starting from compound **E**.

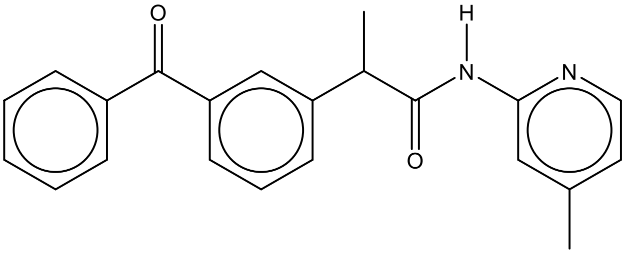


compound **E** *loxoprofen*

[4]

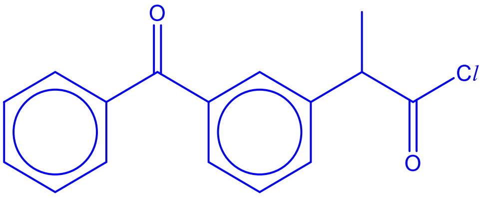


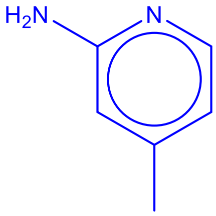
(ii) *Piketoprofen* is produced by the reaction between an acyl chloride and a suitable organic compound. Suggest the structures of the acyl chloride and the organic compound.



piketoprofen

[1]





(iii) The use of acyl chloride requires anhydrous conditions. Explain why acyl chloride undergoes hydrolysis more readily than chloroalkane. [2]

The **carboxyl C** (OR carbonyl C) is bonded to **two** (OR **more**) **electronegative atoms**, **O and C*l*** compared to **chloroalkane where the alkyl C is only bonded to one C*l*** resulting in a **highly electron-deficient** the carboxyl **C atom** and making the C atom highly susceptible to hydrolysis.

Hence, it undergoes hydrolysis more readily than chloroalkane.

[Total: 24]

3 Cobalt is a transition element that plays an important role in hybrid electric vehicles and is also an essential part of vitamin B12. The common oxidation states of cobalt are +2 and +3.

(a) Define *transition element*. [1]

A transition element is a *d* block element that **forms at least one stable ion with partially-filled *d* subshell**

(b) Write the electronic configuration of cobalt(II) ion. [1]

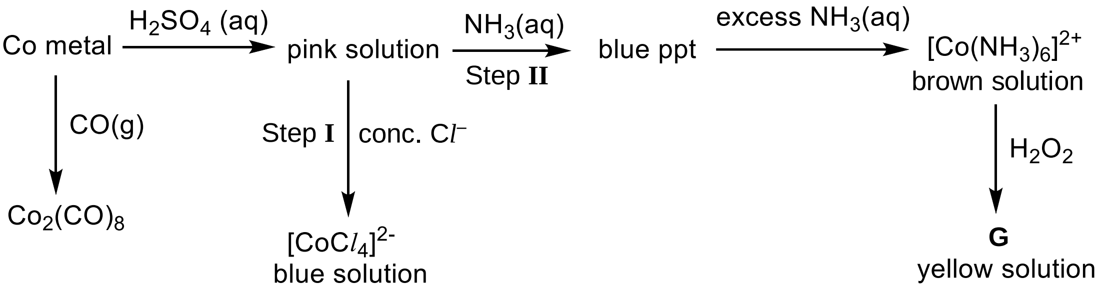
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ Or **$[Ar]3d^7$**

(c) State one **physical** characteristic property of transition elements that is different from the main group metals. Briefly explain why transition elements exhibit this property. [2]

1 Transition metals are **harder/denser**. It has relatively **smaller atomic radius and higher relative atomic mass. Thus it has** have **higher mass per unit volume.**

2 Transition metals have **higher melting points.** In transition metals, **both the 3d and 4s electrons** are involved in delocalization. *For s–block metals*, **only the s electrons are involved in the delocalization.** Thus there is **stronger electrostatic forces of attraction** is present **between the transition metals cations and the sea of delocalised electrons.**

(d) The following sequence of reactions involving cobalt illustrates many of the characteristic properties of transition elements.



(i) State the types of reaction occurring in steps **I** and **II**. [2]

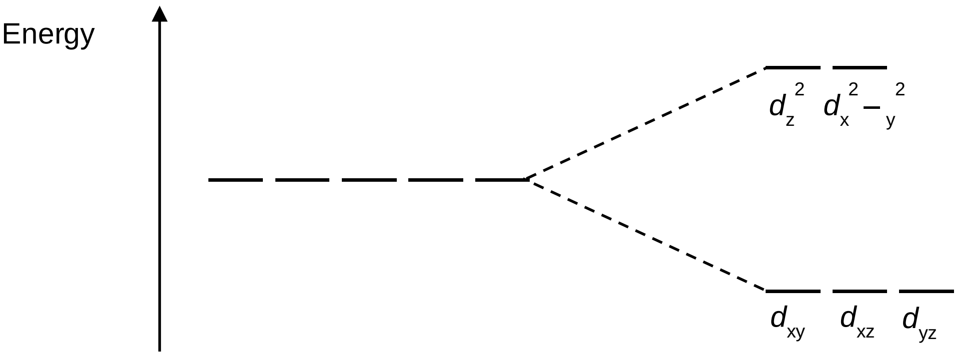
Step **I**: ligand exchange
Step **II**: precipitation

(ii) Suggest the formula of the cobalt-containing species **G**. [1]

Formula for **G**: $[Co(NH_3)_6]^{3+}$

(iii) Cobalt is said to be a d-block element.

The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment as shown.



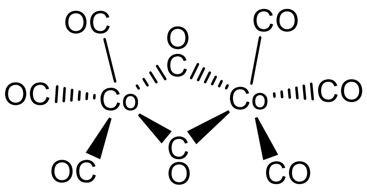
Explain why the splitting occurs. [2]

The **upper energy level d orbitals** (d_{x2-y2} and d_{z2} orbitals) have their **lobes pointing at the ligands along the coordinate axes**. Hence, the **electron pairs in these orbitals will be repelled by the ligands to a greater extent** than those in lower energy d orbitals.

(iv) Given the fact in **(iii)** that d orbitals split into 2 energy levels in the presence of ligands, explain why $[CoCl_4]^{2-}$ solution is blue. [2]

The Co **d electrons in lower energy d orbital is promoted to the higher d orbital by d–d transition**. During the transition, **the d electron absorbs orange wavelength from the visible region of the electromagnetic spectrum** and **the remaining wavelengths not absorbed appear as blue**.

(v) Cobalt can react with carbon monoxide to form $Co_2(CO)_8$, a commonly used reagent and catalyst in organic synthesis.



Suggest the co-ordination number and the oxidation state of cobalt in the complex, $Co_2(CO)_8$. [1]

Co-ordination number: 5
Oxidation state of cobalt: 0

(vi) With the aid of *Data Booklet* and given that $E^{\ominus}{}_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}}$ is +0.10 V, predict the stability of an alkaline solution of $[Co(NH_3)_6]^{2+}$ when left exposed to air. [2]

$$[Co(NH_3)_6]^{3+} + e \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^{\ominus} = +0.10\text{ V} \quad E_{oxid}$$
$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^- \qquad E^{\ominus} = +0.40\text{ V} \quad E_{red}$$

Ecell = 0.40 – 0.10 = +0.30 V > 0

$[Co(NH_3)_6]^{2+}$ is **oxidised to form $[Co(NH_3)_6]^{3+}$** in open air.

(e) A radioactive form of cobalt, ^{60}Co, is used in the inspection of materials to reveal internal structure, flaws, or foreign objects.

(i) State the number of protons, neutrons and electrons present in the isotopic species, ^{60}Co. [1]

Protons = 27
Electrons= 27

Neutrons = 33

(ii) The radioactive decay of ^{60}Co produces beta (β) particles. A simplified balanced decay equation is provided below.

$$^{60}Co \rightarrow \mathbf{L} + \beta$$

Given that β is ${}^{0}_{-1}e$, deduce the identity of the element **L**. [1]

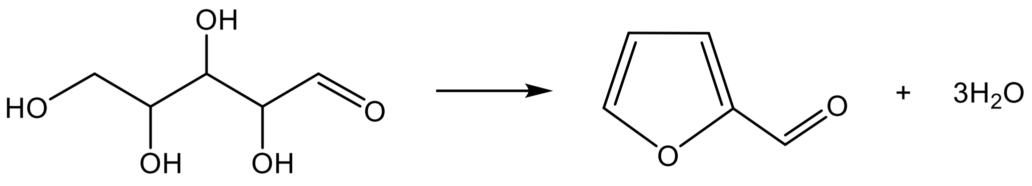
Final proton number = 27 + 1 = **28**
Identity = **Ni or nickel**

[Total: 16]

Section B

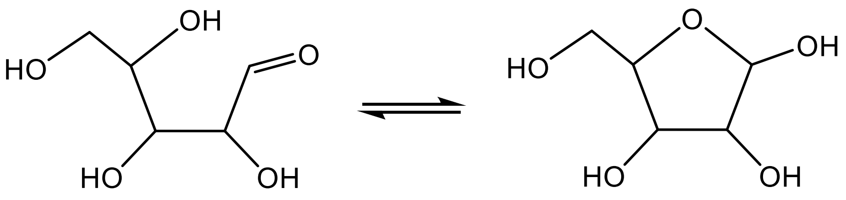
Answer **one** question from this section.

4 Furfural is an aromatic compound with all its carbon atoms lying on the same plane. Today, one of the ways to manufacture furfural is by the acid catalysed dehydration of xylose.



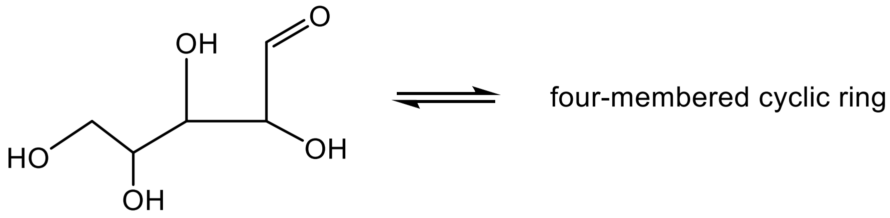
xylose furfural

(a) Xylose exists in more than one form, one of which is the non-cyclic form shown below (i.e. form 1). Form 2 is a five-membered cyclic ring produced as follows.

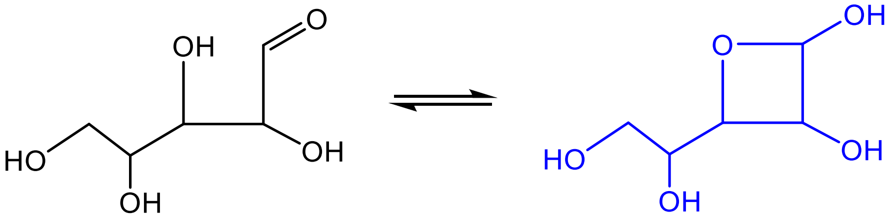


form 1 of xylose form 2 of xylose

It is theoretically possible to produce a four-membered cyclic ring by following a similar pattern of reaction.



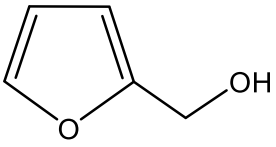
(i) Draw the structure of the theoretical four-membered cyclic ring. [1]



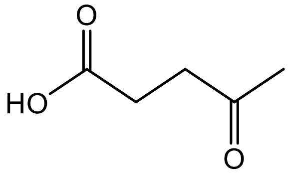
(ii) The four-membered cyclic ring is **not** actually produced because it is unstable. Suggest why it is unstable. [1]

- (greater) **ring / angle strain** in the four-membered-ring
- smaller bond angle than ideal
- compression of bond pair in ring

(b) Furfural can be reduced into furfuryl alcohol. Furfuryl alcohol can then be used to synthesise levulinic acid.



furfuryl alcohol



levulinic acid

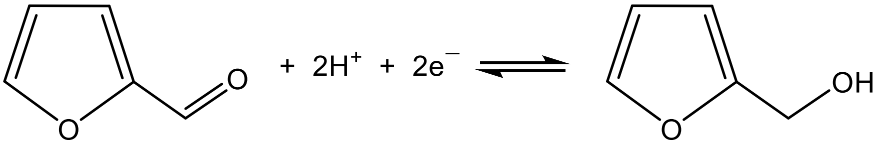
(i) Using the **molecular** formulae of furfuryl alcohol and levulinic acid, write a balanced equation for the synthesis of furfuryl alcohol into levulinic acid. [2]

$C_5H_6O_2 + H_2O \longrightarrow C_5H_8O_3$

(ii) Using your answer in **(i)**, state the type of reaction that has taken place. [1]

hydrolysis

(c) The standard reduction potential involving furfural, $C_5H_4O_2$ measured against the standard hydrogen electrode (S.H.E.) is shown below.

electrode reaction	$E^\ominus$ / V
 furfural furfuryl alcohol	–0.80

A neutral aqueous solution of furfural is prepared. Electrolysis of this solution is performed using copper at both electrodes to increase the percentage yield of the reaction.

When 0.030 A was passed through the cell for 2.0 hours, the *actual* mass of the product formed at the cathode was found to be 0.060 g. Copper is reacted at the anode but not the cathode.

(i) Using the $E^\ominus$ values given above as well as that from the *Data Booklet*, deduce the products formed at the anode and the cathode.
(In your deduction, you may use name or molecular formula to represent the structures of the respective organic compounds.) [3]

At the **anode**:
$E^\ominus_{Cu^{2+}/Cu}$ (+0.34 V) is **less positive / smaller** **than** $E^\ominus_{O_2/H_2O}$ (+1.23 V).
Hence, Cu is preferentially oxidised to **produce Cu^{2+}**.

At the **cathode**:
$E^\ominus_{\text{furfural / furfuryl alcohol}}$ (–0.80 V) **is more positive / less negative / larger** **than** **and** $E^\ominus_{H_2O/H_2}$ (–0.83 V).
Hence, furfural is preferentially reduce to **produce furfuryl alcohol**.

(ii) Write the overall balanced equation for the reaction. [1]

anode: $Cu \longrightarrow Cu^{2+} + 2e^{-}$
cathode: $C_6H_4O_2 + 2H^{+} + 2e^{-} \longrightarrow C_6H_6O_2$

overall: $\underline{\mathbf{C_6H_4O_2 + 2H^{+} + Cu \longrightarrow C_6H_6O_2 + Cu^{2+}}}$

(iii) Calculate the *expected* mass of the product formed at the cathode. [2]

$$n_{\text{furfuryl alcohol}} = \frac{m_{\text{furfuryl alcohol}}}{M_{\text{r, furfuryl alcohol}}} = \frac{It}{zF}$$

$$\frac{m_{\text{furfuryl alcohol}}}{5(12) + 6(1) + 2(16)} = \frac{0.030 \text{ x } (2 \text{ x } 60 \text{ x } 60)}{2 \text{ x } 96500}$$

$m_{\text{furfuryl alcohol}} = \underline{\mathbf{0.110\ g}}$

If H_2 gas produced:

$$\frac{m_{H_2}}{2} = \frac{0.030 \text{ x } (2 \text{ x } 60 \text{ x } 60)}{2 \text{ x } 96500}$$

$m_{H2} = 2.24 \text{ x } 10^{-3}$ g

(iv) Calculate the percentage yield of the product formed at the cathode. [1]

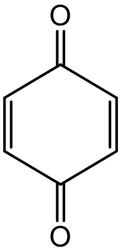
$$\text{percentage yield} = \frac{0.060}{0.110} \text{ x } 100\%$$
$$= \underline{\mathbf{54.5\ \%}}$$

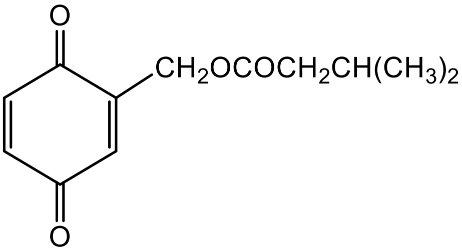
(v) Besides the S.H.E., another standard electrode that can be used is the standard calomel electrode (S.C.E.). When the S.C.E. is compared against the S.H.E., the $E^{\ominus}$ of the S.C.E. is +0.24 V.

Calculate the $E^{\ominus}$ of the furfural / furfuryl alcohol half-cell when measured against the S.C.E.

$E^{\ominus}_{\text{furfural / furfuryl alcohol}}$ against SCE = –0.80 – (+0.24) = $\underline{\mathbf{-1.04}}$ V

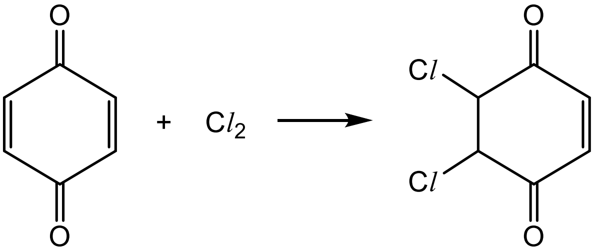
Another compound with all its carbon atoms lying on the same plane is paraquinone, with a characteristic irritating odour of hot plastic. One derivative of paraquinone is blattellaquinone which is a pheromone in cockroaches.


paraquinone



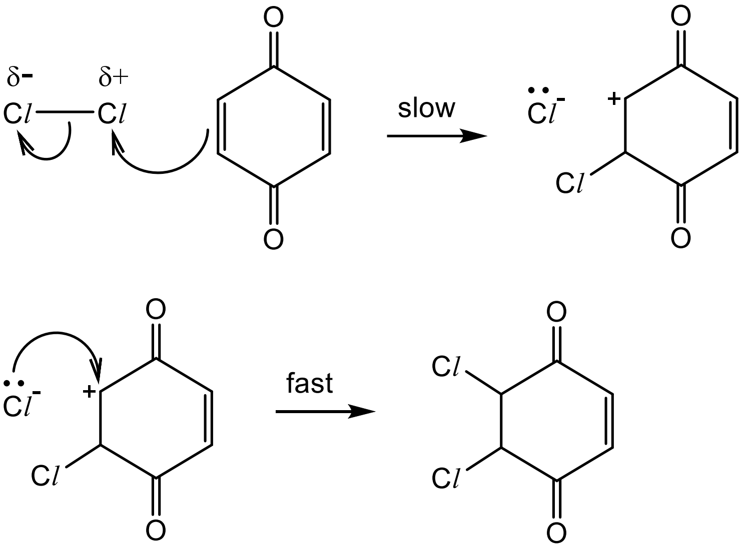
blattellaquinone

(d) Paraquinone and limited chlorine react as follows.



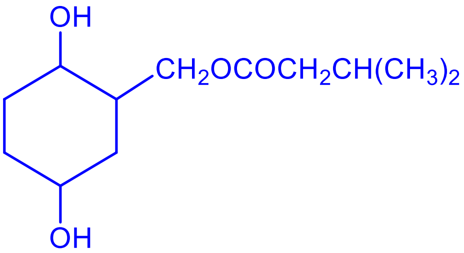
Name and draw the mechanism of this reaction. [3]

electrophilic addition

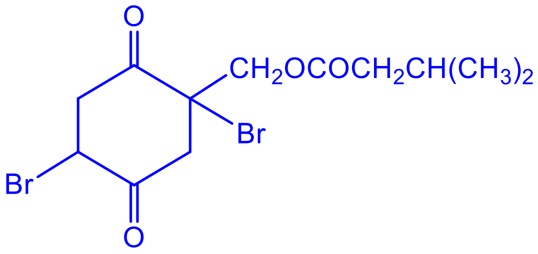


(e) Draw the major products formed when **blattellaquinone** is separately reacted under suitable conditions with each of the following:

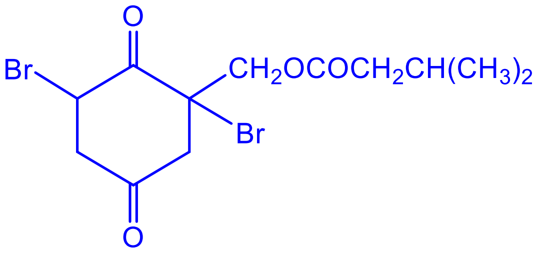
(i) hydrogen gas [1]



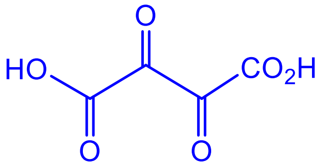
(ii) gaseous hydrogen bromide [1]

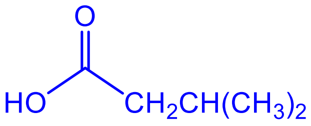


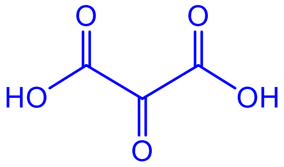
OR



(iii) hot acidified potassium manganate(VII) [2]







[Total: 20]

5 This question concerns the compounds of Period 3 elements.

(a) Properties of the oxides of some Period 3 elements, **P**, **Q** and **R**, are given below.

oxide	physical state at room conditions	electrical conductivity when molten
P	gas	nil
Q	solid	high
R	solid	low

These three oxides, in no particular order, are Al_2O_3, SiO_2 and SO_3.

(i) Identify **P**, **Q** and **R**. [1]

P is SO_3, **Q** is Al_2O_3 and **R** is SiO_2.

(ii) Account for your answer, in terms of their structure and bonding. [4]

P (SO_3) has a **simple molecular structure** with **weak instantaneous dipole – induced dipole interactions** resulting in its **low melting point**. It does not conduct electricity as there are no charged particles in the molten state.

Q (Al_2O_3) has **giant ionic lattice structure** with strong ionic bonds between its cations and anions resulting in its high melting point. It **conducts electricity in the molten state as its ions become mobile**.

R (SiO_2) has a **giant molecular structure** with **strong and extensive covalent bonds between Si and O atoms** resulting in its **high melting point** . It **conducts electricity poorly** as there are **no charged particles in the molten state**.

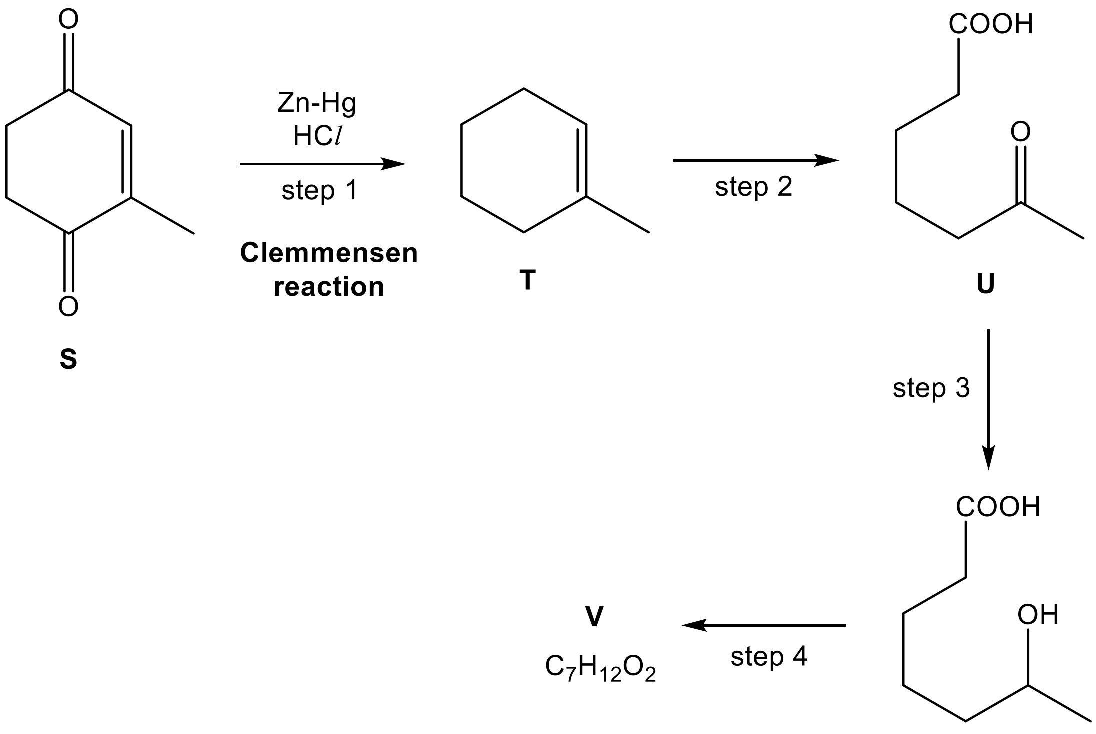
(iii) Al_2O_3 is described as an amphoteric oxide.
Write two equations to show the amphoteric nature of Al_2O_3. [2]

$\mathbf{Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O}$
$\mathbf{Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4}$

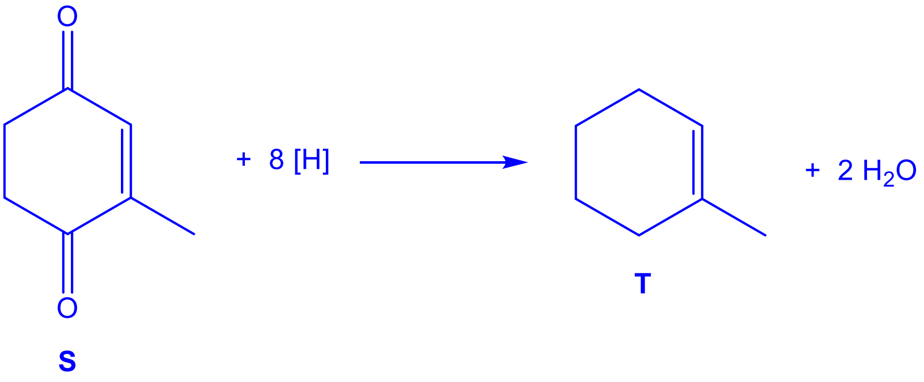
(b) Hydrogen chloride is a colourless gas commonly used in organic synthesis.

In the Clemmensen reaction, carbonyl compounds are reduced to alkanes using zinc-mercury and hydrogen chloride dissolved in an organic solvent.

A reaction scheme involving the Clemmensen reaction is shown below.



(i) Write the balanced equation for the reduction of compound **S** to **T**. Use [H] to represent the formula of the reducing agent. [1]

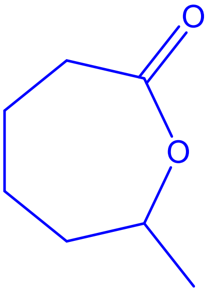


(ii) Suggest a reagent which can determine if the reaction in step 3 is complete. [1]

Brady's reagent/ 2,4-DNPH

(iii) Given that compound **V** is neutral, state the type of reaction occurring in step 4, and suggest the structure of compound **V**. [2]

step 4: **condensation**

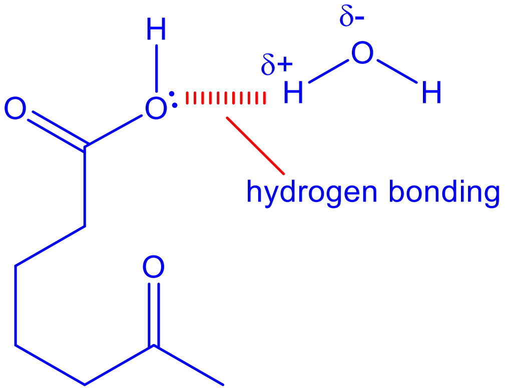


(iv) Compound **U** is more soluble in water than compound **S**.

1. Suggest a reason why this is so. [1]

Compound **U** has more functional groups which **<u>form hydrogen bonding with water to a greater extent</u>**, hence it is more soluble in water than compound **S**.

2. Draw a labelled diagram to show how compound **U** dissolves in water. [1]



(c) HC*l* is stable to heat while HBr and HI, can undergo thermal decomposition. At 700 K, HBr is approximately 10% decomposed but HI, is approximately 20% decomposed.

Explain these differences with reference to relevant data in the *Data Booklet* and the factors that affect them. [3]

Bond energies (kJ mol^{-1}): H-C*l* (431), H-Br (366), H-I (299)
Down Group 17, **<u>extent of thermal decomposition of HX increases</u>/ thermal stability of HX decreases** as **<u>less energy is needed to break H-X bond</u>**/ H-X bond strength decreases.
This is due to an **<u>increase in size of halogen atom</u>** down group 17, resulting in **<u>less effective orbital overlap between H and halogen atom</u>**.

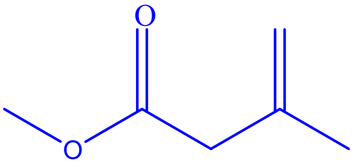
(d) Compound **W**, $C_6H_{10}O_2$ is an ester which decolourises Br_2 in CCl_4 to form $C_6H_{10}Br_2O_2$.

Upon prolonged heating with excess acidified $KMnO_4$, 1 mol of **W** produces 1 mol of **X**, $C_4H_6O_3$ and 2 mol of CO_2.

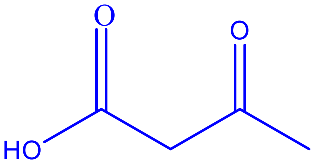
X gives a yellow precipitate **Y** when warmed with aqueous alkaline iodine. **X** also undergoes the Clemmensen reaction to give **Z**, $C_4H_8O_2$. Both **X** and **Z** produce effervescence when reacted with aqueous sodium carbonate.

Suggest structures for the identity of **W**, **X, Y** and **Z**. [4]

W:



X:



Y: **CHI_3**

Z: **$CH_3CH_2CH_2COOH$**

[Total: 20]

End of Paper 3

TAMPINES MERIDIAN JUNIOR COLLEGE

2019 JC2 H2 Chemistry Prelim Exam Paper 4

(Suggested Answers)

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1 Determination of the concentration of a base and the enthalpy change of the neutralisation reaction

FA 1 is 2.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 2 is aqueous sodium hydroxide, NaOH.

The reaction of sulfuric acid and sodium hydroxide is exothermic.
In separate experiments, you will add increasing volumes of **FA 2** to a fixed volume of **FA 1**. In each experiment you will measure the maximum temperature rise, ΔT. As the volume of **FA 2** is increased, this maximum temperature rise, ΔT, will increase and then decrease.

By measuring the maximum temperature rise for different mixtures of the two reagents, you are to determine the following:

- the concentration of sodium hydroxide, NaOH, in **FA 2**
- the enthalpy change when 1 mol of H_2SO_4 is neutralised by NaOH

(a) Method

- Fill the labelled burette with **FA 1**.
- Support a styrofoam cup in the 250 cm^3 beaker.
- Run 10.00 cm^3 of **FA 1** from the burette into the styrofoam cup.
- Measure 20.0 cm^3 of **FA 2** using a measuring cylinder.
- Place the thermometer in the **FA 2** in the measuring cylinder and record the steady temperature of the solution.
- Pour the **FA 2** into the styrofoam cup, stir and record the maximum temperature obtained in the reaction.
- Empty and rinse the styrofoam cup; shake dry the styrofoam cup. Rinse the thermometer.
- Carry out the experiment three more times. Each time use 10.00 cm^3 of **FA 1**.
- Use 30.0 cm^3, 40.0 cm^3 and 50.0 cm^3 of **FA 2** in these different experiments.

Carry out **two further experiments**.
Choose volumes of **FA 2** which will allow you to investigate more precisely the volume of **FA 2** that produces the highest temperature rise when added to 10.00 cm^3 of **FA 1**.

Results
Record your results below in an appropriate form showing, for each experiment, the volumes of solutions used, temperature measurements and the temperature rise, ΔT.

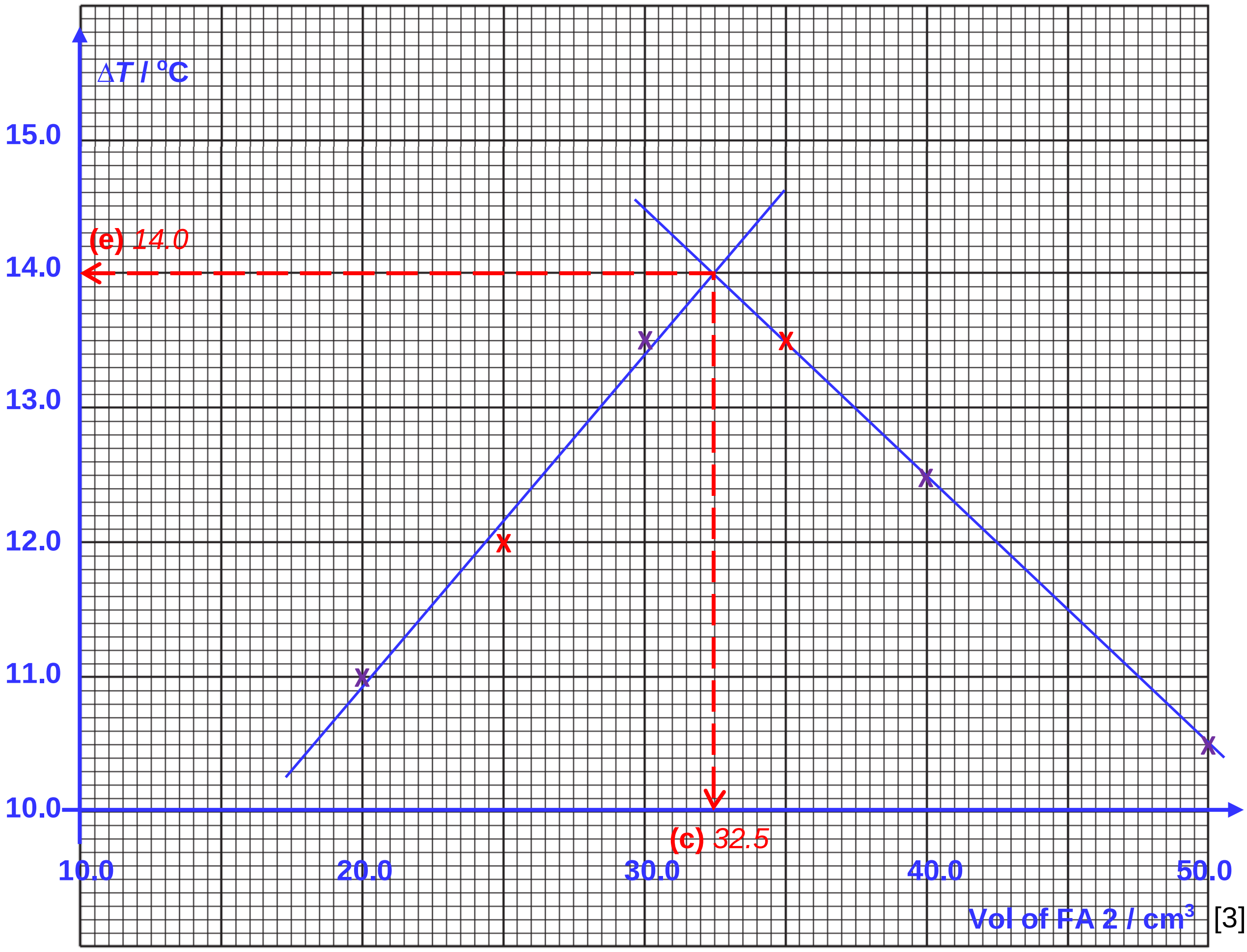
Expt	Volume of FA 1 / cm^3	Volume of FA 2 / cm^3	T_i / °C	T_f / °C	ΔT / °C
1	10.00	20.0	31.5	42.5	11.0
2	10.00	30.0	31.5	45.0	13.5
3	10.00	40.0	31.5	44.0	12.5
4	10.00	50.0	31.5	42.0	10.5
5	10.00	25.0	31.5	43.5	12.0
6	10.00	35.0	31.5	45.0	13.5

[4]

(b) Plot a graph of temperature rise, ΔT, on the y-axis against the volume of **FA 2** added on the x-axis.

Draw a line of best fit through the points where the temperature rise is increasing and another line through the points where the temperature rise is decreasing.

The intersection of these lines represents the temperature rise for the volume of **FA 2** that exactly neutralises the sulfuric acid present in 10.00 cm^3 of **FA 1**.



[3]

(c) Read from the graph the volume of **FA 2** that gives the maximum temperature rise.

Volume of **FA 2** giving the maximum temperature rise = **32.5** cm^3 [1]

(d) **(i)** Calculate the amount of NaOH required to neutralise the amount of H_2SO_4 at the maximum temperature rise.

Amount of $H_2SO_4 = 2.0 \times 0.010$
$= 0.0200$ mol

$H_2SO_4 \equiv 2$ NaOH

Amount of NaOH $= 2 \times 0.020$
$= \underline{\mathbf{0.0400}}$ mol

Amount of NaOH required = **0.0400** mol
[1]

(ii) Hence, calculate the concentration of NaOH in **FA 2**.

Concentration of NaOH in **FA 2** $= 0.0400 \div \frac{32.5}{1000}$
$= \underline{\mathbf{1.23}}$ mol dm^{-3}

Concentration of NaOH in **FA 2** = **1.23** mol dm^{-3}
[1]

(e) Read the maximum temperature rise from the graph and use this to calculate the enthalpy change when 1 mol of H_2SO_4 is neutralised by NaOH. Give your answer in kJ mol^{-1}.

[4.18 J are absorbed or released when the temperature of 1 cm^3 of solution changes by 1 °C.]

Quantity of heat absorbed by solution $= (32.5 + 10.0) \times 4.18 \times 14.0$
= **2487 J** *OR* **2.487 kJ**

Enthalpy change $= -\frac{2.487}{0.0200}$
$= \underline{\mathbf{-124}}$ **kJ mol^{-1}**

Enthalpy change = **–124** kJ mol^{-1}
[2]

(f) The enthalpy change of neutralisation, ΔH_{neut}, between a strong acid and a strong base is –57 kJ mol^{-1}.

Explain why the enthalpy change calculated in **(e)** is significantly more exothermic than ΔH_{neut}.

Enthalpy change in **(e)** is based on **1 mol of H_2SO_4** (or **<u>2 mol of water</u>** formed) while the enthalpy change of neutralisation, ΔH_{neut} (–57 kJ mol^{-1}), is based on **<u>1 mol of water</u>** formed.
[1]

(g) A student suggested that the experiments carried out in **(a)** would be more accurate if volumes of 20.00 cm^3 of 1.0 mol dm^{-3} H_2SO_4 were used instead.

State and explain whether you agree or disagree with the student's suggestion.

Accept any of the following:

- Agree –

Lower (percentage) error as: acid spray is reduced (since reaction will be slower) *OR* smaller temperature rise so less heat loss *OR* larger volume used *(accept other reasons)*

- Disagree –

Higher (percentage) error as: smaller temperature change, so higher (percentage) error of reading *OR* reaction slower so more heat loss *(accept other reasons)*

[1]

[Total: 14]

2 Determination of the percentage by mass of sodium carbonate in a mixture of sodium hydroxide and sodium carbonate

Sodium carbonate is neutralised by hydrochloric acid in two steps:

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$
$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

This step-wise neutralisation can be observed when the acid is added slowly to the sodium carbonate.

The percentage by mass of sodium carbonate in a mixture of sodium hydroxide and sodium carbonate can be determined by carrying out titrations using two different indicators. Since both sodium hydroxide and sodium carbonate react with acids, through careful selection of the indicators used for the titration, the volume of acid required to react with only the sodium carbonate can be found.

FA 3 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 4 is an aqueous solution containing sodium hydroxide, $NaOH$, and sodium carbonate, Na_2CO_3.

You are also provided with bromophenol blue indicator.

In this question, you will carry out titrations to determine the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in solution **FA 4**.

(a) (i) Titration of FA 4 against FA 3 using bromophenol blue

1. Fill a burette with **FA 3**.
2. Pipette 25.0 cm^3 of **FA 4** into a conical flask.
3. Add four to five drops of bromophenol blue indicator.
4. Titrate the mixture in the flask with **FA 3** until the blue-violet colour of the solution changes to yellow.
5. Record your titration results, to an appropriate level of precision, in the space provided.

Repeat steps 2 to 5 to obtain consistent results.

Titration results

	1	2	3
Final burette reading / cm^3	20.70	30.55	20.45
Initial burette reading / cm^3	0.00	10.00	0.00
Volume of **FA 3** / cm^3	20.70	20.55	20.45
		✓	✓

[6]

(ii) From your titration results, obtain a suitable volume of **FA 3**, $V_{\text{FA 3}}$, to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 3**, $V_{\text{FA 3}} = \dfrac{20.55 + 20.45}{2}$

$= \underline{20.50\ \text{cm}^3}$ **(2 d.p.)**

$V_{\text{FA 3}}$ = **20.50 cm^3**

[1]

(b) When the titrations in **(a)** were repeated using **phenolphthalein** as the indicator, 25.0 cm^3 of **FA 4** required 15.00 cm^3 of **FA 3**.

The following explains why different results are obtained using two different indicators.

- When phenolphthalein is used as the indicator, the following reactions have taken place at the end-point of the titration.

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

- When bromophenol blue is used as the indicator in **(a)**, the following reactions have taken place at the end-point of the titration.

Reaction 1 $NaOH + HCl \rightarrow NaCl + H_2O$

Reaction 2 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

Reaction 3 $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

For the titration using **bromophenol blue**, the amount of Na_2CO_3 reacted in *Reaction 2* is equal to the amount of sodium bicarbonate, $NaHCO_3$, reacted in *Reaction 3*. Both the amounts of Na_2CO_3 reacted in *Reaction 2* using **phenolphthalein or bromophenol blue** are the same.

Show your working and use appropriate significant figures in the final answers to all steps of your calculations.

(i) Calculate the amount of HC*l* in the volume of **FA 3**, $V_{\text{FA 3}}$, determined in **(a)(ii)**.

Amount of HC*l* = ***0.125 × ($V_{\text{FA 3}}$ in dm^3) mol***

$= 0.125 \times \dfrac{20.50}{1000}$ **mol** $= \underline{\mathbf{2.56 \times 10^{-3}\ mol}}$

Amount of HC*l* in $V_{\text{FA 3}}$ = **2.56×10^{-3} mol**

(ii) Calculate the amount of HC*l* in 15.00 cm^3 of **FA 3**.

Amount of HC*l* = $\mathbf{0.125} \times \dfrac{15.00}{1000} = \underline{\mathbf{1.88 \times 10^{-3}\ mol}}$

Amount of HC*l* in 15.00 cm^3 of **FA 3** = **1.88×10^{-3} mol**

[1]

(iii) With reference to the information given in **(b)** and your answers to **(b)(i)** and **(b)(ii)**, calculate the amount of HC*l* that reacted with Na_2CO_3 in *Reaction 2* using **phenolphthalein** indicator.

Amount of HC*l* reacted with Na_2CO_3 = ***ans (b)(i) – (1.88 × 10⁻³) mol***

$= 2.56 \times 10^{-3} - 1.88 \times 10^{-3} =$ **$\underline{6.83 \times 10^{-4}\ \text{mol}}$**

Amount of HC*l* reacted with Na_2CO_3 in *Reaction 2*
using phenolphthalein = **6.83×10^{-4} mol**

[1]

(iv) Use your answer to **(b)(iii)** to calculate the mass of Na_2CO_3 present in 25.0 cm^3 of **FA 4**.
[A_r : C, 12.0; O, 16.0; Na, 23.0]

Mass of Na_2CO_3 = ***ans (b)(iii) × 106.0 g***

$= 6.83 \times 10^{-4} \times 106.0 =$ **$\underline{0.0723\ \text{g}}$**

Mass of Na_2CO_3 in 25.0 cm^3 of **FA 4** = **0.0723 g**

[1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HC*l* when **bromophenol blue** is used as indicator is given below.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

Calculate the amount of HC*l* that reacted with Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 4**.

Amount of HC*l* = ***ans (b)(iii) × 2 mol***

$= 6.83 \times 10^{-4} \times 2 =$ **$\underline{1.37 \times 10^{-3}\ \text{mol}}$**

Amount of HC*l* reacted with Na_2CO_3 using bromophenol blue = **1.37×10^{-3} mol**

[1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of NaOH in 25.0 cm^3 of **FA 4**.
[A_r : H, 1.0; O, 16.0; Na, 23.0]

Amount of HC*l* reacted with NaOH = ***(ans (b)(i)) – (ans (b)(v)) mol***

Mass of NaOH = ***[(ans (b)(i)) – (ans (b)(v))] × 40.0 g***

$= (2.56 \times 10^{-3} - 1.37 \times 10^{-3}) \times 40.0 = 1.20 \times 10^{-3} \times 40.0 =$ **$\underline{0.0478\ \text{g}}$**

Mass of NaOH in 25.0 cm^3 of **FA 4** = **0.0478 g**

[1]

(vii) Calculate the percentage by mass of Na_2CO_3 in the mixture of NaOH and Na_2CO_3 in **FA 4**.

% by mass of Na_2CO_3 = *(**ans (b)(iv)**) ÷ [(**ans (b)(iv)**) + (**ans (b)(vi)**)] × **100*** %

$$= \frac{0.0723}{0.0723 + 0.0478} \times 100 = \frac{0.0723}{0.1201} \times 100 = \underline{\mathbf{60.2\%}}$$

FA 4 contains **60.2** % by mass of Na_2CO_3

[2]

(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:	±0.06 cm^3

Calculate the percentage error (uncertainty) when a

- 50.00 cm^3 burette
- 25.0 cm^3 pipette

is used to measure 25 cm^3 of **FA 4** into the conical flask.

Hence explain whether the 50.00 cm^3 burette or the 25.0 cm^3 pipette will be a more accurate apparatus to measure 25 cm^3 of **FA 4**.

% error (uncertainty) of burette = (2 × 0.05)/25 × 100% = **0.40%**

% error (uncertainty) of pipette = 0.06/25 × 100% = **0.24%**

A **25.0 cm^3 pipette** has a **lower % error/uncertainty** and hence is **more accurate** to measure 25 cm^3 of **FA 2**.

[2]

(d) **Planning**

You are to plan an experiment to determine the percentage by mass of sodium carbonate in an unknown solid sample by measuring the volume of carbon dioxide gas evolved on reaction with excess acid at room temperature and pressure.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

You may assume that you are provided with:

- 0.5 mol dm^{-3} hydrochloric acid, HC*l*;
- 0.5 g impure solid sample containing sodium carbonate, Na_2CO_3. Other impurities present are assumed to have no reaction with acid;
- 100 cm^3 gas syringe for gas collection;
- apparatus normally found in a school laboratory.

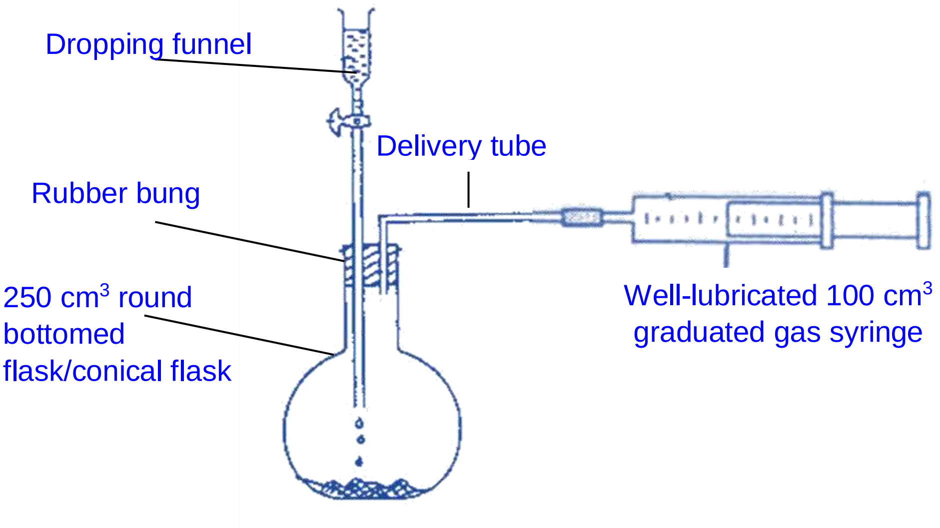
Your plan should include:

- calculations of suitable mass of impure sample and volume of excess hydrochloric acid to be used, based on a 100 cm^3 gas syringe;
- a fully-labelled diagram of the experimental set-up;
- practical details of how you would
  - ensure a known mass of solid sample and volume of acid are measured;
  - determine the volume of carbon dioxide evolved, including the measurements to be made;
  - ensure that an **accurate** and **reliable** volume of gas is obtained.

[M_r : Na_2CO_3, 106.0]

[7]

Diagram



Pre-calculations

Assuming conditions of r.t.p. and 50 to 100 cm^3 of gas collected, eg. 80 cm^3 of CO_2 gas to be collected:

No of mole of $CO_2 = \frac{80}{24000} = 3.33 \times 10^{-3}$ mol

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

$Na_2CO_3 \equiv CO_2$

Mass of $Na_2CO_3 = 3.33 \times 10^{-3} \times 106 = 0.353$ g

Assuming that impure sample is 100% pure, mass of sample required = **0.353 g** ***(about 0.35g)***

$Na_2CO_3 \equiv 2HCl$

Minimum volume of $HCl = \frac{3.33 \times 10^{-3} \times 2}{0.5}$ = **13.32 cm^3** ***(excess acid; any vol > 13.32 cm^3)***

Procedure

Weighing by difference

1. Weigh about **0.35 g** of impure solid sample in a weighing bottle using a mass balance.
2. Transfer the impure sample to a 250 cm^3 round bottom flask/conical flask.
3. Re–weigh the weighing bottle to obtain mass of residual solid.

Alternative

1. Weigh about **0.35 g** of impure solid sample and transfer into a 250 cm^3 round bottom flask/conical flask.

Gas collection

2. Using a **25 cm^3** measuring cylinder, transfer **20** cm^3 of solution into a dry dropping funnel.
3. Read the initial reading of the 100 cm^3 **gas syringe** (or other appropriate apparatus).
4. Run the solution from the dropping funnel into the 250 cm^3 conical flask. Close the tap when all the solution has flowed into the conical flask.
5. Swirl the flask once and leave it to stand.
6. Read the final reading of the **gas syringe** after the reaction is completed, **when there is no further change to the reading of the gas syringe**.

[Total: 23]

3 Qualitative Analysis

Where reagents are selected for use in a test, the **name** or **correct formula** of the element or compound must be given.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

You should indicate clearly at what stage in a test a change occurs.
If there is no observable change, write **no observable change**.

Rinse and reuse test-tubes and boiling tubes where possible.

(a) **FA 5** contains **two** cations and **two** anion from the lists on pages 17 and 18.

- To approximately half a boiling tube of distilled water, add all the **FA 5**.
- Stopper and shake the boiling tube thoroughly for one minute to make sure that no more of the solid will dissolve.
- Filter the mixture into a clean boiling tube.
- Place the filter funnel in a conical flask and wash the residue well with distilled water.
- **Keep both filtrate and residue for (a)(i) and (a)(ii) respectively.**

While you are waiting for the mixture to filter, continue with (b) or (c).

(i) **Tests on the filtrate**

Carry out the following tests and record your observations in Table 3.1 below.

Table 3.1

	test	observations
1.	To a 1 cm depth of the filtrate in a test-tube, add aqueous ammonia, slowly with shaking until no further change is seen;	• **Off-white / beige / pale or light brown** (not cream) **ppt** • Ppt rapidly **turns brown on contact with air / darkens on standing** *OR* **Ppt insoluble in excess NH_3** [1]
	then add aqueous hydrogen peroxide.	• Ppt / solid turns **brown / darker brown / brown-black** • **Effervescence / bubbling** *OR* **Gas evolved relights glowing splint** [1]

(ii) **Tests on the residue**

Carry out the following tests and record your observations in Table 3.2 below.

Table 3.2

	test	observations
2.	Place the funnel containing the residue into a clean test-tube. Pour approximately 5 cm^3 of dilute nitric acid onto the residue. Collect the resultant filtrate. Discard the first 1 cm depth of this resultant filtrate and collect the remaining filtrate in another clean test-tube for test 3.	• **Effervescence** observed when acid is poured onto the residue • **Colourless filtrate** obtained [1]
3.	To 1 cm depth of the solution in a test-tube, add aqueous sodium hydroxide, slowly with shaking until no further change is seen.	• **White ppt** • Ppt **insoluble in excess NaOH** [1]

(iii) Identify the **two** cations present in **FA 5**. Use evidence from your observations in **(a)(i)** and **(a)(ii)** to support your deduction.

cations present .... Mn^{2+} .... and .... Mg^{2+} ....

evidence

In test **1**, **addition of NH_3 formed off-white ppt which turned brown / insoluble in excess**, indicating presence of **Mn^{2+}**.

In test **3**, **addition of NaOH formed white ppt which was insoluble in excess**, indicating presence of **Mg^{2+}**.

[2]

(iv) The tests you have carried out in **(i)** and **(ii)** would have enabled you to identify only one of the two anions present in **FA 5**. Identify this anion.

anion present .... CO_3^{2-} .... [1]

(v) Suggest what type of reaction is happening when hydrogen peroxide is added in test **(b)(i)**.

Redox / decomposition of H_2O_2 / disproportionation of H_2O_2 [1]
(allow oxidation of Mn^{2+} / oxidation or reduction of H_2O_2)

(vi) In test 1 of **(a)(i)**, aqueous ammonia behaved as an Arrhenius base:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In a separate experiment, an equal volume of aqueous ammonium chloride, NH_4Cl was added to a second portion of the filtrate that was used in **(a)(i)**. When aqueous ammonia was then added to this resultant solution, no precipitate formed.

Suggest an explanation for the results of this experiment.

Presence of ammonium chloride increased $[NH_4^+]$ and **shifted position of equilibrium to the left, decreasing $[OH^-]$**.

$[OH^-]$ insufficient to cause precipitation of the metal hydroxide, $(MnOH)_2$.

[2]

(b) **FA 6** is an aqueous solution containing nickel(II) ion.

Carry out the following tests on **FA 6** and record your observations in Table 3.3 below.

Table 3.3

	test	*observations*
(i)	To a 1 cm depth of **FA 6** in a test-tube, add aqueous ammonia, slowly with shaking, until no further change is seen.	• Solution (**FA 6**) turns from green to **blue** (not dark blue) *(Ignore any ppt)* [1]
(ii)	To a 1 cm depth of **FA 6** in a test-tube, add aqueous sodium hydroxide, slowly with shaking, until no further change is seen.	• **Green ppt** • **Ppt insoluble in excess** [1]

(iii) Nickel(II) ions form complexes with ligands such as ammonia and ethylenediamine as shown:

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l) \qquad K_c = 4.8 \times 10^7 \text{ mol}^{-6} \text{ dm}^{18}$$

$$[Ni(H_2O)_6]^{2+}(aq) + 3en(aq) \rightleftharpoons \underset{\text{purple}}{[Ni(en)_3]^{2+}(aq)} + 6H_2O(l) \qquad K_c = 2.0 \times 10^{18} \text{ mol}^{-3} \text{ dm}^9$$

[en ≡ ethylenediamine]

The observation in **(b)(i)** is due to the formation of the nickel-ammonia complex.

Suggest, with reason, what might be observed if aqueous ammonia were added to a solution containing $[Ni(en)_3]^{2+}$ ions instead of $Ni^{2+}(aq)$.

No observable change / no colour change / purple solution remained.

Any one of the following:

- **$[Ni(en)_3]^{2+}$(aq) complex is more stable**
- **$[Ni(NH_3)_6]^{2+}$(aq) complex is less stable**
- **en is a stronger ligand (**and so unable to be displaced by NH_3)
- **NH_3 is a weaker ligand** (and so unable to displace en)

[2]

(c) **FA 7**, **FA 8** and **FA 9** are 1.0 mol dm^{-3} sulfuric acid, 0.1 mol dm^{-3} sulfuric acid and 1.0 mol dm^{-3} hydrochloric acid, but not necessarily in that order.

You are to plan and carry out **two** simple tests, using only the bench reagents provided, which will enable you to determine the identities of **FA 7**, **FA 8** and **FA 9**.

You should record, in a suitable form in the space below, your tests and observations. You should show clearly the observations for each of **FA 7**, **FA 8** and **FA 9** with all test reagents.

TWO tests only	Test	**FA 7**	**FA 8**	**FA 9**
EITHER (allow identification by elimination, sequence may be swapped)	Add aqueous $BaNO_3$	No ppt	White ppt	White ppt
	Add aqueous $AgNO_3$	White ppt	No ppt	No ppt
AND (accept other correct simple tests)	Add Mg strip	Strong / fast effervescence	Strong / fast effervescence	Weak / slow effervescence

FA 7 is **1.0 mol dm^{-3} hydrochloric acid**

FA 8 is **1.0 mol dm^{-3} sulfuric acid**

FA 9 is **0.1 mol dm^{-3} sulfuric acid**

[4]

[Total: 18]

TEMASEK JUNIOR COLLEGE
2019 JC2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

18th September 2019
1 hour

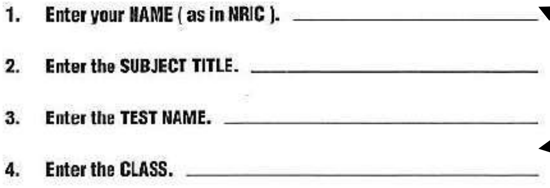
Additional Materials: Multiple Choice Answer Sheet (OMS)
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

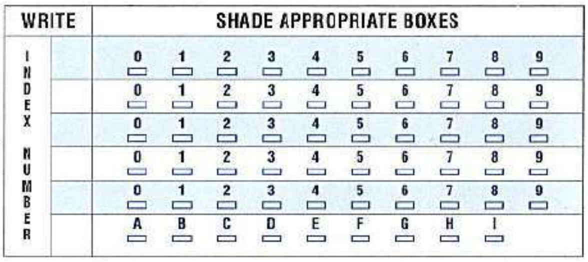
Write your name, Class and index number on the Answer Sheet in the spaces provided.



1. Enter your NAME (as in NRIC). ______________
2. Enter the SUBJECT TITLE. ______________
3. Enter the TEST NAME. ______________
4. Enter the CLASS. ______________

Write your **name** and **Civics Group**

Write and shade your index number



WRITE		SHADE APPROPRIATE BOXES									
I N D E X N U M B E R		0	1	2	3	4	5	6	7	8	9
		0	1	2	3	4	5	6	7	8	9
		0	1	2	3	4	5	6	7	8	9
		0	1	2	3	4	5	6	7	8	9
		0	1	2	3	4	5	6	7	8	9
		A	B	C	D	E	F	G	H	I	

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 including the cover page.

1 The number of neutrons and nucleons for five particles are shown below. The letters of the particles do not correspond to the identity of the elements in the Periodic Table.

Particle	Neutrons	Nucleons
U	16	33
V^-	18	35
S^{2-}	16	32
T^{2+}	17	34
Q^{3-}	16	31

Which of the following sets consists of particles that are isoelectronic?

A U, S^{2-}, T^{2+}

B U, S^{2-}, Q^{3-}

C V^-, S^{2-}, Q^{3-}

D V^-, T^{2+}, Q^{3-}

2 Methane was burned in an incorrectly adjusted burner. The methane was converted into a mixture of carbon dioxide and carbon monoxide in the ratio of 95 : 5, together with water vapour.

What will be the volume of oxygen consumed when x dm^3 of methane is burned?

A $(x - \frac{0.05x}{2})$ dm^3

B $(x - 0.05x)$ dm^3

C $(2x - \frac{0.05x}{2})$ dm^3

D $(2x - 0.05x)$ dm^3

3 Which of the following particles contains the most number of unpaired electrons?

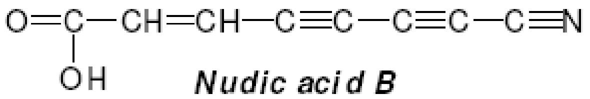
A Na

B P^{3-}

C V

D Mn^{2+}

4 *Nudic acid B* is an acidic antibiotic isolated from the culture medium of the basidiomycete *Tricholoma nudum* (Bull.) Fr.



$\mathrm{O{=}C(OH){-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N}$

Nudic acid B

What is the number of σ and π bonds present in the molecule?

	σ	π
A	16	5
B	13	8
C	13	5
D	10	8

5 A pair of compounds have the following properties as described below.

(i) The first compound has a larger bond angle about the central atom than the second compound.

(ii) The second compound is more polar than the first compound.

Which pair of compounds fit the description above?

A BCl_3, ClO_2^-

B ICl_2^-, CO_2

C HCN, XeF_4

D ClO_2^-, CO_2

6 In which of the following pairs is the melting point of the first member lower than that of the second member?

I diamond, silicon
II H_2O, NH_3
III $SiCl_4$, Al_2O_3
IV Br_2, ICl

A I, II, III, IV

B I, III, IV

C III, IV

D I only

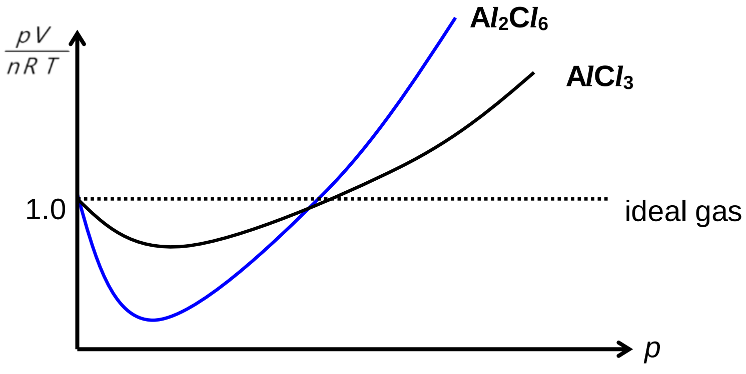
7 Gaseous Al_2Cl_6 decomposes into gaseous $AlCl_3$ in a 250 cm^3 closed reaction vessel maintained at a temperature of 500 K. The system reaches equilibrium with a total pressure of 1.16×10^5 Pa.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

The average M_r of the equilibrium gas mixture in the vessel is found to be 214.9.

Which of the following statements are correct?

1 The bond angle in both molecules is 120°.
2 The mass of the gaseous mixture inside the reaction vessel is 1.50 g.
3 The following graphs depicts the correct behaviour of the two gases under standard conditions.



A 1, 2 and 3 only
B 1 and 2 only
C 2 and 3 only
D 1 only

8 The following information is given.

$2Cr(s) + \frac{3}{2}O_2(g) \longrightarrow Cr_2O_3(s)$ $\Delta H = -1120$ kJ mol^{-1}

$3C(s) + Cr_2O_3(s) \longrightarrow 2Cr(s) + 3CO(g)$ $\Delta H = +790$ kJ mol^{-1}

What is the standard enthalpy change of the following reaction, in kJ mol^{-1}?

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

A −110

B −220

C −637

D −1273

9 In this question, the symbol '<' means 'less positive than' or 'more negative than'.

Both mercury(I) sulfate, Hg_2SO_4, and cadmium(I) sulfate, Cd_2SO_4, are odourless white crystalline solids. Hg_2SO_4 is sparingly soluble while Cd_2SO_4 is very soluble in water. Both sulfates are used in industry for electrochemical and electrolytic processes.

The following data is provided:
$\Delta H_{latt}^{\ominus}$ (Hg_2SO_4) = –2127 kJ mol^{-1}
$\Delta H_{hyd}^{\ominus}$ (Hg^+) = –625 kJ mol^{-1}
$\Delta H_{hyd}^{\ominus}$ (SO_4^{2-}) = –1160 kJ mol^{-1}

Which of the following statements are correct?

1 $\Delta H_{soln}^{\ominus}$ of Hg_2SO_4 equals to a magnitude of 283 kJ mol^{-1}.
2 $\Delta H_{latt}^{\ominus}$ of Hg_2SO_4 is less exothermic than that of Cd_2SO_4.
3 $\Delta G_{soln}^{\ominus}$ of Hg_2SO_4 is < $\Delta G_{soln}^{\ominus}$ of Cd_2SO_4

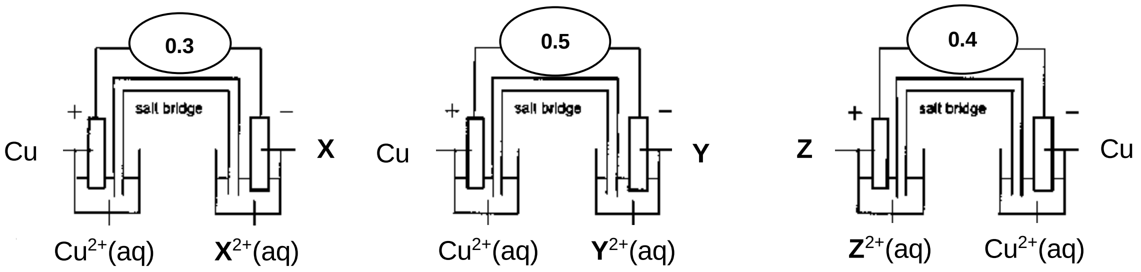
A 1 only

B 1 and 2 only

C 2 and 3 only

D 1,2 and 3 only

10 Three electrochemical cells are set up as shown below. The *e.m.f* in volts at standard conditions is shown on each voltmeter. The concentration of all the solutions are 1 mol dm^{-3}. **X**, **Y** and **Z** are metal electrodes.



The *e.m.f* indicates the order of reactivity of the metals.

The order of the strongest to the weakest oxidising agent is :

A Z^{2+}, Cu^{2+}, X^{2+}, Y^{2+}

B Y^{2+}, X^{2+}, Cu^{2+}, Z^{2+}

C Cu^{2+}, Z^{2+}, Y^{2+}, X^{2+}

D Z, Cu, X, Y

11 The standard reduction potentials, $E^\ominus$, for the electrode reactions NO_3^-/NH_4^+ and NO_3^-/NO_2 are +0.87 V and +0.81 V respectively.

Dilute HC*l* was added to separate beakers containing 1 mol dm^{-3} NO_3^-/NH_4^+ and 1 mol dm^{-3} NO_3^-/NO_2 until a pH of 5 was achieved.

Which of the following statements are correct for the two beakers?

1 The reducing abilities of NH_4^+ and NO_2 decreases.

2 NO_2 is a weaker reducing agent than NH_4^+ at pH 5.

3 The oxidising ability of NO_3^- decreases.

A 1 only

B 3 only

C 1 and 2 only

D 1,2 and 3 only

12 Excess marble chips are added to 30 cm^3 of 1 mol dm^{-3} of nitric acid at room temperature until no further reaction occurs.

How would the experiment be different if it is now repeated with 50 cm^3 of 0.5 mol dm^{-3} of nitric acid at the same temperature?

	Rate of reaction	Amount of products
A	Faster	Lesser
B	Faster	More
C	Slower	More
D	Slower	Lesser

13 CO and H_2 were placed in a reactor fitted with a movable piston and the following equilibrium is established.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Which of the following best explains what happens when some argon gas is added to the mixture at constant volume and temperature?

A The position of equilibrium will not shift as the partial pressure of all gaseous reactants and products remain constant.

B The position of equilibrium will not shift as argon does not react with any substance in the mixture.

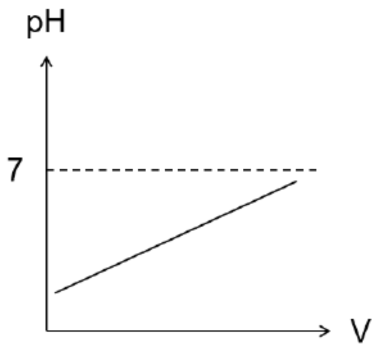
C The position of equilibrium will shift to the right to decrease total pressure.

D The position of equilibrium will shift to the left to increase total pressure.

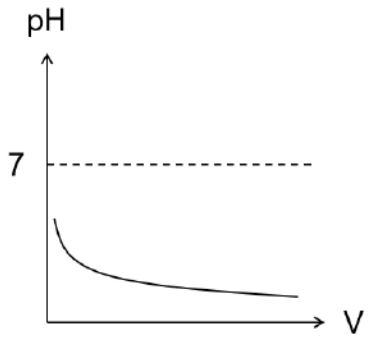
14 A solution of 1 mol dm^{-3} of weak acid is diluted with large excess of water at 25 ^{o}C.

Which of the following graph correctly shows how the pH of the solution varies with volume of mixture, V?

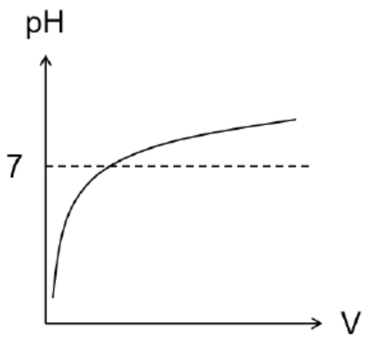
A



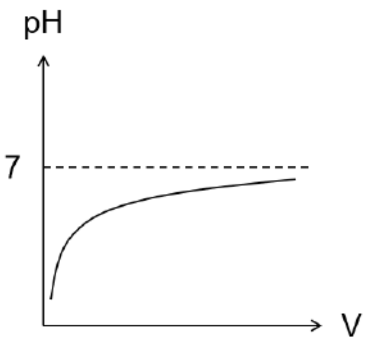
B



C



D

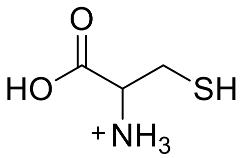


15 Zn^{2+} ions combine with hexacyanoferrate(III), [Fe(CN)$_6$]$^{3-}$, to produce a sparingly soluble salt, Zn$_3$[Fe(CN)$_6$]$_2$.

Given than the K$_{sp}$ value for the salt is **W**, what is the concentration of the anion at equilibrium?

A $\sqrt[3]{\frac{\mathbf{W}}{108}}$ **B** $\sqrt[5]{\frac{\mathbf{W}}{108}}$ **C** $\sqrt[3]{\frac{8\mathbf{W}}{27}}$ **D** $\sqrt[5]{\frac{8\mathbf{W}}{27}}$

16 A solution of cysteine in its *fully protonated* form is titrated against a standard solution of potassium hydroxide. The structure of *fully protonated* cysteine is shown below and its 3 pK_a values are 1.9, 8.1 and 10.3.



Which of the following indicator(s) can be used to detect the isoelectric point of the cysteine?

	Indicator	Working range
1	Bromocresol Green	3.7 – 5.7
2	Methyl Red	4.1 – 6.1
3	Bromothymol Blue	6.0 – 8.0
4	Phenol Red	6.9 – 8.9

A 1 and 2 **B** 2 and 3 **C** 3 and 4 **D** 1 only

17 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table.

The results of some experiments carried out on respective chlorides and oxides of these elements are shown in the table below.

Element	Addition of H_2O(l) to the oxides	Colour of universal indicator upon addition of H_2O(l) to chlorides	Addition of HC*l* to the oxides
X	no reaction	orange	forms chloride salt
Y	forms hydroxide	green	forms chloride salt
Z	no reaction	red	no reaction

Which of the following is correct?

A **X** is A*l* and **Y** is Na.

B **X** is Si and **Y** is Mg

C **Y** is A*l* and **Z** is P.

D **Y** is Na and **Z** is A*l*.

18 $CaCO_3$ decomposes at 825°C to produce CO_2 and the metal oxide.

$BaSO_4$ decomposes at 1580 °C to produce SO_2 and the metal oxide.

Which one of the following statements correctly explains the greater thermal stability of $BaSO_4$?

1 The CO_2 molecule is smaller than SO_2.

2 The CO_3^{2-} ions are more easily polarised than SO_4^{2-}.

3 The charge density of Ca^{2+} is greater than that of Ba^{2+}.

4 The lattice energy of $CaCO_3$ is more exothermic than $CaSO_4$.

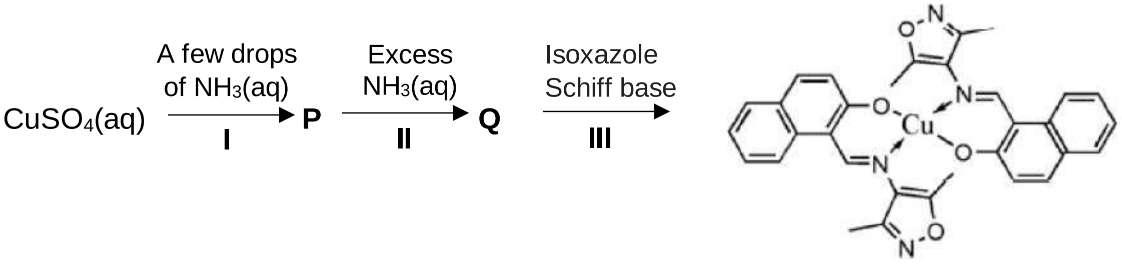
A 2 only

B 3 only

C 1 and 3 are correct.

D 2 and 4 are correct.

19 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **P** and **Q** are copper-containing species.



Copper complex with Isoxazole Schiff base

Which one of the following statements is **incorrect**?

A The copper complex with isoxazole schiff base has a coordination number of 4.

B The copper centre in the complex with isoxazole schiff base has an oxidation state of +2.

C **Q** is a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]SO_4$.

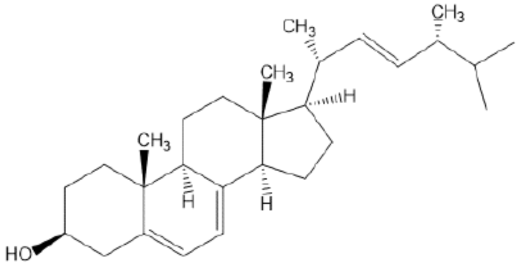
D **Q** undergoes reduction in reaction **III**.

20 An alkane **X** with the molecular formula C_4H_{10} reacts with chlorine gas in the presence of light to form two monochlorinated alkanes **Y** and **Z** in the molar ratio of 9:1.

What are the structures of **X** and **Z**?

	X	**Z**
A	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2Cl$
B	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CHClCH_3$
C	$CH_3CH(CH_3)CH_3$	$CH_3CCl(CH_3)CH_3$
D	$CH_3CH(CH_3)CH_3$	$CH_3CH(CH_3)CH_2Cl$

21 Ergosterol is a compound present in ergot and many other fungi. A steroid alcohol, it is converted to vitamin D_2 when irradiated with ultraviolet light.



Ergosterol

How many possible stereoisomers exist for Ergosterol?

A 2^8 **B** 2^9 **C** 2^{10} **D** 2^{11}

22 A mixture of propyne and propadiene is produced as side products during the cracking of propane. Propyne exists in equilibrium with propadiene.

$$\underset{\text{Propyne}}{H\text{–}C\equiv C\text{–}CH_3} \rightleftharpoons \underset{\text{Propadiene}}{H_2C=C=CH_2}$$

Which of the following statements is **incorrect**?

A Propyne contains a σ bond formed by 1s-2sp overlap.

B Propadiene contains a π bond formed by 2p-2p overlap.

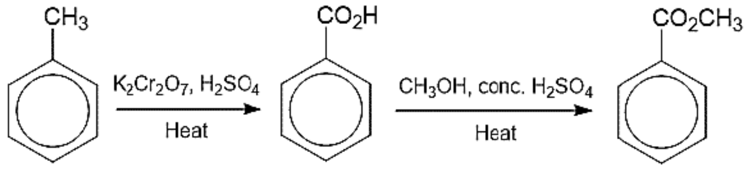
C Both propyne and propadiene contain sp hydridised carbons.

D Propyne has a longer C-C single bond compared to propane.

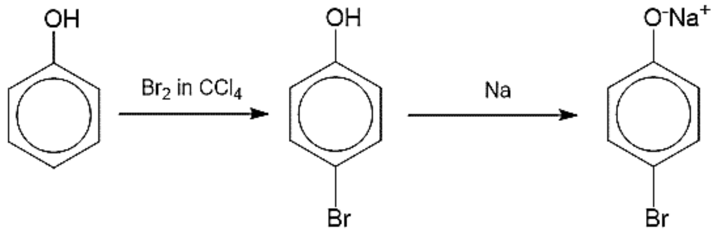
23 The reaction conditions for four different transformations are given below.

Which transformation will give the desired product?

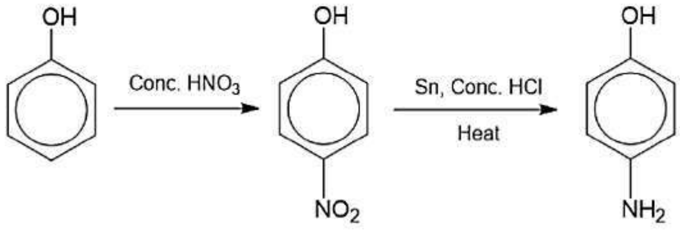
A



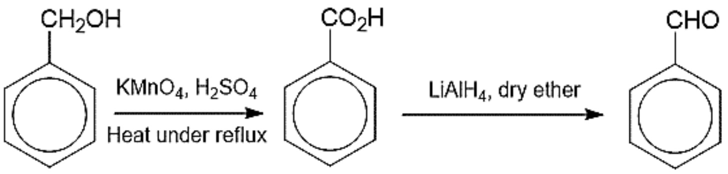
B



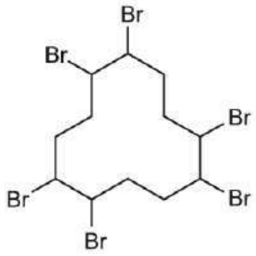
C



D



24 The primary application of hexabromocyclododecane (HBCD) is in polystyrene foam used as thermal insulation in the building industry. Usage of HBCD is under concern due to its toxicity. As HBCD has a number of possible stereoisomers, the substance poses a difficult problem for manufacture and regulation.



HBCD

Which statements about HBCD are correct?

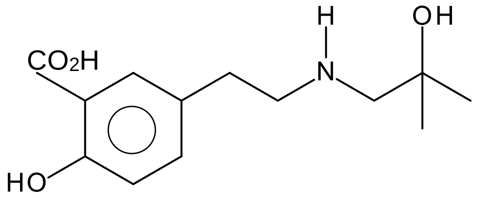
1 The stereoisomers of HBCD have similar chemical and biological properties.

2 The empirical formula of HBCD is C_2H_3Br.

3 The molecule is planar.

A 2 only **B** 3 only **C** 2 and 3 only **D** 1, 2 and 3

25 Compound **G** has the following structure.



Which of the statement is correct about the following reactions with 1 mole of compound **G**?

	Reagent	Result
A	excess sodium metal	3 moles of H_2 produced
B	hot acidified potassium dichromate(VI)	green solution was obtained
C	aqueous sodium hydroxide	anion in the product has a charge of 2-.
D	excess propanoyl chloride	2 moles of HC*l* produced

26 *Use of the Data Booklet is relevant to this question.*

Reduction of **Y** with lithium aluminum hydride produces **Z** with a relative molecular mass 12 less than **Y**, i.e. M_r(**Z**) = M_r(**Y**) - 12.

Which of the following could be compound **Y**?

1 $CH_2{=}CHCO_2H$

2 $CH_3CH_2COCO_2H$

3 $CH_3CH_2CONH_2$

A 1 only **B** 2 only **C** 1 and 2 **D** 1, 2 and 3

27 Which of the following will **not** yield a final organic product containing deuterium? (D = ^2H)

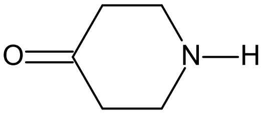
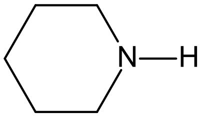
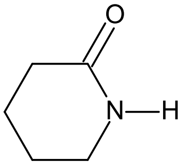
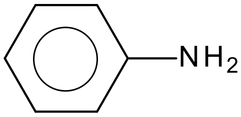
A $CH_3CH_2CH_2CHO \xrightarrow[\text{amount of NaCN}]{\text{DCN, trace}}$

B $CH_3CH_2CH_2COCl \xrightarrow{D_2O}$

C $CH_3CH_2CH_2CON(CH_3)_2 \xrightarrow[\text{heat}]{DCl,\ D_2O}$

D $CH_3CH_2CH_2CN \xrightarrow[\text{heat}]{\text{NaOD, } D_2O}$

28 Consider the following four compounds:

1	2	3	4
			

Which of the following shows the compounds arranged in order of increasing pK_b value?

A 3, 4, 1, 2

B 2, 1, 4, 3

C 2, 1, 3, 4

D 1, 2, 4, 3

29 A peptide contains seven amino acid residues. When it is partially hydrolysed, the following dipeptide and tripeptide fragments are produced.

gly-ser, ala-met, gly-ala-gly, ser-lys, met-gly-ala

What could be the structure of this peptide?

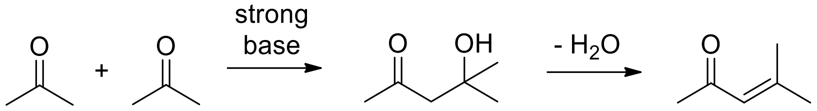
A ala-met-gly-ala-gly-ser-lys

B gly-ser-lys-ala-met-gly-ala

C gly-ala-gly-ser-lys-ala-met

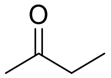
D met-gly-ala-gly-ser-lys-ala

30 The aldol condensation reaction is commonly used in synthetic organic chemistry to obtain a carbonyl compound. In the first step, a carbonyl compound reacts with a strong base at the α carbon to form a nucleophile.

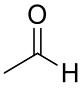


unsaturated carbonyl compound

Which of the following is **not** a possible product when butanone and ethanal reacts with a strong base?

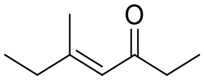


butanone

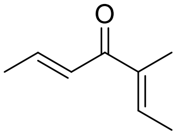


ethanal

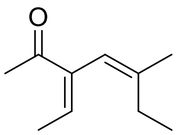
A



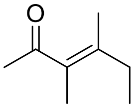
B



C



D



PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME	

CIVICS GROUP			/		

CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY **9729/02**

Paper 2 Structured Questions **28 August 2019**

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	/7
2	/10
3	/10
4	/14
5	/20
6	/14
Total	/ 75

This document consists of **20** printed pages

1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy (kJ mol^{-1})**	**Second Ionisation energy (kJ mol^{-1})**	**Third Ionisation energy (kJ mol^{-1})**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]

(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

[Turn over

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution. [1]

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used. [3]

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H < 0$$

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

[Total: 10]

3 **(a)** Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle. [3]

Shape : ____________________

Bond angle : ________________

(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer. [1]

(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities.

Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I) (II)

(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

Type of bond : ______________________

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

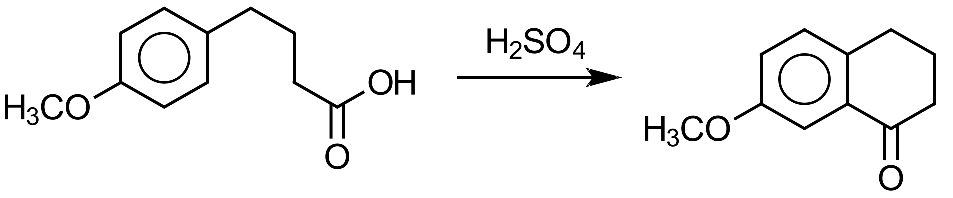
[1]

(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.
Deduce whether Al_2Cl_6 can also function in the same manner.

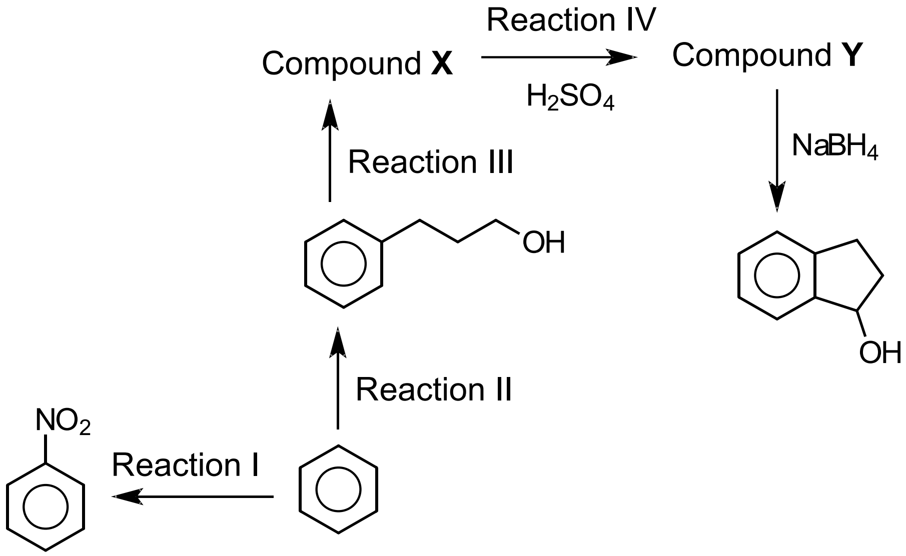
[1]

(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.



The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

Reaction **I**: ____

Reaction **II**: ____

Reaction **III**: ____

Compound **X**

Compound **Y**

[Total: 14]

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

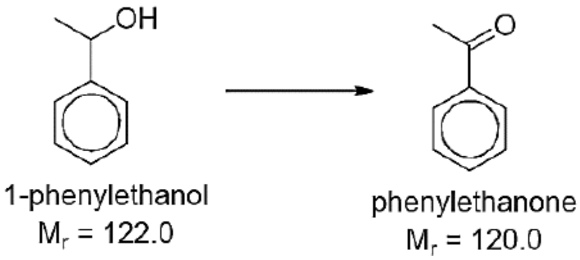
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction or via a catalytic reaction.



Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	*x*

(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone.

[2]

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} \text{E} \times \text{Q}$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

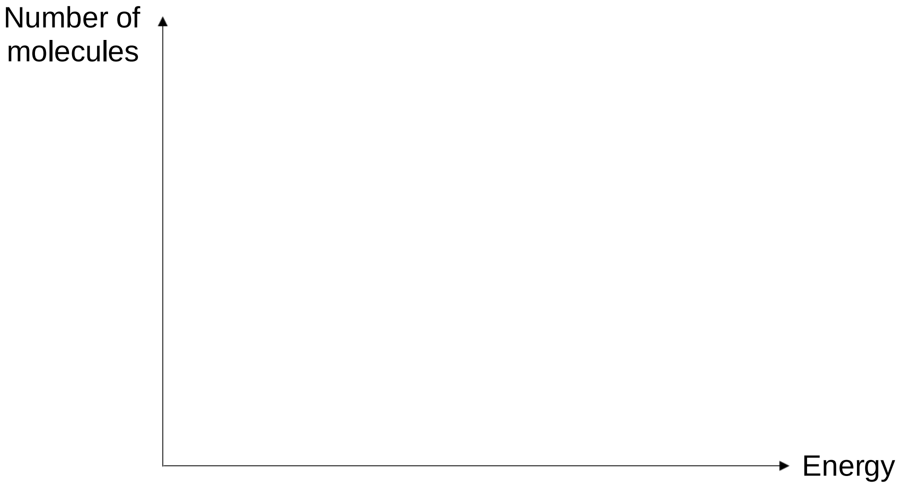
[2]

(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

(ii) Sketch a suitable Boltzmann distribution curve below and hence explain the effect of ruthenium on the rate constant of the reaction.

[3]



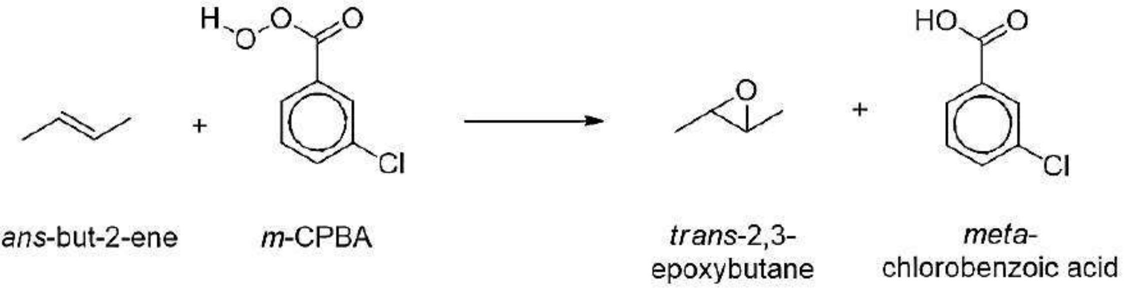
(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

[1]

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an "X" mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the "X" to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for "X" to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

[Turn over

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly.

[2]

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

(iv) State the value of y in experiment 4.

[1]

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data was collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 ^oC

The experiment was only 20% efficient.

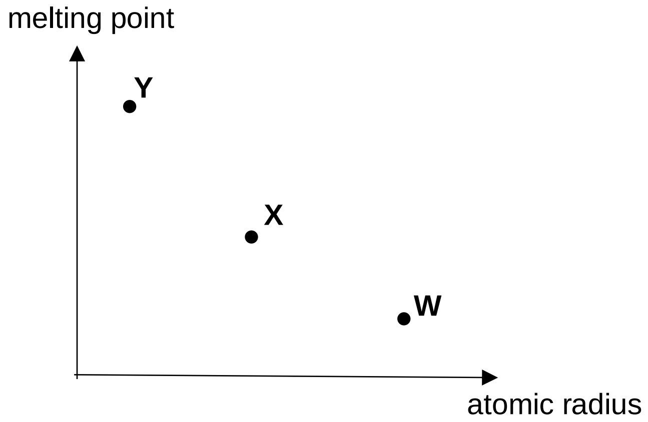
(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

(ii) Suggest one modification to the set-up so that the experiment can be made more efficient. [1]

[Total: 20]

6 (a) **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

(i) Suggest the identities of **Y** and **W**. [1]

(ii) Explain the above observations and write equations for all the reactions that has occurred. [3]

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 Carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained.

[3]

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

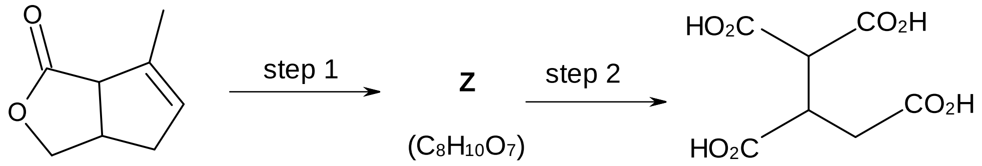
(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]

(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

Step 1: ____

Step 2: ____

Compound **Z**

(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

[Total: 14]

TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CHEMISTRY 9729/03

Paper 3 Free Response 16 September 2019

2 hours

Candidates answer on separate booklet.

Additional Materials: 12-Page Answer Booklet
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 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.

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.

This document consists of **14** printed pages and **2** blank pages.

Section A

Answer **all** the questions from this section.

1 The term *chelates*, originates from the Greek word *chele* for “claw”. It refers to compounds containing ligands bonded to a central metal atom or ion at two or more points.

Ligand exchange occurs when ammonia and ethylenediamine (en), $H_2NCH_2CH_2NH_2$, are added separately to copper sulfate solution.

(a) **(i)** Explain all the changes observed when aqueous ammonia is added dropwise to $Cu^{2+}(aq)$ till in excess. Suggest the formulae of all relevant copper compounds formed and write equations for all reactions. [4]

(ii) Suggest why ethylenediamine can function as a *chelating ligand*. [1]

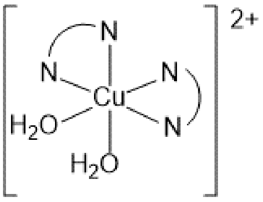
(iii) When ethylenediamine is added to $Cu^{2+}(aq)$, the following occurs.

$$[Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

Predict whether ethylenediamine or ammonia gives a more positive entropy change when added to $Cu^{2+}(aq)$. [2]

(iv) Suggest the coordination number and shape of $[Cu(en)_2(H_2O)_2]^{2+}$. [1]

(v) The complex ion $[Cu(en)_2(H_2O)_2]^{2+}$ can exist as three stereoisomers, **A**, **B** and **C**. Isomers **A** and **B** rotate plane-polarised light but **C** does not. The structure of **A** is represented below.



Isomer **A**

where  represents ethylenediamine (en)

Draw the structure of **C**. [1]

(b) Photochromic glass used for sunglasses contains Ag*Cl* crystals which are added while the glass is in molten state. The glass darkens when exposed to bright light and the following reaction is involved.

$$Ag^{+} + Cl^{-} \rightleftharpoons Ag + Cl$$

(i) Suggest why the glass darkens when exposed to bright light. [1]

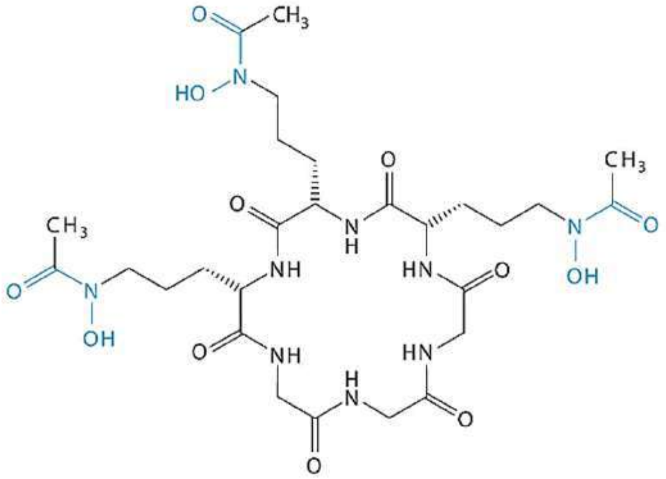
The glass darkens significantly within about a minute of exposure to bright light but takes a longer time to clear when there is less light. Small amount of Cu*Cl* crystals are often added to the glass to speed up the reverse process. No elemental copper is involved in the process.

$$Ag + Cl \rightarrow Ag^{+} + Cl^{-}$$

(ii) Explain why the copper(I) ions can be described as a *homogeneous catalyst*. [2]

(iii) State the property, typical of transition metals, which allows copper(I) ions to behave as a homogenous catalyst in the reverse reaction. Include relevant chemical equations to support your answer. [3]

(c) Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Ferrichrome is a siderophore produced by fungi.



Ferrichrome

(i) Ferrichrome binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

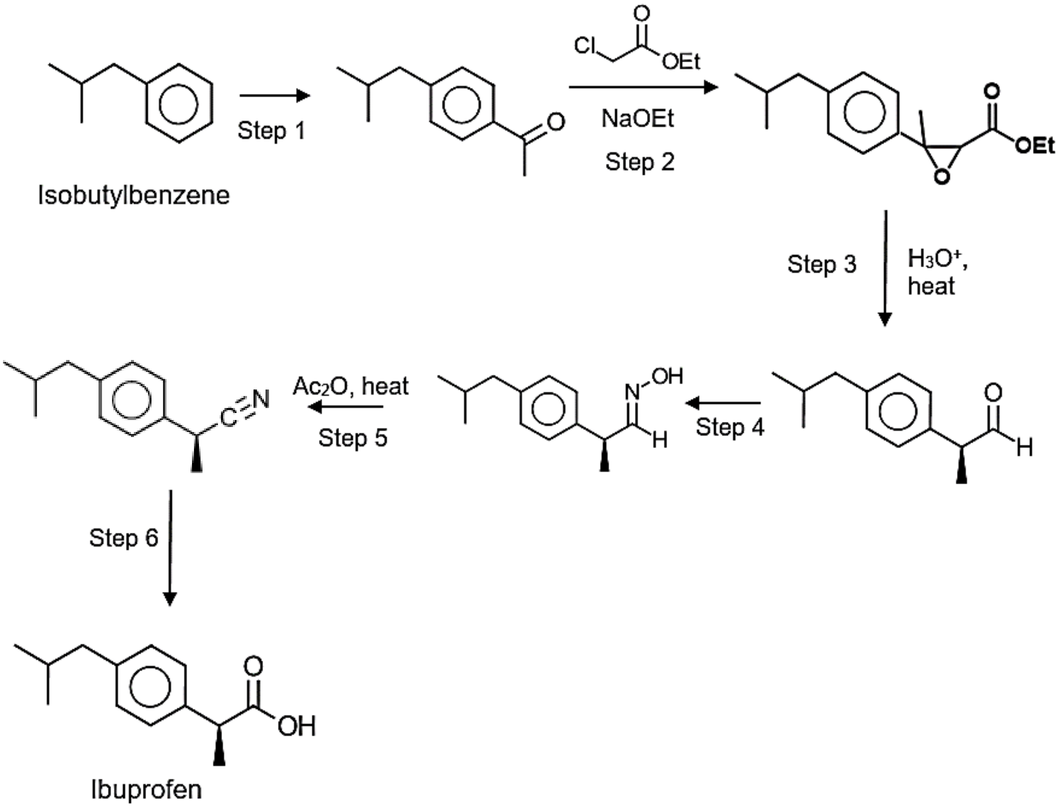
Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in ferrichrome. [2]

(ii) Draw the structures of the products formed when ferrichrome is heated with aqueous sodium hydroxide. [3]

[Total: 20]

2 Ibuprofen is a nonsteroidal anti-inflammatory drug. It works by reducing hormones that cause inflammation and pain in the body. Ibuprofen is used to reduce fever and treat pain or inflammation.

The conventional synthesis of ibuprofen from isobutylbenzene is shown below. Step 4 of the synthesis resembles the reaction between a carbonyl compound and Brady's reagent.

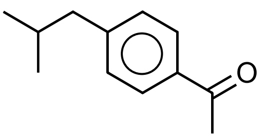


(a) Name the types of reaction that are occurring during steps 4 and 5. [2]

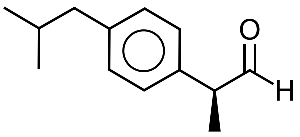
(b) Suggest the reagents and conditions for steps 1, 4 and 6. [3]

(c) Draw the structures of the stereoisomers of the product formed from step 4 and state the type of stereoisomerism exhibited. [2]

(d) Describe a simple chemical test to distinguish between the two compounds, **X** and **Y** obtained from synthesis above. [2]



Compound **X**



Compound **Y**

(e) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

(i) Potassium chloride and concentrated sulfuric acid reacts in an equimolar ratio to produce white fumes of hydrogen chloride.

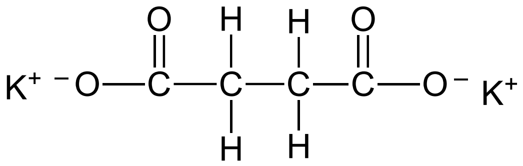
Write an equation for the reaction of potassium chloride with concentrated sulfuric acid. [1]

(ii) Potassium iodide reacts with concentrated sulfuric acid in a similar manner. However, the white fumes of hydrogen iodide would further react with concentrated sulfuric acid to produce violet fumes and hydrogen sulfide gas.

Suggest an explanation for the difference in reactions, and write equations for the above observations. [2]

(f) When aqueous potassium salts of a dicarboxylic acid are electrolysed using inert platinum electrodes, alkenes are formed at the anode.

(i) The electrolysis of aqueous potassium succinate gives ethene at the anode.



$K^+\ {}^-O-C(=O)-CH_2-CH_2-C(=O)-O^-\ K^+$

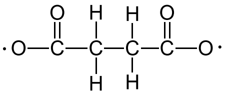
Potassium Succinate

Write an ion-electron half equation for the oxidation of succinate at the anode. [1]

(ii) Write an equation for the reaction at the cathode and for the overall reaction. [2]

(iii) The mechanism of the reaction at the anode involves three steps:

Step 1: There is an initial loss of 2 electrons on succinate ion to form



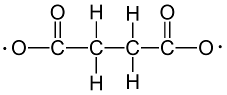
$\cdot O-C(=O)-CH_2-CH_2-C(=O)-O\cdot$

Step 2: This is followed by decarboxylation which involves the homolytic breaking of two C–C bonds, giving a radical intermediate $\bullet CH_2CH_2\bullet$

Step 3: The third step involves forming a covalent bond, producing ethene as the product.

Use the information given above to draw the mechanism for Steps 2 and 3.

You are advised to use structural formulae for all species, such as

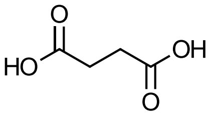
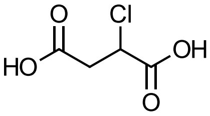


$\cdot O-C(=O)-CH_2-CH_2-C(=O)-O\cdot$

, so that it is clear which bonds are broken and which are formed.

Represent with a half arrow ($\curvearrowright$) for movement of a single unpaired electron and indicate any unpaired electrons by a dot (•). [2]

(g) The strength of a carboxylic acid depends on its structure. An example of this is the comparison of succinic acid and its derivatives.

Acid	pK_{a1}
	4.21
	-

Explain if pK_a of chlorosuccinic acid is lower or higher than the pK_a of succinic acid. [1]

[Total: 18]

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3 On 28 November 2018, an explosion erupted near the Hebei Shenghua Chemical Industrial plant, killing at least 23 people and injuring many more. It was reported that the explosion originated from a truck transporting ethyne gas, C_2H_2, which then set off a chain reaction that engulfed at least 50 other vehicles.

When mixed appropriately with air, C_2H_2 explodes upon ignition as follows.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(g)$$

This explosion may have generated an estimated 20.8 million kilojoules of energy.

(a) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within an ethyne molecule. [3]

(b) **(i)** Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne. [2]

(ii) Using your answer in **(b)(i)**, calculate the volume of ethyne gas transported by the truck at 28°C and 1 bar. [2]

(c) One of the ways that ethyne gas can be produced is via the reaction of calcium carbide, CaC_2, with water, producing solid calcium hydroxide as a by-product.

(i) Using the following information and relevant data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of solid calcium hydroxide. [3]

$$Ca^{2+}(g) + 2OH^{-}(g) \longrightarrow Ca(OH)_2\,(s)$$

standard enthalpy change of atomisation of Ca (s) = + 178 kJ mol^{-1}

standard enthalpy change of formation of OH^{-} (g) = − 230 kJ mol^{-1}

standard enthalpy change of formation of $Ca(OH)_2$ (s) = − 985 kJ mol^{-1}

(ii) Suggest, with reasoning, how the magnitude of the lattice energy of $Ca(OH)_2$ compares with that of calcium carbide, CaC_2, given the following data. [2]

Ion	Radius (pm)
OH^{-}	133
C_2^{2-}	118

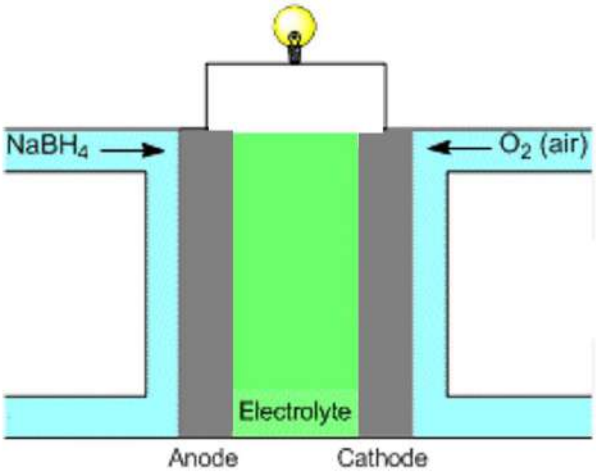
(iii) The value of $\Delta G^{\ominus}$ for the reaction of calcium carbide with water is -148 kJ mol^{-1}.

$$CaC_2\,(s) + 2H_2O\,(l) \longrightarrow Ca(OH)_2\,(s) + C_2H_2\,(g) \qquad \Delta H = -128 \text{ kJ mol}^{-1}$$

Calculate $\Delta S^{\ominus}$ in J mol^{-1} K^{-1} to one decimal place for the reaction. Explain the significance of its sign with reference to the equation. [2]

(d) Similar to calcium carbide, sodium borohydride, $NaBH_4$, can be used in fuel cells.

Direct borohydride fuel cells (DBFCs), are fuel cells which are directly fed by $NaBH_4$ as the fuel and oxygen as the oxidant. The electrolyte used is potassium hydroxide. Sodium metaborate, $NaBO_2$, and water are formed as the only products during the discharging process.



(i) Deduce the ion-electron half–equations for the anode and cathode and hence write the overall cell reaction during discharging. [2]

(ii) A typical DBFC fuel cell generates about 1.64 V. Using the *Data Booklet*, calculate the E^θ involving the $NaBO_2/NaBH_4$ half-cell. [1]

(iii) Use the half–equations you have written in **(d)(i)** to calculate the value of $\Delta G^\ominus$ and comment on the significance of $\Delta G^\ominus$. [1]

(iv) Explain qualitatively what happens to the cell potential, E_{cell} when a small amount of propanal contaminant is accidently added to the anode half-cell.

The contaminant does not take part in the cell reaction. [2]

(v) In a particular DBFC, a current of 1.35×10^{-2} A cm^{-3} was passed through the circuit for 95 minutes.

Calculate the mass of $NaBO_2$ that was produced per 25 cm^3 of solution. [2]

[Total: 22]

Section B

Answer **one** question from this section.

4 Chlorine-containing compounds have many useful applications. One such example is the use of chloric(I) acid, HC*l*O, to disinfect water in swimming pools.

HC*l*O dissociates in water as shown below.

$$\mathrm{HC}l\mathrm{O} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{C}l\mathrm{O^-}$$

(a) **(i)** Write an expression for K_a of HC*l*O. [1]

(ii) A disinfectant solution was prepared by dissolving 10 g of HC*l*O and x g of NaC*l*O in 100 cm^3 of water.

For effective disinfection, a pH of 7.35 was needed to reach the optimal $[\mathrm{C}l\mathrm{O^-}]:[\mathrm{HC}l\mathrm{O}]$ ratio.

Given that the pK_a of HC*l*O is 7.55, determine the optimal $[\mathrm{C}l\mathrm{O^-}]:[\mathrm{HC}l\mathrm{O}]$ ratio and hence the mass of NaC*l*O, x. [2]

(iii) A worker accidentally poured some alkaline solution into the disinfectant solution formed in **(a)(ii)** but found that the pH was still about 7.35.

Write an equation to explain this. [1]

(b) Hydrogen chloride is another chlorine-containing compound.

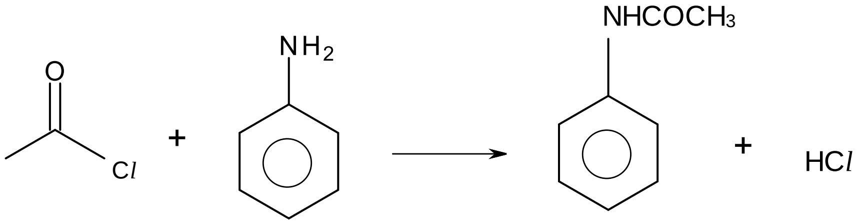
Alkyl chlorides can be synthesised from alcohols using hydrogen chloride. However, acyl chlorides **cannot** be prepared from carboxylic acids in the same way. One key factor is due to the stronger C-O bond present in carboxylic acids.

$$\mathrm{ROH} \xrightarrow{\mathrm{HC}l} \mathrm{RC}l$$

$$\mathrm{RCO_2H} \ \xcancel{\xrightarrow{\mathrm{HC}l}} \ \mathrm{RCOC}l$$

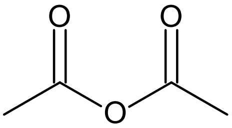
Suggest an explanation for the stronger C-O bond in carboxylic acids. [1]

(c) Acetanilide is an analgesic and can be formed from ethanoyl chloride and phenylamine.



acetanilide

Instead of ethanoyl chloride, ethanoic anhydride is more commonly used in the laboratory to form acetanilide in a similar manner.



ethanoic anhydride

(i) Suggest the other organic product that is produced together with acetanilide. [1]

The experimental procedure for the laboratory synthesis of acetanilide using ethanoic anhydride is given below.

1. Mix phenylamine and hydrochloric acid in a beaker.
2. Stir the mixture until a clear solution is obtained.
3. To the clear solution, add ethanoic anhydride and immediately add a solution of sodium ethanoate.
4. Stir the mixture vigorously.
5. Cool the solution in an ice water bath.
6. Filter the acetanilide formed. Wash with cold water and crystallise using a mixture of water and methanol.

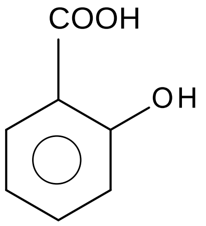
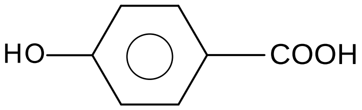
(ii) In step 1, HC*l* was added to increase the solubility of phenylamine in water. Explain. [1]

(iii) Sodium ethanoate is essential to ensure phenylamine is present in step 3 to react with ethanoic anhydride.

Suggest the role of sodium ethanoate. [1]

(iv) Suggest how you could check that the acetanilide obtained in step 6 is pure. [1]

(d) Aspirin is another analgesic and it can be synthesised from salicylic acid. The pK_a values of salicylic acid and its isomer are given below:

Acid	pK_{a1}	pK_{a2}
 Salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

(i) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

(ii) pK_{a2} is larger than pK_{a1} of 4-hydroxybenzoic acid. [1]

(e) When compound **A**, $C_{10}H_{11}NO$, is oxidised with acidified manganate(VII) ions, $[C_7H_8NO_2]^+$ and compound **B**, $C_3H_4O_3$, are formed. Compound **B** produces effervescence when Na_2CO_3 is added to it and gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Compound **A** reacts readily with 4 moles of Br_2(aq) to give compound **C**, $C_{10}H_9NO_2Br_4$.

Compound **A** also gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent and reacts with hot alkaline aqueous iodine to give compound **D**, $C_9H_8NO_2Na$.

Suggest the structures of compounds **A**, **B**, **C** and **D**. Explain the reactions that occur. [9]

[Total: 20]

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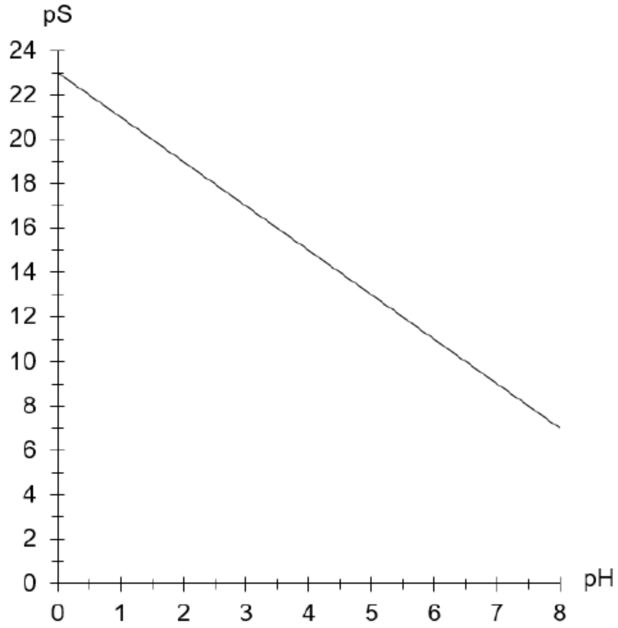
5 **(a)** Hydrogen sulfide gas, H_2S, is a reagent used in qualitative analysis. When H_2S is passed into a solution containing metal cations, metal sulfides are precipitated.

In aqueous medium, H_2S dissociates partially in a step-wise manner to give two equilibrium reactions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The relationship between the H^+ ion concentration and S^{2-} ion concentration, as a result of H_2S dissociation, is shown in the graph below, where $pS = -\log_{10}[S^{2-}]$.



Solution **X** contains 0.1 mol dm^{-3} $CuSO_4$ and 0.05 mol dm^{-3} $MnSO_4$. Hydrogen sulfide gas is bubbled into **X** until saturation and the pH is maintained at 2.0.

The value of the solubility product of CuS and MnS are 1.0×10^{-44} and 1.4×10^{-15}, respectively.

(i) With reference to CuS, define the term *solubility product*. [1]

(ii) Calculate the minimum concentration of sulfide ions needed to precipitate CuS. [1]

(iii) The minimum concentration of sulfide ions needed to precipitate MnS is 2.80×10^{-14} mol dm^{-3}.

Using the graph above and your answer in **(a)(ii)**, explain whether it is possible to separate copper and manganese ions in **X** at pH = 2. [2]

(iv) Determine the maximum pH for solution **X** before separation of copper and manganese ions is no longer possible. [1]

(b) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. The higher the value of K_{stab}, the more likely the complex will be formed.

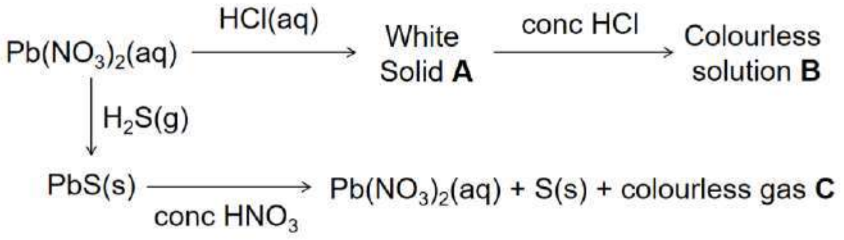
The stability constants for 3 reactions are given below.

Reaction	Colour of complex formed	Value of $\log_{10}(K_{stab})$
$Fe^{3+}(aq) + 6CN^{-}(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$	Yellow	31.0
$Fe^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{-}(aq)$	Brown	25.1
$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$	Red	2.1

Describe the colour change(s) of the solution when excess NaSCN is added to $[Fe(EDTA)]^{-}$, followed by an excess of KCN(aq).

Explain the observation, with reference to the table above. [2]

(c) A solution of $Pb(NO_3)_2$ is subjected to the following reactions.



(i) Suggest the identity of white solid **A** and complex anion present in colourless solution **B**. [2]

(ii) Colourless gas **C** is obtained from the reaction of solid PbS and concentrated HNO_3, which is readily oxidised in air to form a brown acidic gas.

Suggest the identity of **C**. [1]

(d) Thiols are sulfur-containing compounds that can be prepared from alkyl halides and the hydrosulfide nucleophile, ^{-}SH.

Ethanethiol is prepared from chloroethane using NaSH as shown below.

$$CH_3CH_2Cl \xrightarrow{NaSH} CH_3CH_2SH$$

Ethanethiol

(i) Suggest a synthesis of propanethiol starting from propylethanoate.

You should state the reagents and conditions for each step, and show clearly the structure of any intermediate compounds. [3]

CH_3CH_2SH can react with a base, NaH, to give $CH_3CH_2S^-$.

$$CH_3CH_2SH + NaH \rightarrow CH_3CH_2S^-Na^+ + H_2 \quad \text{----- Reaction 1}$$

$CH_3CH_2S^-$ further reacts with chloroethane, to yield diethyl sulfide

$$CH_3CH_2S^-Na^+ + CH_3CH_2Cl \rightarrow \underset{\text{Diethyl sulfide}}{CH_3CH_2SCH_2CH_3} + NaCl \quad \text{----- Reaction 2}$$

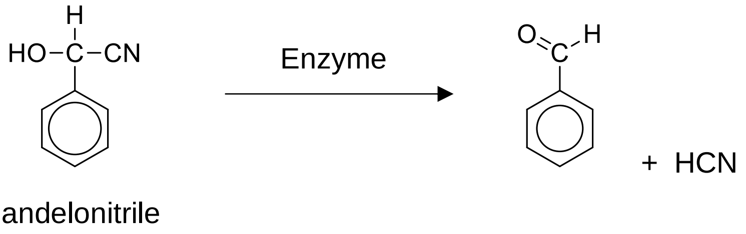
(ii) Suggest why $CH_3CH_2S^-$, is a better nucleophile than $CH_3CH_2O^-$. [1]

(iii) Diethyl sulfide is a good nucleophile.

In Reaction 2, a side product, $C_6H_{15}SCl$, is formed when chloroethane is used in excess. $C_6H_{15}SCl$ gives a white precipitate with aqueous silver nitrate.

Suggest the structural formula of the side product $C_6H_{15}SCl$. [1]

(e) The millipede *Apheeloria corrugate* protects itself by secreting the cyanohydrin mandelonitrile and an enzyme that decompose mandelonitrile into benzaldehyde and HCN.



(i) State the type of reaction for the formation of Mandelonitrile from benzaldehyde. [1]

(ii) Suggest a chemical test that will give a positive test for Mandelonitrile but not for benzaldehyde. [2]

(iii) A student made the following statement, “benzaldehyde can be directly synthesized from phenylmethanol, $C_6H_5CH_2OH$, but not from benzoic acid.”

Based on your knowledge of the reagents and conditions for each reaction, deduce if the statement is true. [2]

[Total: 20]

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

1 **Determination of the concentration of a solution of hydrogen peroxide**

Hydrogen peroxide, H_2O_2, can be oxidised to give oxygen, O_2. This reaction happens rapidly in the presence of acidified potassium manganate(VII), $KMnO_4$.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

To determine the concentration of a solution of hydrogen peroxide, you will first dilute the solution and then carry out a titration using acidified potassium manganate(VII), $KMnO_4$.

FA 1 is aqueous hydrogen peroxide.
FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.

Keep **FA 1** for use in **Question 3**

(a) Method

Dilution

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 volumetric flask.
- Add distilled water to make 250 cm^3 of solution and shake the flask thoroughly.
- Label this diluted solution of hydrogen peroxide as **FA 4**.

Titration

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 4** into a conical flask.
- Use the measuring cylinder to add 25 cm^3 of **FA 3** to the conical flask.
- Titrate **FA 4** against **FA 2** and record your readings in the space below.
- Carry out as many accurate titrations as you think necessary.

Results

[5]

(b) From your titrations, obtain a suitable volume of **FA 2** 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 2** for titration
[1]

(c) Calculations

Show your working and give appropriate significant figures in the final answer for **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 2** calculated in **(b).**

amount of $KMnO_4$ = _________________ [1]

(ii) Calculate the amount of hydrogen peroxide present in 25.0 cm^3 of **FA 4**.

amount of H_2O_2 in 25.0 cm^3 of **FA4** = _________________ [1]

(iii) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 4.**

concentration of H_2O_2 in **FA 4** = _________________ [1]

DO NOT WRITE IN THIS MARGIN

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[Turn over

(iv) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 1.**

concentration of H_2O_2 in **FA 1** = ________________ [1]

(d) Another experiment was conducted to determine the concentration of hydrogen peroxide. Different volumes of hydrogen peroxide were added to identical 25.0 cm^3 samples of 0.0400 mol dm^{-3} aqueous iron(II) solution. Iron(II) is oxidised by hydrogen peroxide as shown by the following equation.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

The remaining iron(II) ions in each of the resulting mixtures were then titrated against potassium manganate(VII) and the results were shown in the table below:

Volume of H_2O_2 added / cm^3	**Volume of $KMnO_4$ / cm^3**
2.00	11.60
12.00	5.20
16.00	2.60
25.00	3.40
30.00	6.70
35.00	10.00

(i) Plot, on the grid on page 5, the values for the volume of potassium manganate(VII) (*y-axis*) against the volume of hydrogen peroxide added (*x-axis*).

Draw two straight lines of best fit, taking into account all of your plotted points.

Your graph should enable you to determine the values for **(d)(ii)**.

[3]

(ii) Hence obtain values for

- the volume of potassium manganate(VII) required, $V_{max}(KMnO_4)$, to react completely with 25.0 cm^3 of iron(II) solution if no hydrogen peroxide is added.
- the volume of hydrogen peroxide required, $V_{max}(H_2O_2)$, to react completely with 25.0 cm^3 of iron(II) solution if no potassium manganate(VII) is added.

[Turn over

$V_{max}(KMnO_4)$ = ____________________

$V_{max}(H_2O_2)$ = ____________________

[1]

[Turn over

(iii) Determine the concentration of hydrogen peroxide, in mol dm^{-3}, in this experiment.

Concentration of hydrogen peroxide = ________________

[4]
[Total: 18]

2 Determination of the enthalpy change of reaction, ΔH$_r$

You are to determine the enthalpy change of reaction, ΔH$_r$, for the following reactions:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_1$$

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

FA 5 is anhydrous sodium carbonate, Na_2CO_3

FA 6 is solid sodium hydrogen carbonate, $NaHCO_3$

You are also provided with 2.0 mol dm^{-3} HC*l*

(a) Reaction of FA 5, Na_2CO_3, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the weighing bottle containing **FA 5**, anhydrous sodium carbonate.
5. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA 5 all at once. The reaction is very vigourous.]

6. Stir and record the highest temperature obtained.
7. Reweigh the weighing bottle containing residual **FA 5**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m$_1$**, of **FA 5** added and the maximum temperature rise, **ΔT$_1$**.

[Turn over

Results

[2]

(b) **(i)** Calculate the temperature rise per gram of **FA 5**, Na_2CO_3, used in the experiment.

$\frac{\Delta T_1}{m_1}$ = ______________________

[2]

(ii) Calculate the enthalpy change, ΔH_1, for the reaction

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl\ (aq) + CO_2\ (g) + H_2O(l)$$

$$\Delta H_1 = -\left(22.79 \times \frac{\Delta T_1}{m_1}\right)\ \text{kJ mol}^{-1}$$

ΔH_1 = ______________________

[1]

(c) Reaction of FA 6, $NaHCO_3$, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support another styrofoam cup in the 250 cm^3 beaker provided.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the empty weighing bottle labelled **"FA 6"**.
5. Weigh approximately 7.0 – 8.0 g of **FA 6**, anhydrous sodium hydrogen carbonate into the empty weighing bottle labelled **"FA 6"**.
6. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA6 all at once. The reaction is very vigourous.]

7. Stir and record the lowest temperature obtained.
8. Reweigh the weighing bottle containing residual **FA 6**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, $\mathbf{m_2}$, of **FA 6** added and the maximum temperature fall, $\mathbf{\Delta T_2}$.

Results

[Turn over

(d) **(i)** Calculate the temperature fall per gram of **FA 6**, $NaHCO_3$, used in the experiment.

$\frac{\Delta T_2}{m_2}$ = ______________________ [2]

(ii) Calculate the enthalpy change, ΔH_2, for the reaction

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_2 = + (18.06 \times \frac{\Delta T_2}{m_2})\ \text{kJ mol}^{-1}$$

ΔH_2 = ______________________ [1]

(e) **(i)** The smallest graduation in reading a –10 °C to +110 °C thermometer is 1.0 °C

Suggest the maximum error of a temperature change calculated with two temperature readings.

Maximum error = ______________________ [1]

(ii)

> The expected fall in temperature when 1.0 g of $NaHCO_3(s)$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is approximately 1.5°C

Determine the maximum percentage error in the calculated temperature change when 1.0 g of $NaHCO_3$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid.

Maximum percentage error = ______________________ [1]

[Turn over

(f) It is not possible to measure experimentally the enthalpy change, ΔH_3, for the following reaction as it does not take place in the laboratory.

$$Na_2CO_3(s) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(s)$$

It is possible, however, to calculate a "theoretical" value of ΔH_3 for this reaction from the results of the experiments you have carried out.

Using an energy cycle and your results from **(b)(ii)** and **(d)(ii),** calculate a value for ΔH_3.

ΔH_3 = ____________________

[2]

[Total: 12]

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.

Rinse and reuse test-tubes where possible.

[Turn over

(a) **FA 7, FA 8** and **FA 9** are aqueous solutions that each have an ion containing one of the metals from those listed in the Qualitative Analysis Notes.

FA 1 from Question 1 is to be used in some of these tests.

Carry out the following tests and record your observations.

	Test	*Observation*
(i)	To a 1 cm depth of **FA 7** in a test-tube, add a 1 cm depth aqueous sodium hydroxide.	
	Then, add several drops of **FA 1**.	
(ii)	To a 1 cm depth of **FA 8** in a test-tube, add a few drops of aqueous sodium hydroxide.	
	Then, add excess aqueous sodium hydroxide.	
(iii)	To a 1 cm depth of **FA 8** in a test-tube, add several drops of **FA 1.**	
	Then, add aqueous sodium hydroxide until in excess.	
(iv)	To a 1 cm depth of **FA 8** in a test-tube, add a 1 cm depth of dilute sulfuric acid, and then a few drops of **FA 9**.	

[Turn over

(v)	To a 1 cm depth of aqueous potassium iodide in a test-tube, add a few drops of **FA 9**.	
	Then, add a few drops of starch solution	

[5]

(b) Identify the cation present in **FA 7** and **FA 8**.

The cation present in **FA 7** is ______________________

The cation present in **FA 8** is ______________________

[2]

(c) Explain the chemistry involved in the effervescence observed in both **(a)(i)** and **(a)(iii).**

[1]

(d) A student added 1 cm^3 of **FA 9** to a test-tube containing **FA 8**. A strip of magnesium ribbon was then added to the mixture. Effervescence was observed.

Deduce the identity of the gas evolved and explain the chemistry involved in this reaction.

[3]

(e) **Figure 1** below shows the thermal decomposition of **FA 10**, which is a solid sample of the compound present in the aqueous solution of **FA 9**.

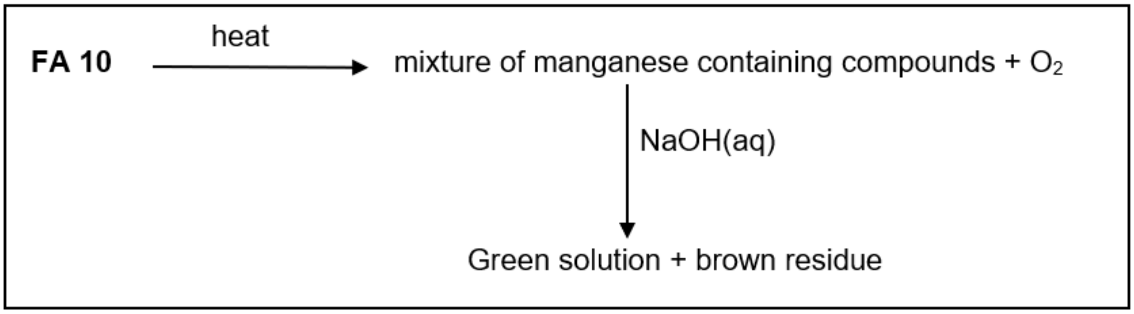


Figure 1

Consider the observations in **Figure 1**, suggest the identity of the manganese-containing species in the green solution and the residue.

[1]

(f) **FA 8** contains one of the anions Cl^-, Br^-, I^-, SO_4^{2-} or SO_3^{2-}.

Plan an experiment to determine the reagents you would use to identify which anion is present in **FA 8**.

Carry out your tests on **FA 8** to identify the anion present. Record your observations in the table below.

Test	**Observation**

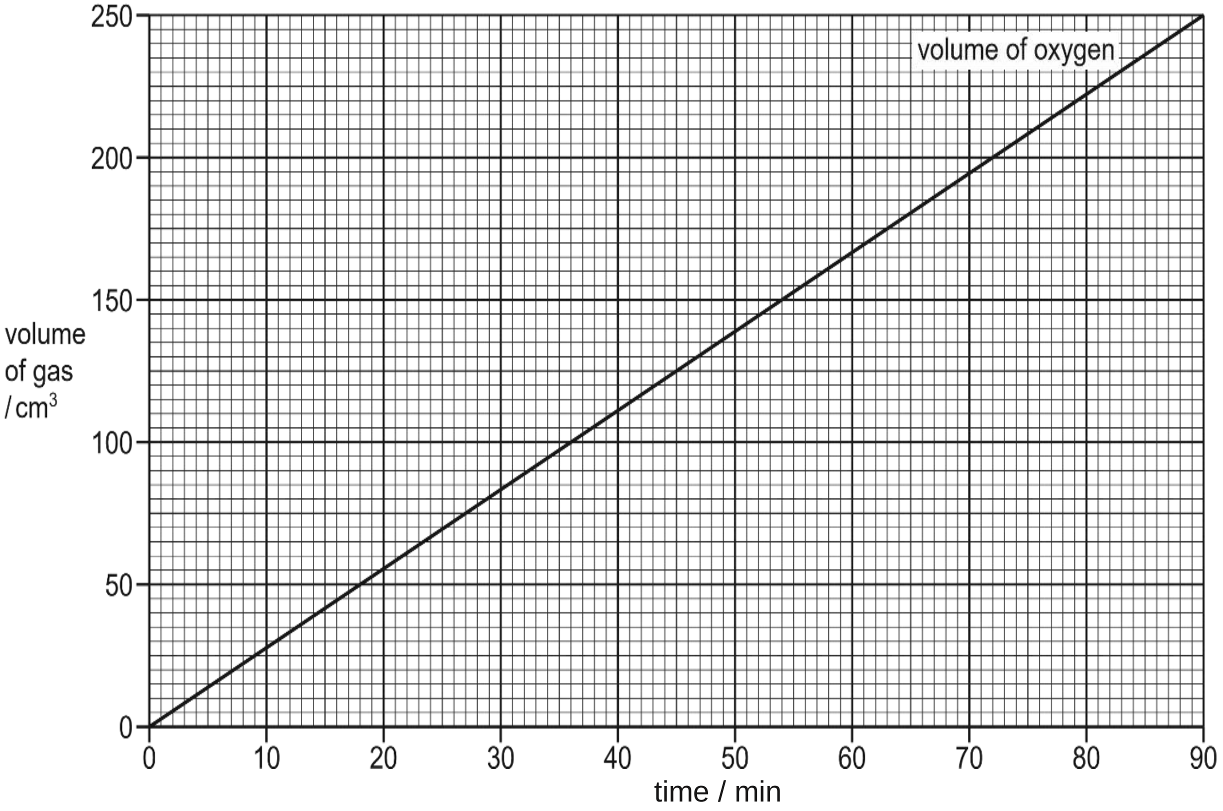
Suggest the identity of the anion present in **FA 8**.

[3]

[Total:15]

4 **(a)** This question is about the electrolysis of different compounds.

During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 minutes, the volume of oxygen gas collected was recorded and is shown in the graph below.



(i) **Table 1** below gives some standard electrode potential values

Electrode reaction	**E⊖ / V**
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Table 1

With reference to the values in the **Table 1**, write equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid.

Cathode: ______________________________

Anode: ______________________________

[2]

[Turn over

On the graph on page 14,

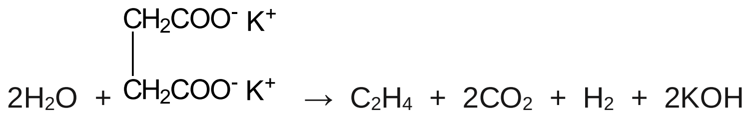
(ii) Draw a straight line to show the volume of hydrogen evolved in the same experiment. Label the line as "hydrogen".

[1]

(iii) Draw a straight line to show the volume of oxygen evolved if a current of 0.45 A was used instead of the 0.75 A used in the original experiment. Label the line as "oxygen".

[1]

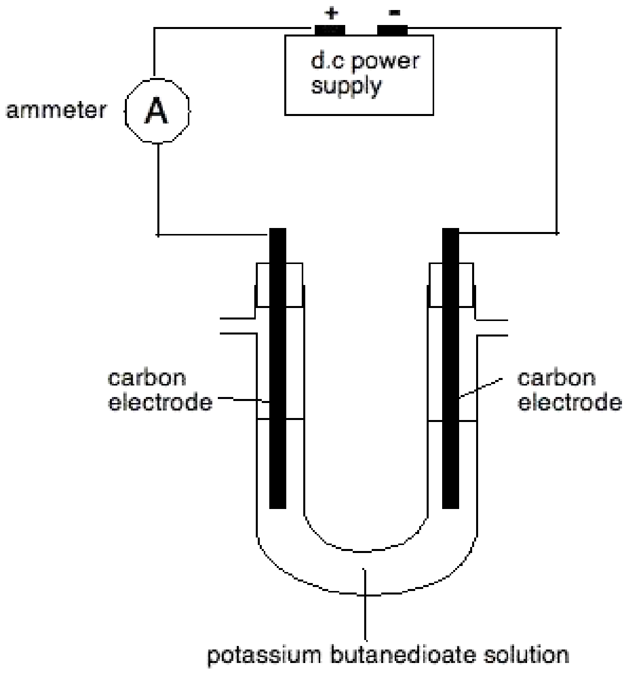
(b) During the electrolysis of potassium butanedioate, the following reaction occurs.



$$2H_2O + \begin{array}{l} CH_2COO^- K^+ \\ | \\ CH_2COO^- K^+ \end{array} \rightarrow C_2H_4 + 2CO_2 + H_2 + 2KOH$$

potassium
butanedioate

An experiment can be conducted to verify the stoichiometric ratio between hydrogen gas and ethene gas collected using the following set-up.



Hydrogen is produced at one electrode, ethene and carbon dioxide are produced at the other. The carbon dioxide can be separated from the ethene by absorbing it using a suitable reagent before the volume of ethene is measured.

(i) Complete the diagram on page 15 to show how:

- the hydrogen could be collected and its volume measured,
- the carbon dioxide could be removed,
- the volume of ethene could be measured.

Your diagram should include appropriate apparatus and the identity of the suitable reagent used to remove carbon dioxide.

[3]

(ii) Calculate the number of coulombs, **N**, that would be required to produce **V** cm^3 of hydrogen at room temperature and pressure.

[Faraday constant, F = 9.65×10^4 C mol^{-1}] [1]

(iii) Write an equation for the reaction that takes place for the removal of carbon dioxide.

[1]

(iv) Predict the organic product that would be obtained at the electrode when a solution of potassium *hexanedioate* is electrolysed.

[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

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[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 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) 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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2019 TJC JC2 H2 Chemistry Prelim MCQ Worked Solutions

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

Question 1 **Answer: C**

Particle	Neutron	Nucleon	Proton	Electron
U	16	33	17	17
V^-	18	35	17	18
S^{2-}	16	32	16	18
T^{2+}	17	34	17	15
Q^{3-}	16	31	15	18

Question 2 **Answer: C**

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
x 0.95x
$CH_4 + 3/2\ O_2 \longrightarrow CO + 2H_2O$
0.05x

If combustion is complete, x dm^3 CH_4 will require 2x dm^3 O_2.
Combustion of 1 mol CH_4 to form CO, requires 3/2 mol O_2 ie ½ mol O_2 less than complete combustion.
To obtain 0.05x mol CO will need 0.05x/2 mol less O_2.
Amt of O_2 needed for incomplete combustion = 2x – 0.05x/2

Or
Volume of methane burnt = y dm^3
5% of methane is burnt to give CO and the remaining 95% is burnt to give CO_2
Vol of methane burnt to give CO = 0.05y
Vol of methane burnt to give CO_2 = (1-0.05)y

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Volume used (1-0.05)y 2(1-0.05)y

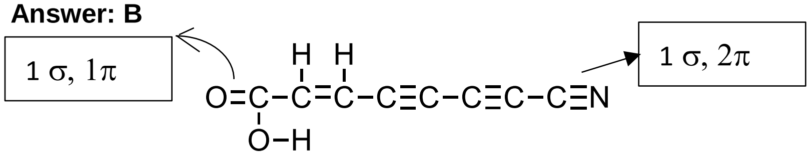
$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O$
Volume used 0.05y 3/2(0.05y)

Vol of O_2 used = 2(1-0.05)y + 3/2(0.05y)
= 2y – 2(0.05)y + 3/2(0.05y)
= 2y – ½ (0.05y)

Question 3 **Answer: D**

Na : $[Ne]3s^1$ (1 unpaired electron)
P^{3-} : [Ar] (0 unpaired electron)
V : $[Ar]3d^34s^2$ (3 unpaired electron)
Mn^{2+}: $[Ar]3d^5$ (5 unpaired electron)

Question 4 **Answer: B**



Question 5 **Answer: A**

ICl_2^- : 2BP + 3 LP, shape linear, Bond angle 180^0, non-polar
CO_2 : 2 BP, shape linear, Bond angle 180^0 , non-polar
BCl_3 : 3 BP shape trigonal planar, Bond angle 120^0 , non-polar
ClO_2^- : 2 BP + 2 LP, shape bent, Bond angle $<109.5^0$, polar
HCN : 2 BP, shape linear, Bond angle 180^0, polar
XeF_4 : 4 BP + 2 LP, shape square planar, Bond angle 90^0, non-polar

Question 6 **Answer: C**

I Both diamond and silicon have giant molecular structures. The atomic radius of C is smaller than Si. C-C bond length is shorter than Si-Si bond. Diamond has a higher mp than silicon as more energy is needed to break the stronger C-C bonds.

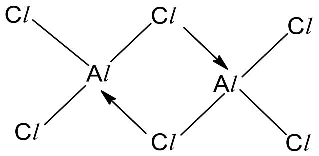
II H_2O is able to form more hydrogen bonds on average compared to NH_3 as it has 2 lone pair of electrons on O.

III $SiCl_4$ has a simple molecular structure and Al_2O_3 has a giant ionic structure. The id-id attractions between $SiCl_4$ molecules is weaker than the strong ionic bonds in Al_2O_3.

IV Both Br_2 and ICl have similar M_r. The id-id attractions between Br_2 molecules is weaker than the pd-pd attractions between ICl molecules.

Question 7 **Answer: C**

1 Structure of dimer Al_2Cl_6



Shape of $AlCl_3$ = Trigonal planar hence bond angle is 120°.

Shape of Al_2Cl_6 = Tetrahedral about each Al atom hence bond angle is not 120°.

2 Using ideal gas equation, pV = nRT
pV = (m/M) RT where M = molar mass
$(1.16 \times 10^5)(250 \times 10^{-6}) = (x / 214.9)(8.31)(500)$
X = 1.50 g

3 Size of electron cloud for : Al_2Cl_6 > $AlCl_3$
Extent of distortion of electron cloud for: Al_2Cl_6 > $AlCl_3$
Strength of intermolecular id-id : Al_2Cl_6 > $AlCl_3$
Deviation from ideality for: Al_2Cl_6 > $AlCl_3$

Question 8 **Answer: B**

$3C(s) + Cr_2O_3(s) \longrightarrow 2Cr(s) + 3CO(g) \quad \Delta H = +790 \text{ kJ mol}^{-1}$

$\Delta H_{rxn} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

$+790 = 3\,\Delta H_f(CO) - \Delta H_f(Cr_2O_3)$

$+790 = 3\,\Delta H_f(CO) - (-1120)$

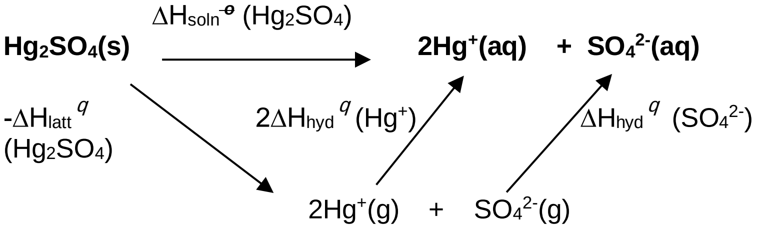
$\Delta H_f(CO) = (+790 - 1120) / 3 =$ **-110 kJ mol^{-1}**

By definition, $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H_f(CO) = -110 \text{ kJ mol}^{-1}$

Hence, $2C(s) + O_2(g) \longrightarrow 2CO(g) \qquad 2\,\Delta H_f(CO) = -220 \text{ kJ mol}^{-1}$

Question 9 **Answer: B**

Energy cycle for ΔH_{soln}^{q} Hg_2SO_4



By Hess' law:

$$\Delta H_{soln}^{q}(Hg_2SO_4) = -\Delta H_{latt}^{q}(Hg_2SO_4) + 2\Delta H_{hyd}^{q}(Hg^+) + \Delta H_{hyd}^{q}(SO_4^{2-})$$
$$= -(-2127) + 2(-625) + (-1160)$$
$$= \underline{\mathbf{-\,283\ kJ\ mol^{-1}}}$$

Since the calculated value of ΔH_{soln}^{q} (Hg_2SO_4) is a negative value at r.t.p., it means that:

1. **Correct.** Magnitude is 283 kJ mol^{-1}
2. **Correct.** $\Delta H_{latt}^{q} \propto \frac{q_+ q_-}{r_+ + r_-}$, since <u>Hg^+ has a bigger ionic radius as compared to Cd^+</u> (q^+, q^-, r^- same), ΔH_{latt}^{q} of Hg_2SO_4 is less exothermic than that of Cd_2SO_4.
3. **Incorrect.** <u>$\Delta G_{soln}^{\ominus}$ of Hg_2SO_4 is less negative than $\Delta G_{soln}^{\ominus}$ of Cd_2SO_4</u> since Hg_2SO_4 is less soluble than Cd_2SO_4.

Question 10 **Answer: A**

$E^{q}_{cell} = E^{q}_{red} - E^{q}_{oxi}$
$0.3\ V = E^{\ominus}_{Cu^{2+}/Cu} - E^{\ominus}_{X^{2+}/X}$
$0.5\ V = E^{\ominus}_{Cu^{2+}/Cu}{}^{q} - E^{\ominus}_{Y^{2+}/Y}$
$0.4\ V = E^{\ominus}_{Z^{2+}/Z} - E^{\ominus}_{Cu^{2+}/Cu}{}^{q}$

From the data in the terms of increasing positive value: $E^{\ominus}_{Z^{2+}/Z} > E^{\ominus}_{Cu^{2+}/Cu} > E^{\ominus}_{X^{2+}/X} > E^{\ominus}_{Y^{2+}/Y}$
Tendency to be reduced for : $\mathbf{Z^{2+}}$, Cu^{2+}, $\mathbf{X^{2+}}$, $\mathbf{Y^{2+}}$
Thus, the strongest to the weakest oxidising agents is $\mathbf{Z^{2+}}$, Cu^{2+}, $\mathbf{X^{2+}}$, $\mathbf{Y^{2+}}$

Question 11 **Answer: C**

$NO_3^- + 10H^+\ 8e \rightleftharpoons \mathbf{NH_4^+} + 3H_2O$ $E^{q} = 0.87\ V$ -- (1)
$NO_3^- + 2H^+ + e \rightleftharpoons \mathbf{NO_2} + H_2O$ $E^{q} = 0.81\ V$ --(2)

As [H^+] increases. By *Le Chatelier's Principle*, the <u>position of both equilibria shifts to the right to decrease [H^+], favouring reduction</u>

Oxidising ability of NO_3^- <u>increases</u> while <u>reducing abilities of NO_2 and NH_4^+ decreases</u>.

Since for eqm (2), <u>a lesser number of moles of H^+ is required for one mole of NO_3^- to be reduced, there is greater tendency for equilibrium (2) to shift to the right hence backward reaction is less favoured. Hence, NO_2 is a weaker reducing agent</u> where [H^+] = 10^{-5} mol dm^{-3} < standard condition of 1 mol dm^{-3}).

Question 12 **Answer: D**

Rate would be slower as concentration of nitric acid is lower. Amount of products would be lesser as nitric acid is the limiting agent and there are less amount of nitric acid used in the 2nd scenario (0.025 mol vs 0.030 mol)

Question 13 **Answer: A**

Total pressure increases at constant volume but *partial pressure* of individual product and reactant remains constant. So position of equilibrium will NOT shift at all.

Question 14 **Answer: D**

$[H^+] = \sqrt{K_a C}$
When the acid is diluted, the conc of acid drops, so $[H^+]$ will drop too → pH increases, following a logarithm function since pH = $-\lg[H^+]$.

However at infinitely dilute condition, $[H^+]_{overall} = [H^+]_{acid} + [H^+]_{water}$, where $[H^+]_{acid} << [H^+]_{water}$, so $[H^+]_{overall} \approx [H^+]_{water} = 10^{-7}$ mol dm^{-3} at 25 °C. So the pH at infinitely dilute condition will reach a constant value of 7.

Question 15 **Answer: D**

$Zn_3[Fe(CN)_6]_2 \rightleftharpoons 3Zn^{2+} + 2[Fe(CN)_6]^{3-}$

At eqm, there are 3y mol of Zn^{2+} and 2y mol of $[Fe(CN)_6]^{3-}$.

$K_{sp} = [Zn^{2+}]^3 [Fe(CN)_6{}^{3-}]^2$

$= (3y)^3(2y)^2 = 108y^5 = \mathbf{W}$

$y = \sqrt[5]{\frac{\mathbf{W}}{108}}$

$[Fe(CN)_6{}^{3-}] = 2 \times \sqrt[5]{\frac{\mathbf{W}}{108}} = \sqrt[5]{\frac{\mathbf{8W}}{27}}$

Question 16 **Answer: A**

pK_a value of –COOH = 1.9, –SH = 8.1 and $-NH_3^+$ = 10.3.
At isoelectric point, only $-COO^-$ and $-NH_3^+$ exist, so pI = ½ (1.9+8.1) = 5.0

Hence only Bromocresol Green and Methyl Red can detect the isoelectric point of cysteine as the pI is within the working range of both indicators.

Question 17 **Answer: A**

X is A*l*:
- Al_2O_3 has no reaction with water due to high lattice energy.
- $AlCl_3$ undergoes hydrolysis with water to give an acidic solution of pH 3
- Al_2O_3, an amphoteric oxide, reacts with HC*l* to form $AlCl_3$ (chloride salt) and water.

Y is Na
- Na_2O reacts with water to forms NaOH (formation of hydroxide).
- NaC*l* undergoes only hydration with water to form a solution with pH = 7
- Na_2O, a basic oxide, reacts with HC*l* to form NaC*l* and H_2O.

Z is Si
- SiO_2 does not react with water due to its giant covalent structure
- $SiCl_4$ reacts with water to give an acidic solution pH 1
- SiO_2 does not react with HC*l*.

Question 18 **Answer: B**

Thermal stability is increased by (a) lower polarising power of the cation and (b) lower polarisability of the anion.

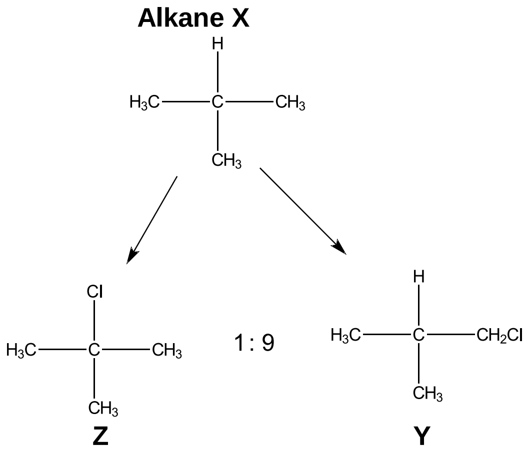
Ba^{2+} has a lower polarising power than Ca^{2+} due to its larger ionic radius. As $BaSO_4$ requires a higher temperature for decomposition, it is thermally more stable due to the lower polarising power of Ba^{2+}. It is not due to the polarisability of the SO_4^{2-} anion because the SO_4^{2-} anion is larger and more polarisable than CO_3^{2-}.

Statement 1 and 4 are incorrect as it does not help to explain thermal stability. Statement 2 is incorrect because SO_4^{2-} is more easily polarised than CO_3^{2-} ions.

Question 19 **Answer: D**

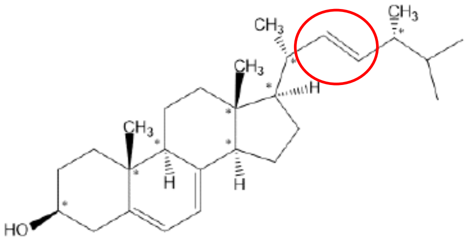
Option **A** is correct as there are 4 dative bonds formed in the complex to the central copper ion, hence coordination number is 4.
Option **B** is correct as these are ligand exchange reactions with no change in oxidation state. Copper (**II**) complexes are formed in this reaction scheme.
Option **C** is correct as **Q** is formed in presence of excess ammonia and the complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is formed.
Option **D** is incorrect as reduction reaction does not occur during a ligand exchange reaction (Reaction **III**).

Question 20 **Answer: C**

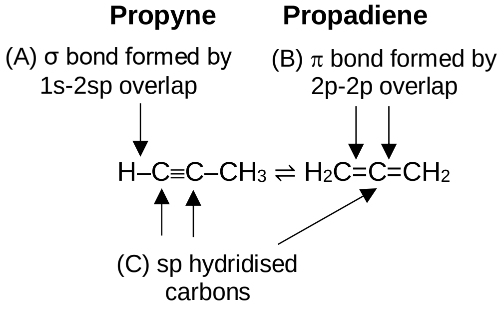


Question 21 **Answer: B**

Max number of stereoisomers = $2^{8+1} = 2^9$ [Note: C=C in ring does not exhibit cis-trans isomerism]



Question 22 **Answer: D**



D is incorrect as the C-C single bond in propyne is sp-sp^3 overlap, while that in propane ($CH_3–CH_2–CH_3$) is sp^3-sp^3 overlap. The bond length in propyne is shorter as sp orbital has more s character, resulting in more effective overlap.

Question 23 **Answer: B**

A is incorrect as oxidation of methylbenzene to benzoic acid requires $KMnO_4/H_2SO_4$, heat.
C is incorrect as aqueous NaOH needs to be added to liberate the free phenylamine and concentrated HNO_3 will result in substitution at 2, 4 position.
D is incorrect as $LiAlH_4$ will reduce carboxylic acid back to primary alcohol.

Question 24 **Answer: A**

Option 1 is incorrect as stereoisomers have different biological properties.
Option 2 is correct. Molecular formula = $C_{12}H_{18}Br_6$, Empirical formula = C_2H_3Br
Option 3 is incorrect as the carbon atoms are tetrahedral.

Question 25 **Answer: C**

A 1 mole of compound **G** reacts with Na (alcohol, phenol, carboxylic acid) to produce 1.5 mole of H_2.
B Tertiary alcohol cannot be oxidised so no green solution obtained.
C 1 mole of compound **G** reacts with 2 moles of NaOH (carboxylic acid and phenol) so product has a charge of 2-.
D 1 mole of compound **G** reacts with 3 moles of CH_3COCl (alcohol, phenol, amine) to produce 3 moles of HCl.

Question 26 **Answer: B**

1 $CH_2=CHCO_2H$ gives $CH_2=CHCH_2OH$ (gains 2 H and loses 1 O). Alkene is not reduced.
→ net change in $M_r = +2 - 16 = -14$

2 $CH_3CH_2COCO_2H$ gives $CH_3CH_2CH(OH)CH_2OH$ (gains 4H and lose 1 O)
→ net change in $M_r = +4 - 16 = -12$

3 $CH_3CH_2CONH_2$ gives $CH_3CH_2CH_2NH_2$ (gains 2H and lose 1 O)
→ net change in $M_r = +2 -16 = -14$

Question 27 **Answer: D**

A Product is $CH_3CH_2CH_2CHCN(OD)$
B Product is $CH_3CH_2CH_2CO_2D$
C Product is $CH_3CH_2CH_2CO_2D$ and $^{+}ND_2(CH_3)_2$
D Product is $CH_3CH_2CH_2CO_2^{-}$ which does not contain deuterium.

Question 28 **Answer: B**

Increasing pK_b: arrange from most basic to least basic.
1 and 2 are both secondary amines. However, 1 has an electron-withdrawing group (C=O) attached to it which reduces the electron density on the nitrogen and hence it is less basic than 2.
3 is neutral.
4 is less basic than 1 and 2 since the lone pair of electrons on the nitrogen is delocalised into the benzene ring and hence less available for dative bonding with a proton.

Question 29 **Answer: A**

ala-met
    met-gly-ala
        gly-ala-gly
            gly-ser
                ser-lys

Therefore, the structure of the polypeptide is ala-met-gly-ala-gly-ser-lys

Question 30 **Answer: C**

Working backwards via pattern recognition: "break C=C bond and place back O at C=C bond" to get first carbonyl compound and the remaining fragment belongs to the second carbonyl compound.

A & D: forms from 2 molecules of butanone

B: forms from 1 molecule of butanone and 2 molecules of ethanal

C: C=C on the right is NOT at C2 and C3 from C=O group

1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy (kJ mol^{-1})**	**Second Ionisation energy (kJ mol^{-1})**	**Third Ionisation energy (kJ mol^{-1})**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

The first and second I.E of the transition elements involves the removal of 4s electrons. Across the period, • nuclear charge increases due to increasing number of protons. Screening effect increases as electrons are added to the penultimate 3d subshell, providing a shield between nucleus and outer 4s electrons. • Increase in nuclear charge is only *slightly* more significant than the increase in screening effect. Hence, small increase in both the first and second I.E.

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

• Electronic Configuration of Fe: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^6$ $4s^2$

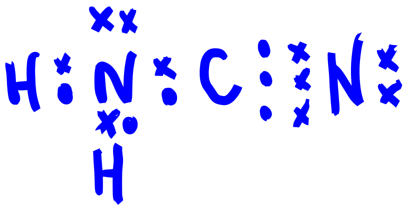
Electronic Configuration of Ca: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$

• The third ionisation energy of calcium is more than that of iron because an electron is removed from a 3p orbital of Ca^{2+} whereas an electron is removed from a 3d orbital of the Fe^{2+}. The 3p electron is nearer to the nucleus compared to the 3d electron and hence required more energy to remove.

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]



(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

- **NH_2CN has simple molecular structure with hydrogen bonds between its molecules.**

$CaCN_2$ has a giant ionic lattice structure held by strong electrostatic forces of attraction/ionic bonds between the oppositely charged ions.

- **Melting involves the breaking of the stronger electrostatic forces of attraction between the oppositely charges ions (Ca^{2+} and CN_2^{2-}) as compared to the (or) weaker hydrogen bonds between NH_2CN molecules. Hence more energy is required to melt $CaCN_2$, hence higher melting point.**

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

Oxidation :$HCO_2^- \rightarrow CO_2 + H^+ + 2e^-$ (x5)

Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x2)

- **$2MnO_4^- + 11H^+ + 5HCO_2^- \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$**

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution.

[1]

- **$[HCO_2^-]$ in saturated solution = $\frac{143}{24.3+2(1+12+2\times16)}\times 2$**
= 2.50 mol dm^{-3}

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used.

[3]

Assuming the titre volume of potassium manganate(VII) solution to be 25.00 cm^3 (accept 20.00 to 25.00 cm^3),

No. of moles of HCO_2^- in 25.0 cm^3 of diluted solution
$= \frac{25}{1000} \times 0.05 \times \frac{5}{2} = 3.125 \times 10^{-3}$ mol
No. of moles of HCO_2^- in 250 cm^3 of diluted solution = 3.125×10^{-2} mol

- **Volume of saturated HCO_2^- solution needed for dilution**
  $= \frac{3.125 \times 10^{-2}}{2.5} \times 1000 = 12.50$ cm^3

••
Using a <u>burette</u>, transfer <u>12.50 cm^3</u> of saturated magnesium methanoate solution into a <u>250 cm^3 standard flask</u>. <u>Make up to the mark with water and shake well</u>.

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H < 0$$

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

Since P ∝ T,

- **$P_{CO_2} = P_{H_2} = 6$ atm at 900K**

	$CO_2(g)$ +	$H_2(g)$ ⇌	$H_2O(g)$ +	$CO(g)$
Initial partial pressure /atm	6	6	0	0
Change in partial pressure /atm	-x	-x	+x	+x
Equilibrium partial pressure /atm	6-x	6-x	x	x

$K_p = \frac{P_{H_2O} \times P_{CO}}{P_{CO_2} \times P_{H_2}}$

- **$0.641 = \frac{x^2}{(6-x)^2}$**
  x = 2.67 atm
- **$P_{H_2} = 6 - 2.67 = 3.33$ atm**

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

• The value of K_p at 300 K is <u>higher than 0.641</u>.
• By Le Chatelier's Principle, at the lower temperature of 300 K, the system will <u>favour the exothermic forward reaction to produce more heat</u>. Thus <u>position of equilibrium shifts to the right</u> and K_p increases.

[Total: 10]

3 **(a)** Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

[3]

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle.

There are 2 bond pairs and 2 lone pairs of electrons around S. To minimize repulsion and maximize stability, the 4 electron pairs are directed to the corners of a tetrahedron. The shape is bent.

√ 2 bond pairs and 2 lone pairs around S.

√ 4 electrons pairs arranged tetrahedrally to

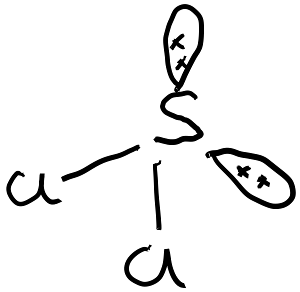
√ minimize repulsion and maximize stability.

√ bent

√ diagram

√ bond angle : any angle between 90^0 & 109.5^0.

2 √ : 1m



(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer.

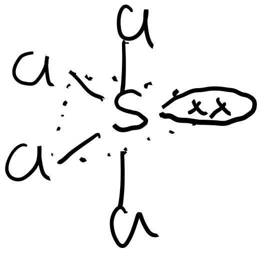
[1]

Cl is less electronegative than F. The bond pair of electrons is closer to S for SCl_2 resulting in a greater bond pair-bond pair repulsion. Hence the bond angle of SCl_2 is larger.

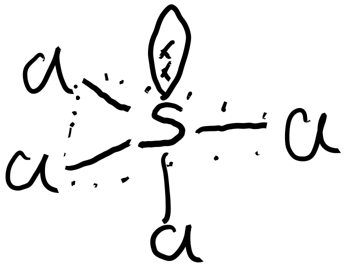
(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities. Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I)



(II)



(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

- **Since electron pairs exert repulsion on one another in the following order:**

lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion

<u>Arrangement I</u> gives the more stable molecule when the lone pair is placed in the equatorial positions (120^0 apart).

(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

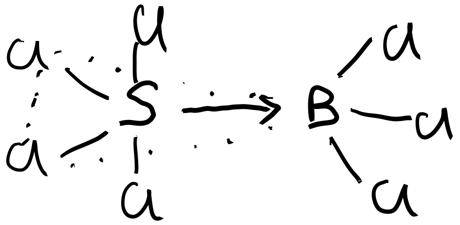
	S	**B**	**C*l***
Mole ratio	**11/32.1**	**3.7/10.8**	**85.3/35.5**
	0.343	**0.343**	**2.40**
Simplest ratio	**1**	**1**	**7**

Empirical formula : $SBCl_7$

(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

•



•Type of bond : Dative/co-ordinate

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

● Order of boiling point : HI > HBr > HC*l*
● Down the group, <u>size of electron cloud of HX increases</u>, leading to <u>greater distortion of electron cloud</u>. Extent of <u>instantaneous dipole-induced dipole interactions becomes stronger</u> and more extensive. Larger amount of energy required to break these intermolecular forces of attraction between the molecules.

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

● Bond energy of H-C*l*, H-Br and H-I are <u>431, 366 and 299 kJ mol^{-1}</u> respectively.
● As seen from the data, the <u>H-X bond energy decreases down the group</u> resulting in <u>a decrease in the strength of the H-X bond</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group. *OR*
● Radius of Cl, Br, I are <u>0.099, 0.114, 0.133 nm</u> respectively.
● <u>H-X bond length increases down the group</u>, <u>extent of effective orbital overlap decreases</u> and the <u>H-X bond strength decreases</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group.

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

• Orange & pH = 3 to 4
• $AlCl_3$ undergoes both hydration and hydrolysis as Al^{3+} 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.
Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$
1m for both equation

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

[1]

• $SiCl_4$ is a covalent chloride that undergoes hydrolysis in water. Hydrolysis occurs due to energetically accessible & vacant 3d-orbitals available for dative bonding with water/accept lone pair electron from water.

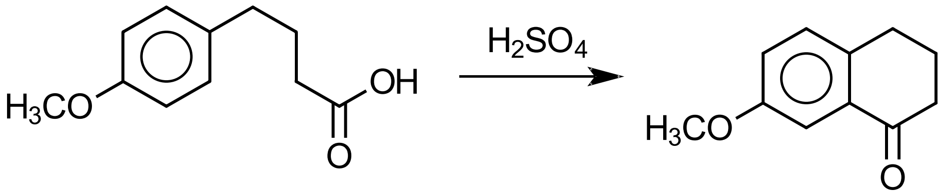
(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.
Deduce whether Al_2Cl_6 can also function in the same manner.

[1]

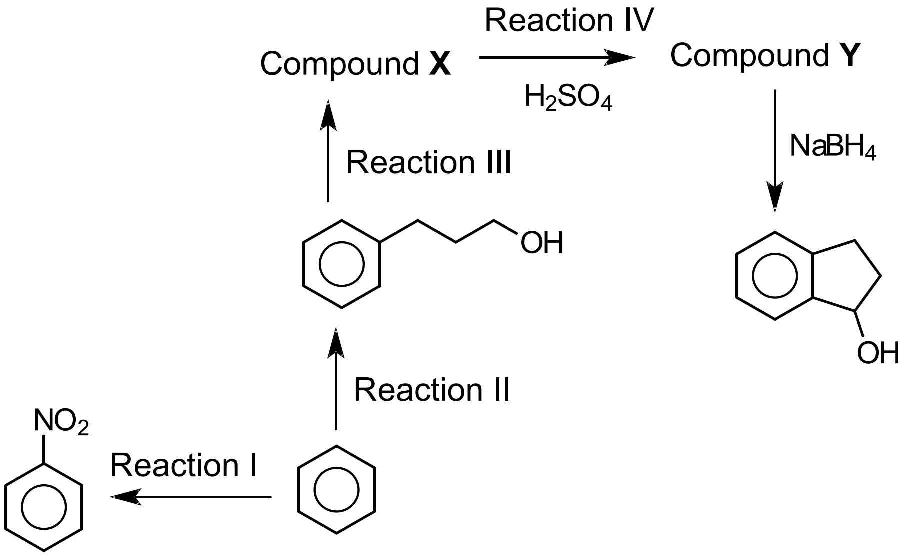
• No, because Al_2Cl_6 is not electron-deficient/has achieved octet structure and is less likely to accept a lone pair of electrons to form a dative bond.

(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.



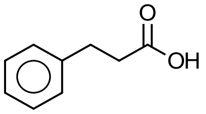
The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



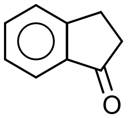
Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

- **Reaction I: concentrated nitric acid, concentrated sulfuric acid, heat < 60°C**
- **Reaction II: $ClCH_2CH_2CH_2OH$, anhydrous $AlCl_3$ as catalyst, rtp**
- **Reaction III: acidified $K_2Cr_2O_7$, heat under reflux (cannot use $KMnO_4$)**
- **X:**



- **Y:**



[Total: 14]

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

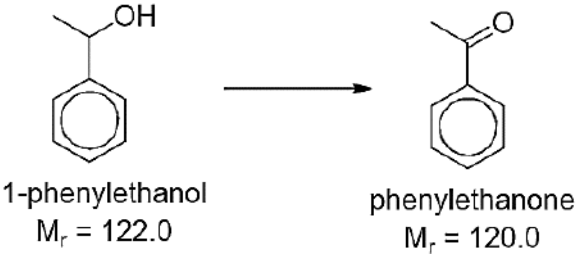
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction using chromium(VI) oxide in acidic medium or via a catalytic reaction using oxygen in the presence of ruthenium metal catalyst.



Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	x

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(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone. [2]

- **Atom Utilisation for the catalytic reaction**
  = M_r of phenylethanone / (M_r of phenylethanone + M_r of water)
  = 120/(120+18) = 87.0%

- **Catalytic reaction is more efficient as the Atom Utilisation value is higher implying less waste is produced from the reaction.**

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} E \times Q$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

[2]

- **Bulk chemical industry: 1000x2 + 1x2 = 2002**
  Pharmaceutical industry: 1000x50 + 1x50 = 50,050

- **Hence, the bulk chemical industry is more environmental friendly as the EQ value is lower, implying less amount of toxic waste is generated.**

(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

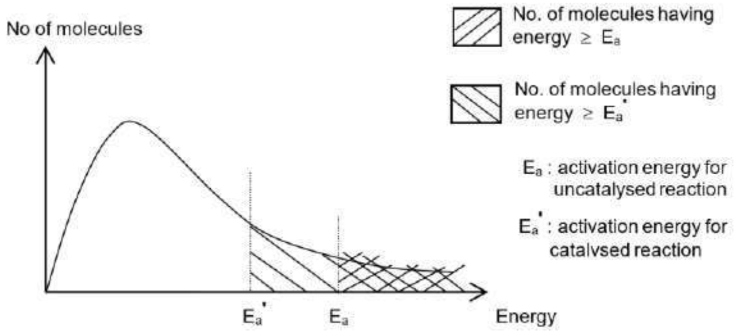
- **Ruthenium provides the surface in which adsorption of reactant molecules and desorption of product molecules take place.**

- **The activation energy is lower than that of the uncatalysed reaction because the effective surface concentration of oxygen and 1-phenylethanol on the catalyst is higher and the intramolecular bonds of reactants are weakened by the adsorption effect.**

[Turn over

(ii) With a sketch of a suitable Boltzmann distribution curve below, explain the effect of ruthenium on the rate constant of the reaction.

[3]



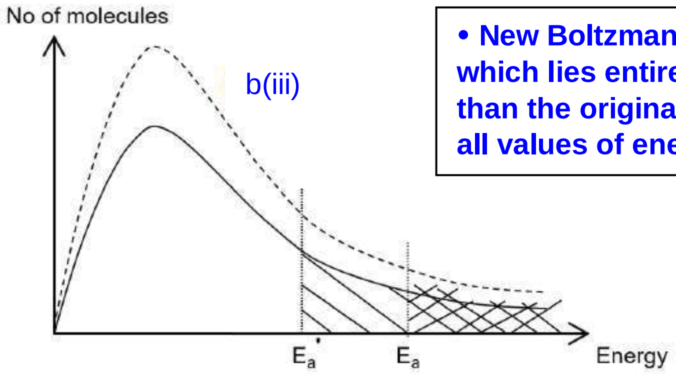
- **Correct Boltzmann curve with legends and correct Ea and Ea' shown**

- **The ruthenium catalyst provides an alternative pathway which involves <u>a lower activation energy, E_a'</u>. The <u>number of reactant molecules having energy greater than or equal to Ea' increases significantly</u>.**
- **<u>Frequency of effective collisions increases</u> and <u>rate constant increases</u>, hence rate increases.**

(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

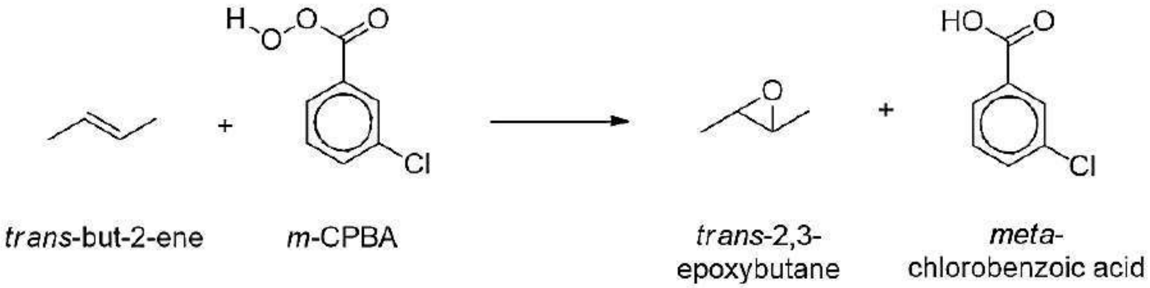
[1]



- **New Boltzmann curve which lies entirely higher than the original curve at all values of energy**

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an “X” mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the “X” to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for “X” to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

Formation of • id-id interaction between meta-chlorobenzoic acid and hexane release insufficient energy to overcome the • hydrogen-bonding interactions between molecules of meta-chlorobenzoic acid and id-id interactions between hexane molecules.

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly. [2]

Total volume is constant at 45 cm^3, so the volume ∝ concentration. Rate of reaction ∝ 1/t.

[Turn over

Relative rate for expt 1 = 1/10 = 0.100

Relative rate for expt 2 = 1/6.7 = 0.149

Relative rate for expt 3 = 1/40 = 0.025

• Comparing expt 1 and 2, keeping conc of trans-but-2-ene constant, when conc of m-CPBA increases by 1.5 times, rate increases by 1.5 times → 1st order reaction wrt m-CPBA.

• Comparing expt 1 and 3, when conc of m-CPBA and trans-but-2-ene each halves, rate decreases by 4 times → 1st order reaction wrt trans-but-2-ene.

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

• Rate = k[trans-but-2-ene][m-CPBA]

(iv) State the value of y in experiment 4.

[1]

• 10s

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data are collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 °C

The experiment was only 20% efficient.

(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

• Total heat gained by water & calorimeter = 400x4.18x32 + 154x32 = 58432 J

• Total heat given out by burning 10cm^3 of trans-2,3-epoxybutane = 58432 x 100/20 = 292160 J

Amount of trans-2,3-epoxybutane burnt = 8.26/(4x12+8+16) = 0.1147 mol

• Enthalpy change of combustion = -292 160 / 0.1147 = -2550 kJ mol^{-1}

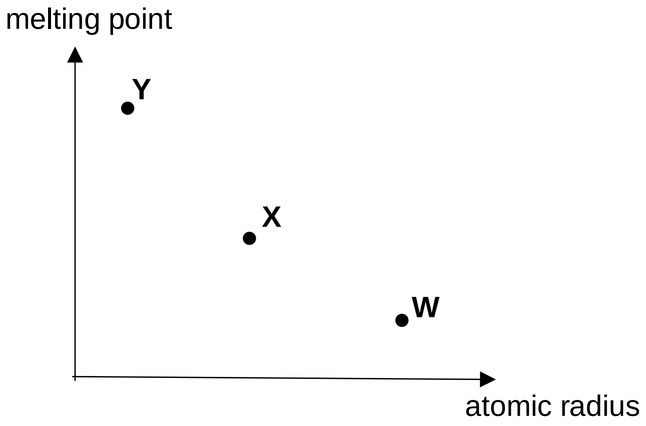
(ii) Suggest one modification to the set-up so that the experiment can be made more efficient.

[1]

Install windshield / conduct the experiment in a draught-free room / insulate the copper calorimeter

[Total: 20]

6 **(a)** **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

(i) Suggest the identities of **Y** and **W**.

- **Y is <u>aluminum</u> and W is <u>Sodium</u> (X: Magnesium)**

(ii) Explain the above observations and write equations for all the reactions that has occurred. [3]

- **Al_2O_3 is insoluble in water due to its high lattice energy.**

  When Na_2O dissolves in water, it forms NaOH(aq).

- **$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$**

  Since Al_2O_3 is an amphoteric oxide, it can react with NaOH(aq) and hence dissolves.

- **$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$**

Note: Y is not Si because SiO_2 does not dissolve in weakly alkaline solution.

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained. [3]

- **The ionic radius of Mg^{2+}, Sr^{2+} and Ba^{2+} are 0.065 nm, 0.113 nm and 0.135 nm respectively.**

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

Down Group 2, the ionic charge of the cation remains the same while the ionic radius increases, hence √ charge density decreases down the group.

Hence, Mg^{2+} has the greatest polarising power and can √ distort the electron cloud of CO_3^{2-}/polarise the C-O bond to the greatest extent, √ weakening the C–O bond the most.

As a result, $MgCO_3$ √ decomposes most readily/is least stable to heat than $SrCO_3$ and $BaCO_3$ and requires the least amount of time to for the white ppt to be formed with calcium hydroxide.

•• Every 2√ 1 mark

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

The time needed for the white ppt to be observed is 70 s (accept any value between 40 – 240).

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

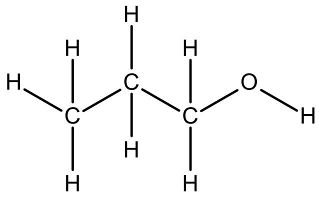
(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

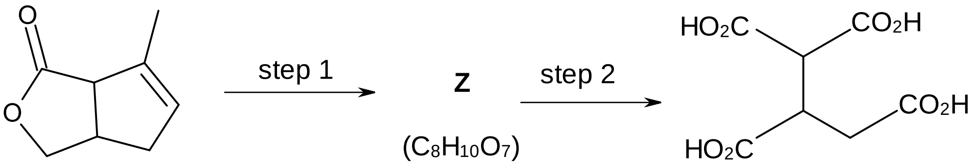
LiA*l*H$_4$ is a stronger reducing agent than NaBH$_4$ as the H in the A*l*-H bond is more electron rich. This is due to the greater electronegativity difference between A*l* and H in the A*l*-H bond (electronegativity difference is 2.1-1.5).

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]



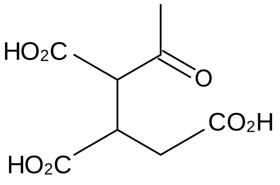
(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

- **Step 1: $KMnO_4$, H_2SO_4, heat**

- **Z:**



- **Step 2: alkaline I_2(aq), heat, followed by acidification using H_2SO_4(aq) or HC*l*(aq)**

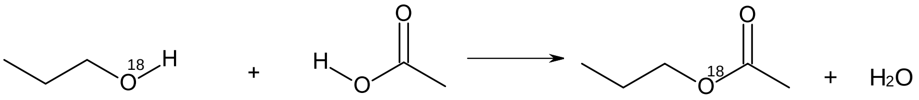
(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

-



[Total: 14]

TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CHEMISTRY 9729/03

Paper 3 Free Response 16 September 2019

2 hours

Candidates answer on separate booklet.

Additional Materials: 12-Page Answer Booklet
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 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.

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.

This document consists of **14** printed pages and **2** blank pages.

Section A

Answer **all** the questions from this section.

1 The term *chelates*, originates from the Greek word *chele* for "claw". It refers to compounds containing ligands bonded to a central metal atom or ion at two or more points.

Ligand exchange occurs when ammonia and ethylenediamine (en), $H_2NCH_2CH_2NH_2$, are added separately to copper sulfate solution.

(a) **(i)** Explain all the changes observed when aqueous ammonia is added dropwise to $Cu^{2+}(aq)$ till in excess. Suggest the formulae of all relevant copper compounds formed and write equations for all reactions. [4]

When aqueous ammonia is added dropwise to blue $Cu^{2+}(aq)$ solution, a blue precipitate of $Cu(OH)_2$ is formed. Ammonia acts as a base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l) \quad \text{— (1)}$$

Blue ppt

$$\text{OR } Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$$

In excess ammonia, blue precipitate $Cu(OH)_2(s)$ dissolves to give a dark blue solution due to the formation of the complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.

Ammonia acts as a ligand (or ligand exchange has taken place).

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l) \quad \text{— (2)}$$

Dark blue solution

Formation of the complex shifts the equilibrium in equation (1) to the left, thus, the blue precipitate dissolves.

(ii) Suggest why ethylenediamine can function as a *chelating ligand*. [1]

- **Ethylenediamine molecule has two lone pair of electrons on the nitrogen atoms to form two dative bonds with the Cu^{2+} ion.**

(iii) When ethylenediamine is added to $Cu^{2+}(aq)$, the following occurs.

$$[Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

Predict whether ethylenediamine or ammonia gives a more positive entropy change when added to $Cu^{2+}(aq)$. [2]

$$Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

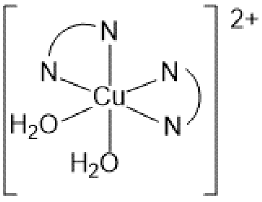
$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

- **Ethylenediamine (a bidentate ligand) gives a more positive change in entropy when added to $Cu^{2+}(aq)$ as**
- **there is an increase in number of particles (from 3 to 5) and thus more way of arranging the particles.**

(iv) Suggest the coordination number and shape of $[Cu(en)_2(H_2O)_2]^{2+}$. [1]

- **Coordination number = 6, Shape = Octahedral**

(v) The complex ion $[Cu(en)_2(H_2O)_2]^{2+}$ can exist as three stereoisomers, **A**, **B** and **C**. Isomers **A** and **B** rotate plane-polarised light but **C** does not. The structure of **A** is represented below.

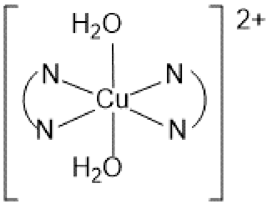


Isomer **A**

where  represents ethylenediamine (en)

Draw the structure of **C**. [1]

- **Isomer C**



(b) Photochromic glass used for sunglasses contains $AgCl$ crystals which are added while the glass is in molten state. The glass darkens when exposed to bright light and the following reaction is involved.

$$Ag^+ + Cl^- \rightleftharpoons Ag + Cl$$

(i) Suggest why the glass darkens when exposed to bright light. [1]

- **In presence of UV light, colorless Ag^+ cations form elemental Ag and the glass appear darker.**

The glass darkens significantly within about a minute of exposure to bright light but takes a longer time to clear when there is less light. Small amount of $CuCl$ crystals are often added to the glass to speed up the reverse process. No elemental copper is involved in the process.

$$Ag + Cl \rightarrow Ag^+ + Cl^-$$

(ii) Explain why the copper(I) ions can be described as a *homogeneous catalyst*. [2]

The copper(I) ions are in the •same phase as the reactants, and is •not consumed/used up by the reaction.

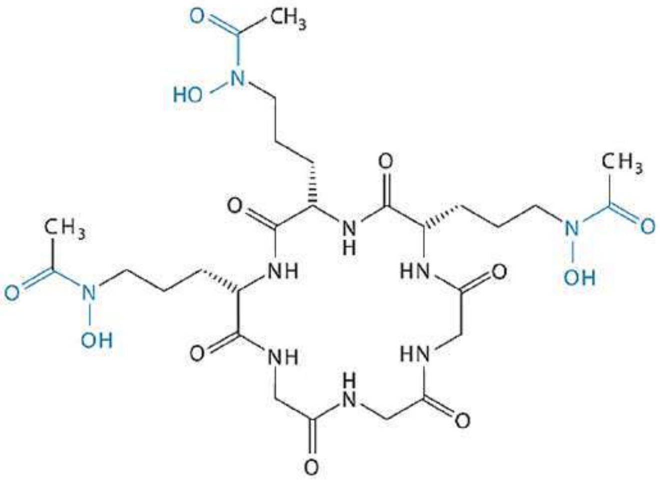
(iii) State the property, typical of transition metals, which allows copper(I) ions to behave as a homogenous catalyst in the reverse reaction. Include relevant chemical equations to support your answer. [3]

- **The catalytic activity of transition metals in homogenous catalysis depends on their ability to exist in variable oxidation states.**

The catalysed pathway for the reverse reaction.

- **$Cu^+ + Cl \rightarrow Cu^{2+} + Cl^-$**
- **$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$**

(c) Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Ferrichrome is a siderophore produced by fungi.



Ferrichrome

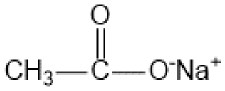
(i) Ferrichrome binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in ferrichrome. [2]

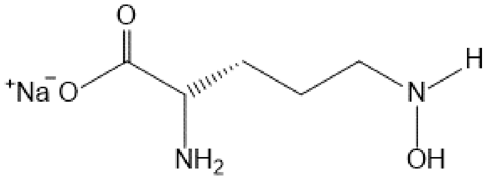
- **Ferrichrome binds to iron(III) ions through the formation of dative bonds between oxygen atoms and iron(III) ions.**
- **Lone pair of electrons on the nitrogen atoms are delocalised over the C=O group and are not available for dative bonding to iron(III) ions.**

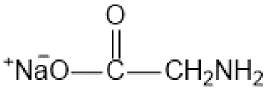
(ii) Draw the structures of the products formed when ferrichrome is heated with aqueous sodium hydroxide. [3]

●●● 1 mark for each structure



$CH_3-\overset{O}{\overset{\|}{C}}-O^-Na^+$



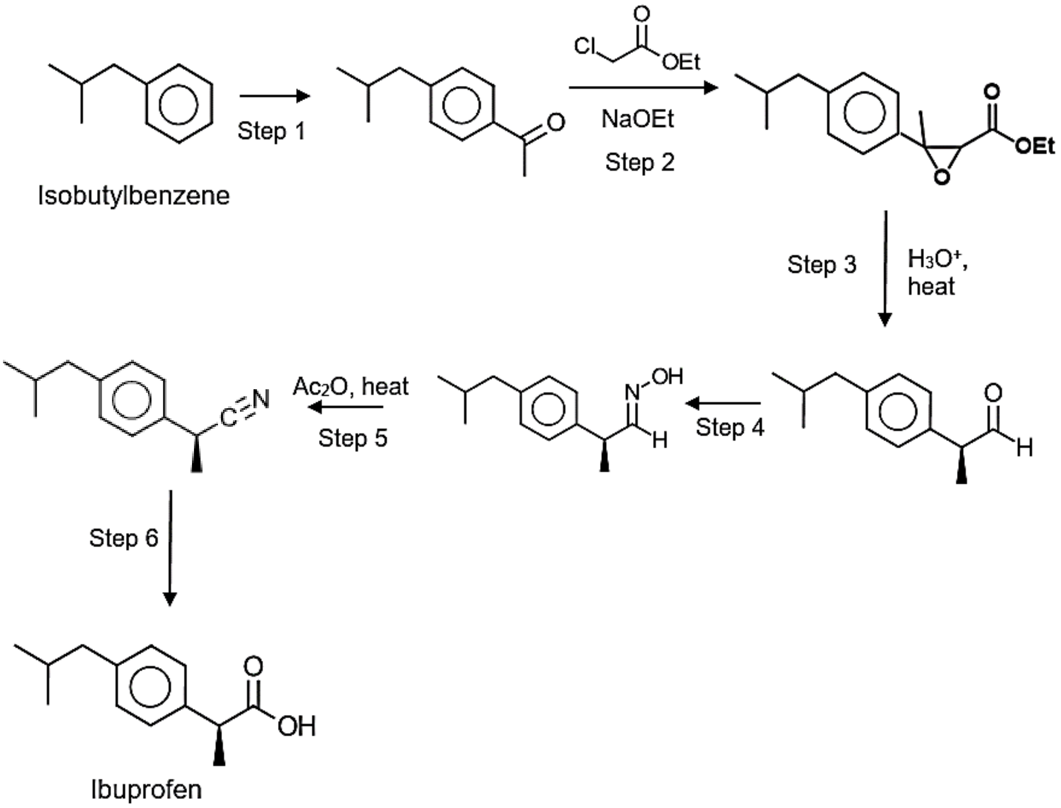


$^+Na^-O-\overset{O}{\overset{\|}{C}}-CH_2NH_2$

[Total: 20]

2 Ibuprofen is a nonsteroidal anti-inflammatory drug. It works by reducing hormones that cause inflammation and pain in the body. Ibuprofen is used to reduce fever and treat pain or inflammation.

The conventional synthesis of ibuprofen from isobutylbenzene is shown below. Step 4 of the synthesis resembles the reaction between a carbonyl compound and Brady's reagent.



(a) Name the types of reaction that are occurring during steps 4 and 5. [2]

•Step 4 : condensation reaction

•Step 5 : elimination

(b) Suggest the reagents and conditions for steps 1, 4 and 6. [3]

•Step 1 : CH_3COCl , anhydrous $AlCl_3$, r.t.p

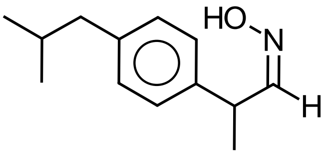
•Step 4 : NH_2OH, r.t.p

•Step 6 : dilute HC*l*, heat

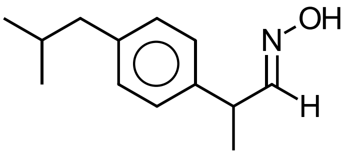
(c) Draw the structures of the stereoisomers of the product formed from step 4 and state the type of stereoisomerism exhibited. [2]

•Type : cis-trans isomerism

•



and



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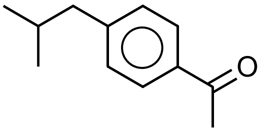
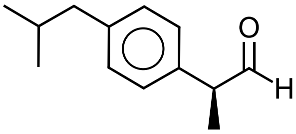
(d) Describe a simple chemical test to distinguish between the two compounds, **X** and **Y** obtained from synthesis above. [2]



Compound **X**



Compound **Y**

●**Add Tollens reagent** (diammine silver(I) complex), **HEAT** to separate samples.

●**Silver mirror observed for compound Y. No silver mirror for compound X.**

Alternative tests :

*** Alkaline aq. Iodine and warm. Yellow ppt observed for compound X and no yellow ppt for compound Y.**

*** Fehling's reagent, heat. Brick-red observed for compound Y and no brick-red ppt for compound X**

*** Acidified $K_2Cr_2O_7$, heat. Orange dichromate turned green when added to compound Y. No colour change for compound X.**

(e) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

(i) Potassium chloride and concentrated sulfuric acid reacts in an equimolar ratio to produce white fumes of hydrogen chloride.

Write an equation for the reaction of potassium chloride with concentrated sulfuric acid. [1]

Reaction of KCl and H_2SO_4

●$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$

(ii) Potassium iodide reacts with concentrated sulfuric acid in a similar manner. However, the white fumes of hydrogen iodide would further react with concentrated sulfuric acid to produce violet fumes and hydrogen sulfide gas.

Suggest an explanation for the difference in reactions, and write equations for the above observations. [2]

Reaction of KI and H_2SO_4

$KI + H_2SO_4 \longrightarrow HI + KHSO_4$

Half equations:

$2I^- \rightarrow I_2 + 2e^-$ (x4)

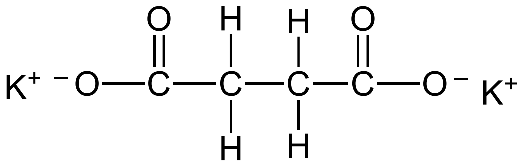
$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$

● **Overall:** $8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$

● I^- **being a stronger reducing agent (than Cl^-) will reduce H_2SO_4 to H_2S and itself oxidised to I_2. OR ● $E^\ominus_{I_2/I^-}$ is more negative than $E^\ominus_{Cl_2/Cl^-}$, thus more easily oxidized, stronger reducing agent than Cl^-. $E^\ominus_{I_2/I^-} = +0.54V$; $E^\ominus_{Cl_2/Cl^-} = +1.36V$.**

(f) When aqueous potassium salts of a dicarboxylic acid are electrolysed using inert platinum electrodes, alkenes are formed at the anode.

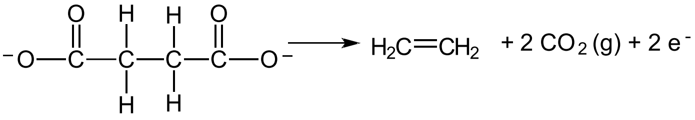
(i) The electrolysis of aqueous potassium succinate gives ethene at the anode.



$$K^+\ {}^-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O^-\ K^+$$

Potassium Succinate

Write an ion-electron half equation for the oxidation of succinate at the anode. [1]

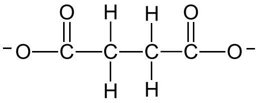
- 

$${}^-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O^- \longrightarrow H_2C{=}CH_2\ + 2\,CO_2\,(g) + 2\,e^-$$

(ii) Write an equation for the reaction at the cathode and for the overall reaction. [2]

•At the cathode: $\mathbf{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$

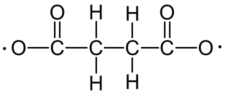
[Explanation: Since $E^\ominus_{H_2O/H_2}$ *is more positive than* $E^\ominus_{K^+/K}$*,* H_2O *is preferentially reduced at the cathode, liberating* H_2*.]*

•Overall reaction: 

$${}^-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O^- \mathbf{+ 2H_2O \rightarrow} H_2C{=}CH_2 \mathbf{+ 2CO_2 + H_2 + 2OH^-}$$

(iii) The mechanism of the reaction at the anode involves three steps:

Step 1: There is an initial loss of 2 electrons on succinate ion to form

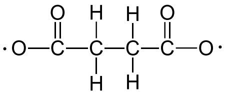


$$\cdot O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O\cdot$$

Step 2: This is followed by decarboxylation which involves the homolytic breaking of two C–C bonds, giving a radical intermediate $\bullet CH_2CH_2\bullet$

Step 3: The third step involves forming a covalent bond, producing ethene as the product.

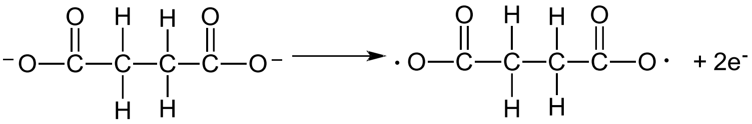
Use the information given above to draw the mechanism for Steps 2 and 3.

You are advised to use structural formulae for all species, such as 

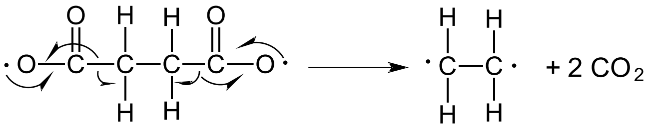
$$\cdot O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O\cdot$$

, so that it is clear which bonds are broken and which are formed.

Represent with a half arrow (⇀) for movement of a single unpaired electron and indicate any unpaired electrons by a dot (•). [2]



$${}^-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O^- \longrightarrow \cdot O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O\cdot\ + 2e^-$$



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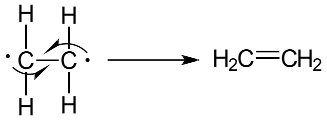
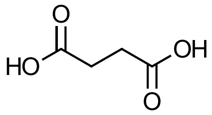
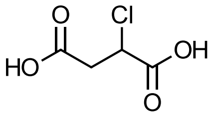


●

(g) The strength of a carboxylic acid depends on its structure. An example of this is the comparison of succinic acid and its derivatives.

Acid	pK_{a1}
	4.21
	-

Explain if pK_a of chlorosuccinic acid is lower or higher than the pK_a of succinic acid. [1]

●pK_a of chlorosuccinic acid is lower (a stronger acid)

Reason: presence of electron-withdrawing Cl-atom disperse the negative charge on anion more, better stabilising the anion more, so chlorosuccinic acid is a stronger acid (lower pK_a).

[Total: 18]

3 On 28 November 2018, an explosion erupted near the Hebei Shenghua Chemical Industrial plant, killing at least 23 people and injuring many more. It was reported that the explosion originated from a truck transporting ethyne gas, C_2H_2, which then set off a chain reaction that engulfed at least 50 other vehicles.

When mixed appropriately with air, C_2H_2 explodes upon ignition as follows.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(g)$$

This explosion may have generated an estimated 20.8 million kilojoules of energy.

(a) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within an ethyne molecule. [3]

- ○ One of the 2s electrons in each C atom is promoted to the vacant 2p orbital, and **the s and one p orbital then hybridise/mix to give two sp hybrid orbitals** which contain one electron each.
- ○ One **σ bond** between adjacent C atoms formed through / bonded by **head –on overlap of** one **sp hybrid orbital of each C atom**.

○ Two <u>π **bonds** are formed through **sideway overlap of the**</u> two unhybridised <u>**p orbitals of each C atom.**</u>

(b) **(i)** Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne. [2]

$$\text{H–C≡C–H} + \frac{5}{2}\,\text{O=O} \longrightarrow 2\,\text{O=C=O} + \text{H–O–H}$$

- $\Delta H_c^{\ominus} = [2\,\text{BE(C–H)} + \text{BE(C≡C)} + \frac{5}{2}\,\text{BE(O=O)}] - [4\,\text{BE(C=O)} + 2\,\text{BE(O–H)}]$

$\Delta H_c^{\ominus} = [2(410) + (840) + \frac{5}{2}(496)] - [4(805) + 2(460)]$

- = –<u>**1240 kJ mol**</u>$^{-1}$

(ii) Using your answer in **(b)(i)**, calculate the volume of ethyne gas transported by the truck at 28°C and 1 bar. [2]

- Amount of ethyne gas used for combustion = $\dfrac{20.8\times10^{6}}{1240}$ = 16774 mol

Using pV=nRT

- Vol. of ethyne gas produced = $\dfrac{16774\times8.31\times(273+28)}{1.00\times10^{5}}$ = <u>420 m^3</u>

(c) One of the ways that ethyne gas can be produced is via the reaction of calcium carbide, CaC_2, with water, producing solid calcium hydroxide as a by-product.

(i) Using the following information and relevant data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of solid calcium hydroxide. [3]

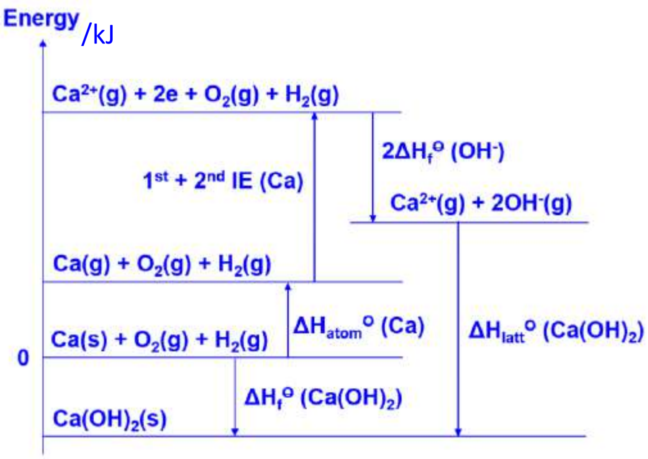
$$Ca^{2+}(g) + 2OH^{-}(g) \longrightarrow Ca(OH)_2(s)$$

standard enthalpy change of atomisation of Ca (s) = + 178 kJ mol^{-1}

standard enthalpy change of formation of OH^{-} (g) = − 230 kJ mol^{-1}

standard enthalpy change of formation of $Ca(OH)_2$ (s) = − 985 kJ mol^{-1}

Energy Level Diagram

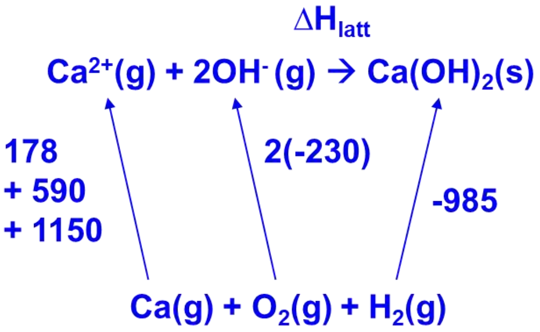


By Hess' Law,

$\Delta H_f^{\ominus} (Ca(OH)_2)$ $= \Delta H_{at}^{\ominus} (Ca) + 1^{st}$ IE (Ca) + 2^{nd} IE (Ca) + $2\Delta H_f^{\ominus}(OH^-) + \Delta H_{latt} (Ca(OH)_2)$

-985 $= 178 + 590 + 1150 + 2(-230) + \Delta H_{latt} (Ca(OH)_2)$

• $\Delta H_{latt} (Ca(OH)_2)$ = **<u>– 2443 kJ mol</u>**$^{-1}$



(ii) Suggest, with reasoning, how the magnitude of the lattice energy of $Ca(OH)_2$ compares with that of calcium carbide, CaC_2, given the following data. [2]

Ion	Radius (pm)
OH^-	133
C_2^{2-}	118

$|\Delta H_{latt}| \propto \dfrac{q_+q_-}{r_+ + r_-}$ **for ionic compound**

Ionic radius or r^- : $OH^- > C_2^{2-}$ q_+, r_+ constants

Ionic charge or r^- : $OH^- < C_2^{2-}$ •

Magnitude/value of the lattice energy CaC_2 is larger than that of $Ca(OH)_2$

(iii) The value of $\Delta G^{\ominus}$ for the reaction of calcium carbide with water is -148 kJ mol^{-1}.

$$CaC_2\,(s) + 2H_2O\,(l) \longrightarrow Ca(OH)_2\,(s) + C_2H_2\,(g) \qquad \Delta H = -128 \text{ kJ mol}^{-1}$$

Calculate $\Delta S^{\ominus}$ in J mol^{-1} K^{-1} to one decimal place for the reaction. Explain the significance of its sign with reference to the equation. [2]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

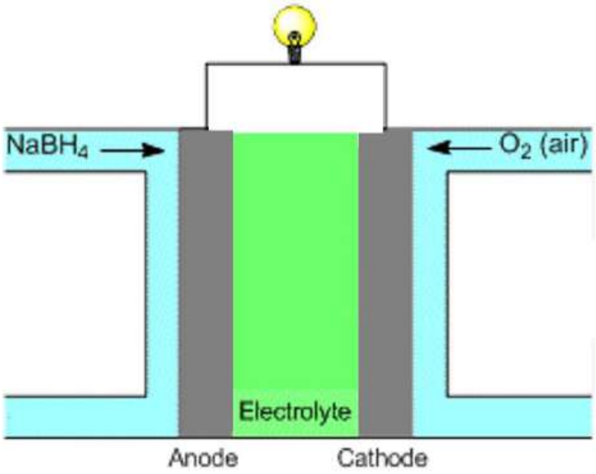
$-148 = -128 - (298)\,\Delta S^{\ominus}$

• $\Delta S^{\ominus}$ = <u>+67.1 J mol^{-1} K^{-1}</u> (to 1 dp)

• $\Delta S^{\ominus}$ is positive because there is **<u>an increase in the number of moles of gaseous molecules</u>** produced in the chemical reaction (from 0 in reactants to 1 in products) **and <u>hence an increase in disorder</u>** of the system.

(d) Similar to calcium carbide, sodium borohydride, $NaBH_4$, can be used in fuel cells.

Direct borohydride fuel cells (DBFCs), are fuel cells which are directly fed by $NaBH_4$ as the fuel and oxygen as the oxidant. The electrolyte used is potassium hydroxide. Sodium metaborate, $NaBO_2$, and water are formed as the only products during the discharging process.



(i) Deduce the ion-electron half–equations for the anode and cathode and hence write the overall cell reaction during discharging. [2]

- **Anode:** $NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-$

  Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- **Overall:** $NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O$

(ii) A typical DBFC fuel cell generates about 1.64 V. Using the *Data Booklet*, calculate the E^{θ} involving the $NaBO_2/NaBH_4$ half-cell. [1]

$E^{\theta}_{cell} = E^{\theta}_{red} - E^{\theta}_{oxid}$

$1.64 = 0.40 - E^{\theta}_{oxid}$

• E^{θ} = <u>-1.24 V</u>

(iii) Use the half–equations you have written in **(d)(i)** to calculate the value of $\Delta G^{\ominus}$ and comment on the significance of $\Delta G^{\ominus}$. [1]

n = **8**

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

$\Delta G^{\ominus} = -(8 \times 1.64 \times 96500) =$ **–1266080 J mol^{-1}**

ΔG^{e} is negative or G < 0 hence the **reaction is spontaneous** or energetically **feasible**

(iv) Explain qualitatively what happens to the cell potential, E_{cell} when a small amount of propanal contaminant is accidently added to the anode half-cell.

The contaminant does not take part in the cell reaction. [2]

$NaBO_2 + 6H_2O + 8e^- \rightleftharpoons NaBH_4 + 8OH^-$ -- (1) **E_{oxid}**

The **$NaBH_4$ is used to reduce the propanal** to propanol, causing the $[NaBH_4]$ to decrease.

By *Le Chatelier's Principle*, the **equilibrium position (1) will shift right to increase $NaBH_4$, favouring the reduction reaction.**

E_{oxid} or **$E_{NaBO2/NaBH4}$ will become more positive/less -ve**

Hence, producing a less positive E_{cell} or **a value less than 1.64 V** .

(v) In a particular DBFC, a current of 1.35×10^{-2} A cm^{-3} was passed through the circuit for 95 minutes.

Calculate the mass of $NaBO_2$ that was produced per 25 cm^3 of solution. [2]

- Quantity of charge, $Q = It = (1.35 \times 10^{-2}\ \text{A cm}^{-3})(25) \times (95 \times 60) =$ **1923.8 C**

No of moles of electrons transferred $= \dfrac{1923.75}{96500} = 1.993 \times 10^{-2}$ mol

$$\left.\begin{aligned} &\text{No of moles of } NaBO_2 = \frac{0.01993}{8} = 2.49 \times 10^{-3} \text{ mol} \\ &\text{Mass of } NaBO_2 = 2.49 \times 10^{-3} \times (23.0 + 10.8 + 32) = \underline{\mathbf{0.164\ g}} \end{aligned}\right\} \bullet$$

[Total: 22]

Section B

Answer **one** question from this section.

4 Chlorine-containing compounds have many useful applications. One such example is the use of chloric(I) acid, HC*l*O, to disinfect water in swimming pools.

HC*l*O dissociates in water as shown below.

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

(a) **(i)** Write an expression for K_a of HC*l*O. [1]

- $K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$

(ii) A disinfectant solution was prepared by dissolving 10 g of HC*l*O and *x* g of NaC*l*O in 100 cm^3 of water.

For effective disinfection, a pH of 7.35 was needed to reach the optimal $[ClO^-]$:[HC*l*O] ratio.

Given that the pK_a of HC*l*O is 7.55, determine the optimal $[ClO^-]$:[HC*l*O] ratio and hence the mass of NaC*l*O, *x*. [2]

pH = pKa + lg $\frac{[ClO^-]}{[HClO]}$ **or**

7.35 = 7.55 + lg $\frac{[ClO^-]}{[HClO]}$

$\frac{[ClO^-]}{[HClO]}$ = • 0.631

[C*l*O$^-$] = 0.631 x $\frac{\left(\frac{10}{1+35.5+16}\right)}{\frac{100}{1000}}$

= 1.20 mol dm^{-3}

$K_a = \frac{[H_3O^+][ClO^-]}{[HClO]}$

$10^{-7.35} = \frac{(10^{-7.35})[ClO^-]}{[HClO]}$

$\frac{[ClO^-]}{[HClO]}$ = 0.631

Mass of C*l*O$^-$ which needs to be added **= $\frac{100}{1000}$ x 1.20 x (23 + 35.5 + 16)**

= • 8.95 g

(iii) A worker accidentally poured some alkaline solution into the disinfectant solution formed in **(a)(ii)** but found that the pH was still about 7.35.

Write an equation to explain this. [1]

- **$HClO + OH^- \rightarrow ClO^- + H_2O$**

Since OH^- is neutralised by the weak acid, there is negligible change in pH.

(b) Hydrogen chloride is another chlorine-containing compound.

Alkyl chlorides can be synthesised from alcohols using hydrogen chloride. However, acyl chlorides **cannot** be prepared from carboxylic acids in the same way. One key factor is due to the stronger C-O bond present in carboxylic acids.

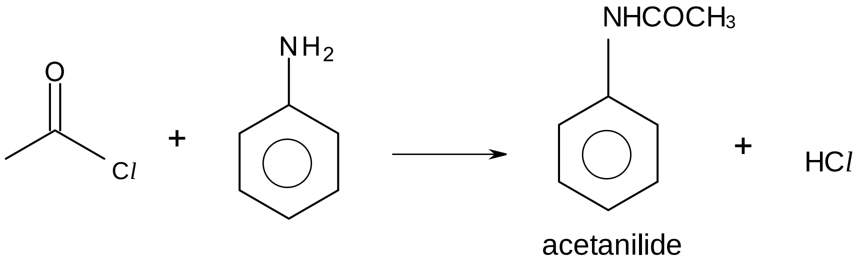
$$\mathrm{ROH} \xrightarrow{\mathrm{HC}l} \mathrm{RC}l$$

$$\mathrm{RCO_2H} \overset{\mathrm{HC}l}{\cancel{\longrightarrow}} \mathrm{RCOC}l$$

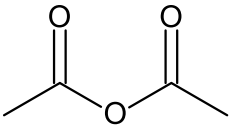
Suggest an explanation for the stronger C-O bond in carboxylic acids. [1]

- **The strengthening of the C-O bond is due to the effective <u>overlap/delocalisation of the lone pair of electrons on the O of the O-H into the C=O</u> resulting in a <u>partial double bond character</u>.**

(c) Acetanilide is an analgesic and can be formed from ethanoyl chloride and phenylamine.



Instead of ethanoyl chloride, ethanoic anhydride is more commonly used in the laboratory to form acetanilide in a similar manner.



ethanoic anhydride

(i) Suggest the other organic product that is produced together with acetanilide. [1]

- **CH_3CO_2H**

The experimental procedure for the laboratory synthesis of acetanilide using ethanoic anhydride is given below.

1. Mix phenylamine and hydrochloric acid in a beaker.
2. Stir the mixture until a clear solution is obtained.
3. To the clear solution, add ethanoic anhydride and immediately add a solution of sodium ethanoate.
4. Stir the mixture vigorously.
5. Cool the solution in an ice water bath.
6. Filter the acetanilide formed. Wash with cold water and crystallise using a mixture of water and methanol.

(ii) In step 1, HC*l* was added to increase the solubility of phenylamine in water. Explain. [1]

- **$C_6H_5NH_3^+$ is formed which forms ion-dipole interactions with water and hence is more soluble than $C_6H_5NH_2$ which has a non-polar benzene ring.**

(iii) Sodium ethanoate is essential to ensure phenylamine is present in step 3 to react with ethanoic anhydride.

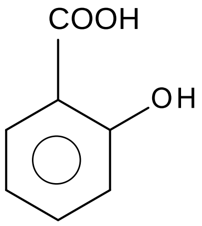
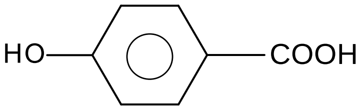
Suggest the role of sodium ethanoate. [1]

- **Sodium ethanoate acts as a base to react with $C_6H_5NH_3^+$ to regenerate the free amine so that it can act as a nucleophile.**

(iv) Suggest how you could check that the acetanilide obtained in step 6 is pure. [1]

- **Determine the melting point of the acetanilide obtained. If the melting point has a narrow range/fixed temperature, it is pure.**

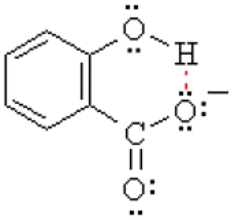
(d) Aspirin is another analgesic and it can be synthesised from salicylic acid. The pK_a values of salicylic acid and its isomer are given below:

Acid	pK_{a1}	pK_{a2}
 Salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

(i) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **This is because the 2-hydroxybenzoate ion is stabilised by intramolecular hydrogen bonding. In 4-hydroxybenzoate ion, the –OH group is too far away for hydrogen bonding to form.**



(ii) pK_{a2} is larger than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **Electrostatically unfavourable / more difficult to remove H^+ from a negatively charged anion, conjugate base less likely to dissociate 2nd H^+.**

OR

- **Removal of 2nd H^+ would destabilise the anion as stabilisation by intramolecular H-bonding is no longer present.**

(e) When compound **A**, $C_{10}H_{11}NO$, is oxidised with acidified manganate(VII) ions, $[C_7H_8NO_2]^+$ and compound **B**, $C_3H_4O_3$, are formed. Compound **B** produces effervescence when Na_2CO_3 is added to it and gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Compound **A** reacts readily with 4 moles of $Br_2(aq)$ to give compound **C**, $C_{10}H_9NO_2Br_4$.

Compound **A** also gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent and reacts with hot alkaline aqueous iodine to give compound **D**, $C_9H_8NO_2Na$.

Suggest the structures of compounds **A**, **B**, **C** and **D**. Explain the reactions that occur. [9]

[✔] A has a high C:H ratio, hence a benzene ring is present.

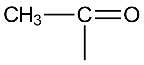
[✔] B undergoes acid-carbonate/acid-base/neutralisation reaction with Na_2CO_3, it has –CO_2H group or it is a carboxylic acid.

[✔] B undergoes condensation reaction with 2,4-dinitrophenylhydrazine. B is a product of strong oxidation, it is a ketone not aldehyde.

[✔] A undergoes condensation reaction with 2,4-dinitrophenylhydrazine. It can be a ketone or aldehyde/ carbonyl compound.

[✔]A undergoes electrophilic addition with aq Br_2, one Br atom and one OH atom are added at the carbon-carbon double bond of A (or confirm A has alkene group).

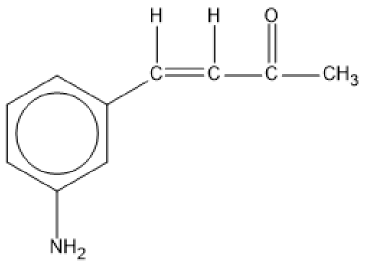
[✔] A undergoes electrophilic substitution with $Br_2(aq)$. Since C has 4 Br atoms, the remaining 3 Br atoms are at the benzene ring, implying that A is a phenylamine/ has activating group like NH_2 bonded to benzene and the [✔] 2-, 4- and 6- positions with respect to NH_2 group are unsubstituted.

[✔] A is undergoes <u>oxidation</u> with by alkaline aq iodine, suggesting that it <u>has</u>

$CH_3-\underset{|}{C}=O$
<u>group</u> and it forms a salt of carboxylic acid E.

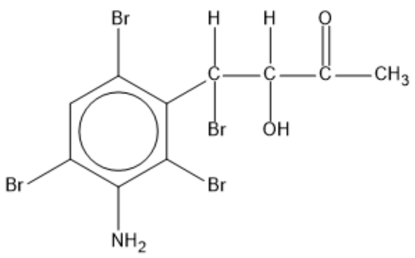
Every [✔]: 1 mark [Max: 5m]

A:

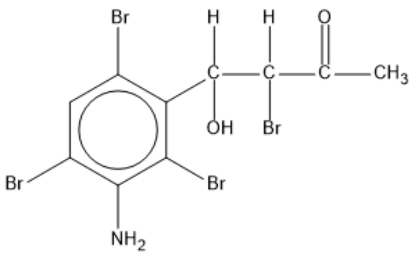
B: CH_3COCO_2H



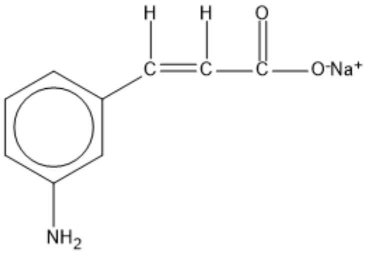
C:



or



D:



[Each structure 1m]

[Total: 20]

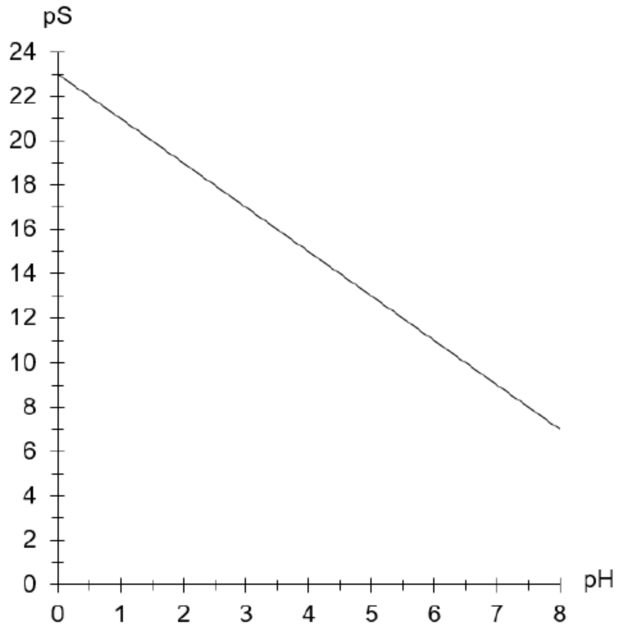
5 **(a)** Hydrogen sulfide gas, H_2S, is a reagent used in qualitative analysis. When H_2S is passed into a solution containing metal cations, metal sulfides are precipitated.

In aqueous medium, H_2S dissociates partially in a step-wise manner to give two equilibrium reactions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The relationship between the H^+ ion concentration and S^{2-} ion concentration, as a result of H_2S dissociation, is shown in the graph below, where $pS = -\log_{10}[S^{2-}]$.



Solution **X** contains 0.1 mol dm^{-3} $CuSO_4$ and 0.05 mol dm^{-3} $MnSO_4$. Hydrogen sulfide gas is bubbled into **X** until saturation and the pH is maintained at 2.0.

The value of the solubility product of CuS and MnS are 1.0×10^{-44} and 1.4×10^{-15}, respectively.

(i) With reference to CuS, define the term *solubility product*. [1]

K_{sp} of CuS is the • <u>product of the concentrations of Cu^{2+} ions and S^{2-} ions</u> in a <u>saturated solution</u> at a <u>given temperature</u>.

(ii) Calculate the minimum concentration of sulfide ions needed to precipitate CuS. [1]

K_{sp} of CuS = $[Cu^{2+}][S^{2-}] = 1.0\times10^{-44}$ mol^2 dm^{-6}

• Min $[S^{2-}]$ for precipitation of CuS = $1.0\times10^{-44}/0.1 = 1.0\times10^{-43}$ mol dm^{-3}

(iii) The minimum concentration of sulfide ions needed to precipitate MnS is 2.80×10^{-14} mol dm^{-3}.

Using the graph above and your answer in **(a)(ii)**, explain whether it is possible to separate copper and manganese ions in **X** at pH = 2. [2]

• From graph, when pH = 2, pS = 19 → $[S^{2-}] = 10^{-19}$ mol dm^{-3}

- **Since [S^{2-}] at pH = 2 is greater than min [S^{2-}] for precipitation of CuS but smaller than min [S^{2-}] for precipitation of MnS, ionic product of CuS exceeds its K_{sp}. Hence, only CuS will be precipitated and separation of the 2 ions is possible at pH = 2.**

OR

- **At pH = 2, pS = 19 → [S^{2-}] = 10^{-19} mol dm^{-3}**

- **Ionic product of CuS = 0.1×10^{-19} = $1.00 \times 10^{-20} > K_{sp}$**
  Ionic product of MnS = 0.05×10^{-19} = $5.00 \times 10^{-21} < K_{sp}$
  Only CuS is precipitated, so separation is possible.

(iv) Determine the maximum pH for solution **X** before separation of copper and manganese ions is no longer possible. [1]

Max [S^{2-}] before MnS is precipitated = 2.80×10^{-14} mol dm^{-3}

pS = -lg 2.80×10^{-14} ≈ 13.5 *[accept range 13 to 14]*

From graph, when pS = 13.5, • pH = 4.75 *[Accept 4.5 < pH < 5.0]*

(b) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. The higher the value of K_{stab}, the more likely the complex will be formed.

The stability constants for 3 reactions are given below.

Reaction	Colour of complex formed	Value of $\log_{10}(K_{stab})$
$Fe^{3+}(aq) + 6CN^{-}(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$	Yellow	31.0
$Fe^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{-}(aq)$	Brown	25.1
$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$	Red	2.1

Describe the colour change(s) of the solution when excess NaSCN is added to $[Fe(EDTA)]^{-}$, followed by an excess of KCN(aq).

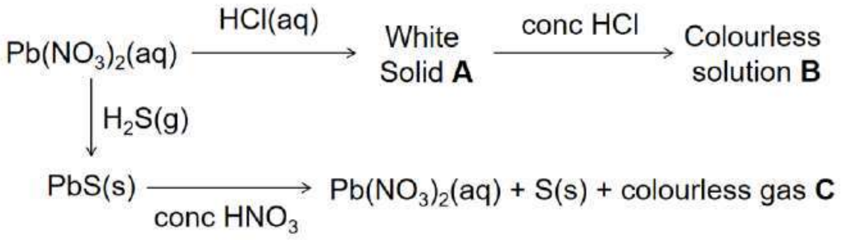
Explain the observation, with reference to the table above. [2]

Brown to yellow.

SCN^{-} cannot substitute $EDTA^{4-}$ as $[Fe(SCN)]^{2+}$ is less stable than $[Fe(EDTA)]^{-}$ from a lower K_{stab} value, so colour remains brown.

CN^{-} can substitute $EDTA^{4-}$ ligands as $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(EDTA)]^{-}$ from a larger K_{stab} value, so colour changes from brown to yellow.

(c) A solution of $Pb(NO_3)_2$ is subjected to the following reactions.



(i) Suggest the identity of white solid **A** and complex anion present in colourless solution **B**. [2]

A is • $PbCl_2$

B is • $[PbCl_4]^{2-}$

(ii) Colourless gas **C** is obtained from the reaction of solid PbS and concentrated HNO_3, which is readily oxidised in air to form a brown acidic gas.

Suggest the identity of **C**. [1]

• NO

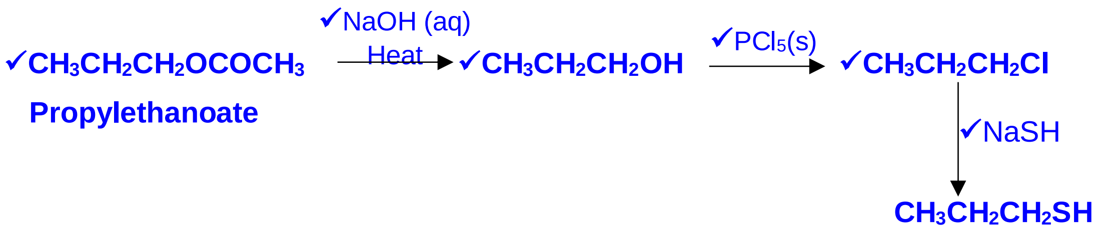
(d) Thiols are sulfur-containing compounds that can be prepared from alkyl halides and the hydrosulfide nucleophile, ^{-}SH.

Ethanethiol is prepared from chloroethane using NaSH as shown below.

$$CH_3CH_2Cl \xrightarrow{NaSH} \underset{\text{Ethanethiol}}{CH_3CH_2SH}$$

(i) Suggest a synthesis of propanethiol starting from propylethanoate.

You should state the reagents and conditions for each step, and show clearly the structure of any intermediate compounds. [3]



6 ✓ 3m 3-5 ✓ 2m 2✓ 1m

CH_3CH_2SH can react with a base, NaH, to give $CH_3CH_2S^-$.

$CH_3CH_2SH + NaH \rightarrow CH_3CH_2S^-Na^+ + H_2$ ----- Reaction 1

$CH_3CH_2S^-$ further reacts with chloroethane, to yield diethyl sulfide

$CH_3CH_2S^-Na^+ + CH_3CH_2Cl \rightarrow CH_3CH_2SCH_2CH_3 + NaCl$ ----- Reaction 2

Diethyl sulphide

(ii) Suggest why $CH_3CH_2S^-$, is a better nucleophile than $CH_3CH_2O^-$. [1]

• The valence electron (3p) on S are <u>further away and less tightly held</u>, hence they are stronger nucleophiles.

[Alternative answers: Oxygen is <u>more electronegative</u> than Sulfur and hence <u>less likely to donate the lone pair of electrons</u>. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.

or Oxygen is <u>smaller</u> than sulfur and the electrons are <u>closer and more strongly held</u> than that in sulfur. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.]

(iii) Diethyl sulfide is a good nucleophile.

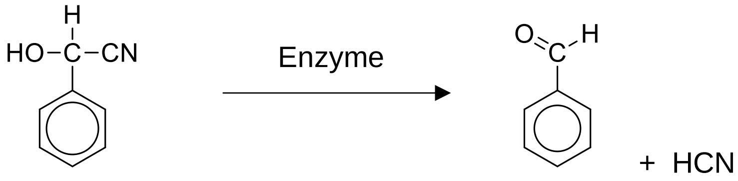
In Reaction 2, a side product, $C_6H_{15}SCl$, is formed when chloroethane is used in excess. $C_6H_{15}SCl$ gives a white precipitate with aqueous silver nitrate.

Suggest the structural formula of the side product $C_6H_{15}SCl$. [1]

Free Cl^- anion is present and the white ppt formed is AgCl

• $(CH_3CH_2)_3S^+ Cl^-$ (Similar to RX reaction with ammonia)

(e) The millipede *Apheeloria corrugate* protects itself by secreting the cyanohydrin mandelonitrile and an enzyme that decompose mandelonitrile into benzaldehyde and HCN.



Mandelonitrile

(i) State the type of reaction for the formation of Mandelonitrile from benzaldehyde. [1]

• Nucleophilic addition

(ii) Suggest a chemical test that will give a positive test for Mandelonitrile but not for benzaldehyde. [2]

1. **Na(s),**

   Observation: H_2(g) evolved with Mandelonitrile but not benzaldehyde
2. **PCl_5(s)**

   Observation: White fumes of HCl(g) evolved with Mandelonitrile but not benzaldehyde
3. **NaOH(aq), heat**

   Observation: NH_3(g) evolved with Mandelonitrile but not benzaldehyde

(iii) A student made the following statement, “benzaldehyde can be directly synthesized from phenylmethanol, $C_6H_5CH_2OH$, but not from benzoic acid.”

Based on your knowledge of the reagents and conditions for each reaction, deduce if the statement is true. [2]

The statement made by the student is true.

- **Benzaldehyde can be formed from phenylmethanol via oxidation using acidified $K_2Cr_2O_7$ warm with immediate distillation. Upon distillation, the aldehyde can be separated and not be further oxidized to propanoic acid.**

- **Benzoic acid can only be reduced by $LiAlH_4$ and it reduces directly back to phenylmethanol and benzaldehyde cannot be isolated.**

[Total: 20]

TEMASEK
JUNIOR COLLEGE

2019 JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	

CIVICS GROUP			/		

CENTRE NO. / INDEX NO.					/				

CHEMISTRY **9729/04**

Paper 4 Practical **2 September 2019**

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 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	/ 18
2	/12
3	/15
4	/ 10
Total	/ 55

This document consists of 18 printed pages and 2 blank pages.

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

1 Determination of the concentration of a solution of hydrogen peroxide

Hydrogen peroxide, H_2O_2, can be oxidised to give oxygen, O_2. This reaction happens rapidly in the presence of acidified potassium manganate(VII), $KMnO_4$.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

To determine the concentration of a solution of hydrogen peroxide, you will first dilute the solution and then carry out a titration using acidified potassium manganate(VII), $KMnO_4$.

FA 1 is aqueous hydrogen peroxide.
FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.

Keep **FA 1** for use in **Question 4.**

(a) Method

Dilution

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 volumetric flask.
- Add distilled water to make 250 cm^3 of solution and shake the flask thoroughly.
- Label this diluted solution of hydrogen peroxide as **FA 4**.

Titration

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 4** into a conical flask.
- Use the measuring cylinder to add 25 cm^3 of **FA 3** to the conical flask.
- Titrate **FA 4** against **FA 2** and record your readings in the space below.
- Carry out as many accurate titrations as you think necessary.

Results

Final burette reading /cm^3	**20.70**	**20.80**
Initial burette reading /cm^3	**0.00**	**0.00**
Volume of FA 2 /cm^3	**20.70**	**20.80**
	√	√

- Appropriate headings and units.
- All accurate burette readings recorded to 0.05 cm^3.
- Has two uncorrected, accurate titres value within ±0.10 cm^3.

●● 2m – accuracy

[5]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

- **Average titre = $\frac{20.70+20.80}{2}$**

= 20.75 cm^3

25.0 cm^3 of **FA 4** required 20.75 cm^3 of **FA 2** for titration

[1]

(c) Calculations

Show your working and give appropriate significant figures in the final answer for **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 2** calculated in **(b).**

- **Amount of MnO_4^- present in 20.75 cm^3 of FA 2**

$= \frac{20.75}{1000} \times 0.0200$

= 4.15 x 10^{-4} mol

amount of $KMnO_4$ = **4.15 x 10^{-4} mol** [1]

(ii) Calculate the amount of hydrogen peroxide present in 25.0 cm^3 of **FA 4**.

$2MnO_4^-(aq) \equiv 5H_2O_2(aq)$

- **Amount of H_2O_2 in 25 cm^3 of FA 4**

= 4.15 x 10^{-4} x $\frac{5}{2}$

= 1.04 x 10^{-3} mol (3sf)

amount of H_2O_2 in 25.0 cm^3 of **FA4** = **1.04 x 10^{-3} mol** [1]

(iii) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 4.**

- **Concentration of H_2O_2 in FA 4**

= 1.04 x 10^{-3} x $\frac{1000}{25}$

= 0.0415 mol dm^{-3} (3sf)

concentration of H_2O_2 in **FA 4** = **0.0415 mol dm^{-3}** [1]

(iv) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 1.**

Amount of H_2O_2 in 250 cm^3 of FA 4 = Amount of H_2O_2 in 25 cm^3 of FA 1

= $1.04 \times 10^{-3} \times \frac{250}{25}$ mol

= 0.0104 mol

● Concentration of H_2O_2 in FA 1

= $0.0104 \times \frac{1000}{25}$

= 0.415 mol dm^{-3} (3sf)

OR

Dilution factor = 250 / 25 = 10

● Concentration of H_2O_2 in FA 1 = 0.0415 x 10 = 0.415 mol dm^{-3}

concentration of H_2O_2 in **FA 1** = **0.415 mol dm^{-3}** [1]

(d) Another experiment was conducted to determine the concentration of hydrogen peroxide. Different volumes of hydrogen peroxide were added to identical 25.0 cm^3 samples of 0.0400 mol dm^{-3} aqueous iron(II) solution. Iron (II) is oxidised by hydrogen peroxide as shown by the following equation.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

The remaining iron(II) ions in each of the resulting mixtures were then titrated against potassium manganate(VII) and the results are shown in the table below:

Volume of H_2O_2 added / cm^3	**Volume of $KMnO_4$ / cm^3**
2.00	11.60
12.00	5.20
16.00	2.60
25.00	3.40
30.00	6.70
35.00	10.00

(i) Plot, on the grid on page 5, your values for the volume of potassium manganate(VII) (*y-axis*) against the volume of hydrogen peroxide added (*x-axis*).

Draw two straight lines of best fit, taking into account all of your plotted points.

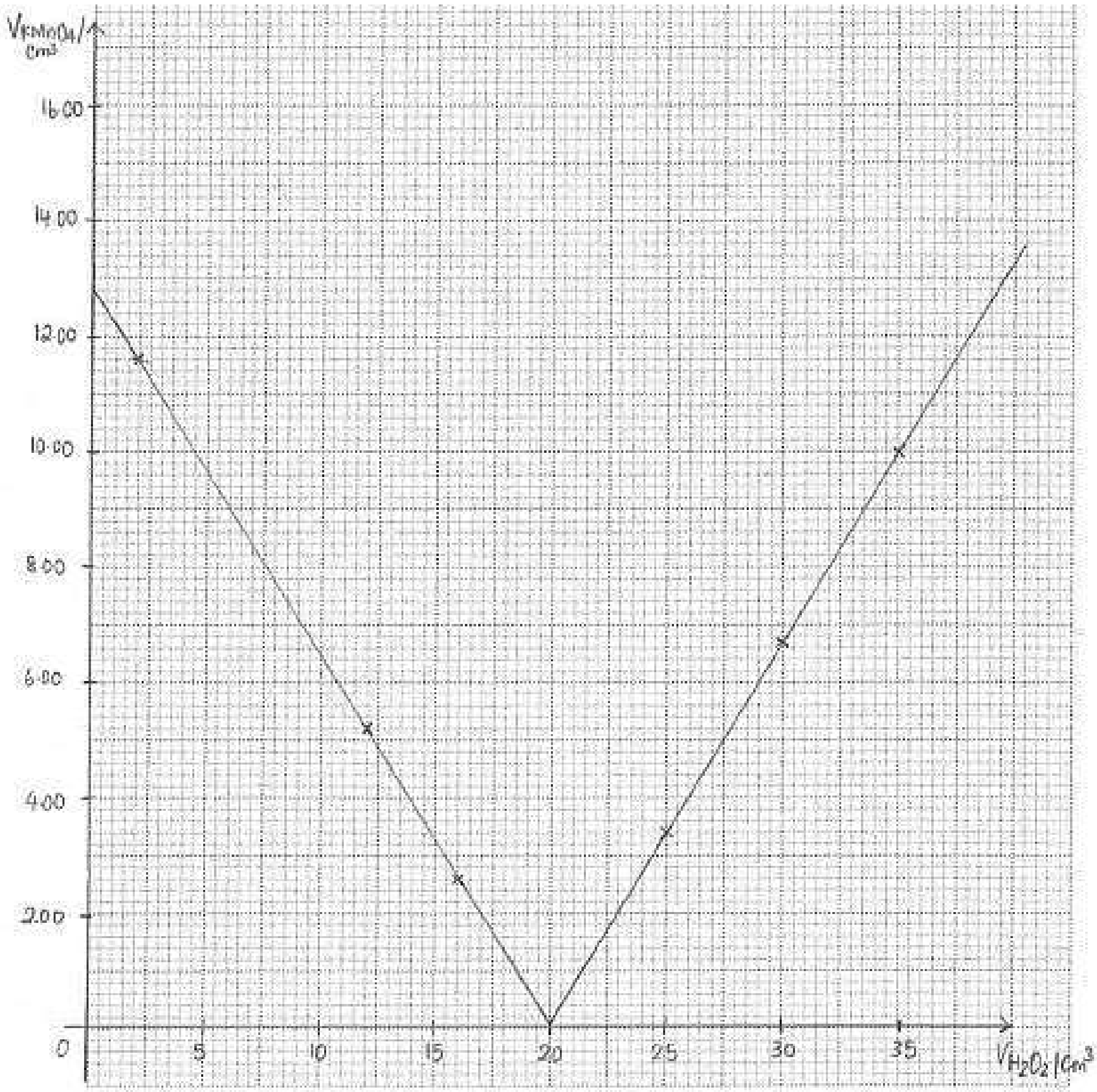
Your graph should enable you to determine the values for **(d)(ii)**.

[3]

(ii) Hence obtain values for

- the volume of potassium manganate(VII) required, $V_{max}(KMnO_4)$, to react completely with 25.0 cm^3 of iron(II) solution if no hydrogen peroxide is added.
- the volume of hydrogen peroxide required, $V_{max}(H_2O_2)$, to react completely with 25.0 cm^3 of iron(II) solution if no potassium manganate(VII) is added.

[1]



●Clearly labelled axes. Appropriate scale starting from origin and allowing the plotted points to be more than half given grid.

●correctly plotted points

●2 best-fit straight lines

$V_{max}(KMnO_4)$ = **12.8 cm^3**

$V_{max}(H_2O_2)$ = **20.0 cm^3**

● 1 mark for both values (only if the 2 lines intersect at x-axis)

(iii) Determine the concentration of hydrogen peroxide in mol dm^{-3} in this experiment.

$2Fe^{2+} \equiv H_2O_2$

Amount of Fe^{2+} in 25.0 cm^3 of solution = $\frac{25}{1000} \times 0.04$ = 1.00×10^{-3} mol

●Amount of H_2O_2 in 20 cm^3 of solution = $1.00 \times 10^{-3} \times ½ = 5.00 \times 10^{-4}$ mol

(●using Vmax(H_2O_2)) Concentration of H_2O_2 solution = $5.00 \times 10^{-4} \times \frac{1000}{20}$

= 0.0250 mol dm^{-3}

(*allow ecf from (ii)*)

● All calculations to 3 significant figures

● correct units for all calculated values

Concentration of hydrogen peroxide = **0.0250 mol dm^{-3}**

[4]
[Total: 18]

2 Determination of the enthalpy change of reaction, ΔH$_r$

You are to determine the enthalpy change of reaction, ΔH$_r$, for the following reactions:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_1$$
$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

FA 5 is anhydrous sodium carbonate, Na_2CO_3

FA 6 is solid sodium hydrogen carbonate, $NaHCO_3$

You are also provided with 2.0 mol dm^{-3} HC*l*

(a) Reaction of FA 5, Na_2CO_3, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the weighing bottle containing **FA 5**, anhydrous sodium carbonate.
5. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA 5 all at once. The reaction is very vigourous.]

6. Stir and record the highest temperature obtained.
7. Reweigh the weighing bottle containing residual **FA 5**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m_1**, of **FA 5** added and the maximum temperature rise, **ΔT_1**.

Results

Mass of weighing bottle and FA 5	**/ g**	**51.64**
Mass of weighing bottle and residual FA 5	**/ g**	**45.60**
Mass of FA5 (Na_2CO_3) added to acid (m_1)	**/ g**	**6.04**

Initial temperature of HC*l*	**/ °C**	**29.5**
Maximum temperature	**/ °C**	**37.5**
Maximum temperature rise (ΔT_1)	**/ °C**	**8.0**

- **(for both (a) and (c)): mass table and table recording temperature changes with appropriate headers**
- **Record every mass reading to 2 dp and temperature recorded to 1dp**

[2]

(b) **(i)** Calculate the temperature rise per gram of **FA 5**, Na_2CO_3, used in the experiment.

- **$\frac{\Delta T_1}{m_1}$ = 8.0 / 6.04 = 1.32 °C g^{-1}**
- **Accuracy**

Calculate the difference between the Supervisor and candidate values of ∆T/m. Give 1 mark for a difference up to ±0.2 °C g^{-1}.

$\frac{\Delta T_1}{m_1}$ = **1.32 °C g^{-1}**

[2]

(ii) Calculate the enthalpy change, ΔH_1, for the reaction

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_1 = -(22.79 \times \frac{\Delta T_1}{m_1})\ \text{kJ mol}^{-1}$$

$\Delta H_1 = -(22.79 \times \frac{\Delta T_1}{m_1})$

•$\Delta H_1 = -(22.79 \times 1.32) =$ <u>– 30.2 kJ mol^{-1}</u>

ΔH_1 = **– 30.2 kJ mol^{-1}**

[1]

(c) Reaction of FA 6, $NaHCO_3$, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support another styrofoam cup in the 250 cm^3 beaker provided.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the empty weighing bottle labelled **"FA 6"**.
5. Weigh approximately 7.0 – 8.0 g of **FA 6**, anhydrous sodium hydrogen carbonate into the empty weighing bottle labelled **"FA 6"**.
6. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA6 all at once. The reaction is very vigourous.]

7. Stir and record the lowest temperature obtained.
8. Reweigh the weighing bottle containing residual **FA 6**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m_2**, of **FA 6** added and the maximum temperature fall, **ΔT_2**.

Results

Mass of empty weighing bottle	**/ g**	**44.89**
Mass of weighing bottle and FA 6	**/ g**	**52.49**
Mass of weighing bottle and residual FA 6	**/ g**	**44.90**
Mass of FA 6 ($NaHCO_3$) added to acid (m_2)	**/ g**	**7.59**

Initial temperature of HC*l*	**/ °C**	**29.5**
Minimum temperature	**/ °C**	**18.0**
Fall in temperature (ΔT_2)	**/ °C**	**11.5**

[Marks awarded together with (a)]:

mass table and table recording temperature changes with appropriate headers
Record every mass reading to 2 dp and temperature recorded to 1dp

(d) (i) Calculate the temperature fall per gram of **FA 6**, $NaHCO_3$, used in the experiment.

●$\frac{\Delta T_2}{m_2}$ **= (11.5/ 7.59) = 1.52 °C g^{-1}.**

●**Accuracy**

Calculate the difference between supervisors' value and the candidate's value of ΔT/m.

Give 1 mark for a difference up to ±0.2 °C g^{-1}

$\frac{\Delta T_2}{m_2}$ = 1.52 °C g^{-1}

[2]

(ii) Calculate the enthalpy change, ΔH_2, for the reaction

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_2 = +\left(18.06 \times \frac{\Delta T_2}{m_2}\right) \text{ kJ mol}^{-1}$$

$\Delta H_2 = +\left(18.06 \times \frac{\Delta T_2}{m_2}\right)$

- **$\Delta H_2 = +(18.06 \times 1.52) =$ + 27.5 kJ mol^{-1}**

ΔH_2 = **+ 27.5 kJ mol^{-1}**

[1]

(e) (i) The smallest graduation in reading a –10 °C to +110 °C thermometer is 1.0 °C

Suggest the maximum error of the temperature change calculated with two temperature readings.

Error = ½ of smallest graduation = ±0.5 °C

- **Maximum error = 2 x 0.5 = ±1.0°C**

Maximum error = ±1.0°C

[1]

(ii) The expected fall in temperature when 1.0 g of $NaHCO_3(s)$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is approximately 1.5°C

Determine the maximum percentage error in the calculated temperature change when 1.0 g of $NaHCO_3$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid.

- % error = $\frac{1.0}{1.5}$ x 100% = 66.7%

Maximum percentage error = 66.7%

[1]

(f) It is not possible to measure experimentally the enthalpy change, ΔH_3, for the following reaction as it does not take place in the laboratory.

$$Na_2CO_3(s) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(s)$$

It is possible, however, to calculate a “theoretical” value of ΔH_3 for this reaction from the results of the experiments you have carried out.

Using an energy cycle and your results from **(b)(ii)** and **(d)(ii),** calculate a value for ΔH_3.

●Energy cycle with state symbols

$$\begin{tikzcd}
2HCl(aq) + Na_2CO_3(s) + H_2O(l) + CO_2(g) \arrow[rr, "\Delta H_3"] \arrow[dr, "\Delta H_1"'] & & 2NaHCO_3(s) + 2HCl(aq) \arrow[dl, "2\Delta H_2"] \\
& 2NaCl(aq) + 2CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

● By Hess’ Law,

$\Delta H_3 = \Delta H_1 - (2 \times \Delta H_2)$

$\Delta H_3 = (-30.2) - 2(+27.5) = -85.2$ kJ mol^{-1}

ΔH_3 = **-85.2 kJ mol^{-1}**

[2]

[Total: 12]

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.

Rinse and reuse test-tubes and boiling tubes where possible.

(a) **FA 7, FA 8** and **FA 9** are aqueous solutions that each have an ion containing one of the metals from those listed in the Qualitative Analysis Notes.

FA 1 from Question 1 are to be used in some of these tests.

Carry out the following tests and record your observations.

	Test	*Observation*
(i)	To a 1 cm depth of **FA 7** in a test-tube, add a 1 cm depth aqueous sodium hydroxide. Then, add several drops of **FA 1**.	**√ Off-white ppt formed turns brown on contact with air, insoluble in excess NaOH** **√ Black or brown solid (ppt) formed** **Effervescence seen.** √(Colourless, odourless) **gas evolved relights a glowing splint**
(ii)	To a 1 cm depth of **FA 8** in a test-tube, add a few drops of aqueous sodium hydroxide. Then, add excess aqueous sodium hydroxide.	**√ Green ppt formed, turns brown on standing, insoluble in excess NaOH**
(iii)	To a 1 cm depth of **FA 8** in a test-tube, add several drops of **FA 1,** and then add aqueous sodium hydroxide.	**√ Solution turned darker yellow.** **√ Red-brown ppt formed insoluble in excess NaOH** **Effervescence seen.** **√ (colourless, odourless) gas evolved relights a glowing splint**
(iv)	To a 1 cm depth of **FA 8** in a test-tube, add a 1 cm depth of dilute sulfuric acid, and then a few drops of **FA 9**.	**√ Purple FA 9 decolourises to form a colourless/ (pale-yellow/ pale-orange) solution.**
(v)	To a 1 cm depth of aqueous potassium iodide in a test-tube, add a few drops of **FA 9**. Then, add a few drops of starch solution	**√ Brown solution formed / black ppt formed.** **√Solution turned blue-black** **Every 2 √ = 1m**

[5]

(b) Identify the cation present in **FA 7** and **FA 8**.

The cation present in **FA 7** is **•Mn^{2+}**

The cation present in **FA 8** is **•Fe^{2+}**

[2]

(c) Explain the chemistry involved in the effervescence observed in both **(a)(i)** and **(a)(iii).**

[1]

●Gas evolved is O_2. Mn^{2+} and Fe^{3+} present in the solution acts as a catalyst for the decomposition of H_2O_2. Hence, O_2 is produced.

(d) A student added 1 cm^3 of **FA 9** to a test-tube containing **FA 8**. A strip of magnesium ribbon was then added to the mixture. Effervescence was observed.

Deduce the identity of the gas evolved and explain the chemistry involved in this reaction.

[3]

●Gas evolved is H_2.

●Fe^{2+} in FA 8 was oxidized to Fe^{3+} by FA 9 (oxidizing agent)

●Fe^{3+} has a high polarizing power (high charge density), thus polarize the electron cloud of water, weaken the O-H bond, releasing H^+ into the solution, thus FA8 is acidic. Reactive metal Mg reacts with an acidic solution to release H_2 (g).

(e) **Figure 1** below shows the process of thermal decomposition of **FA 10**, which is a solid sample of the compound present in the aqueous solution of **FA 9**.

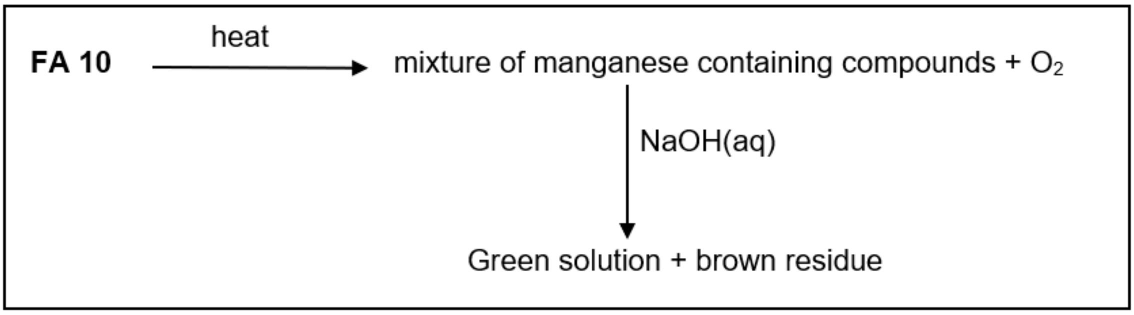


Figure 1

Consider the observations in **Figure 1**, suggest the identity of the manganese-containing species in the green solution and the residue.

● MnO_4^{2-}(solution) and MnO_2(residue)

[1]

(f) **FA 8** contains one of the anions Cl^-, Br^-, I^-, SO_4^{2-} or SO_3^{2-}.

Plan an experiment to determine the reagents you would use to identify which anion is present in **FA 8**.

Carry out your tests on **FA 8** to identify the anion present. Record your observations in the table below.

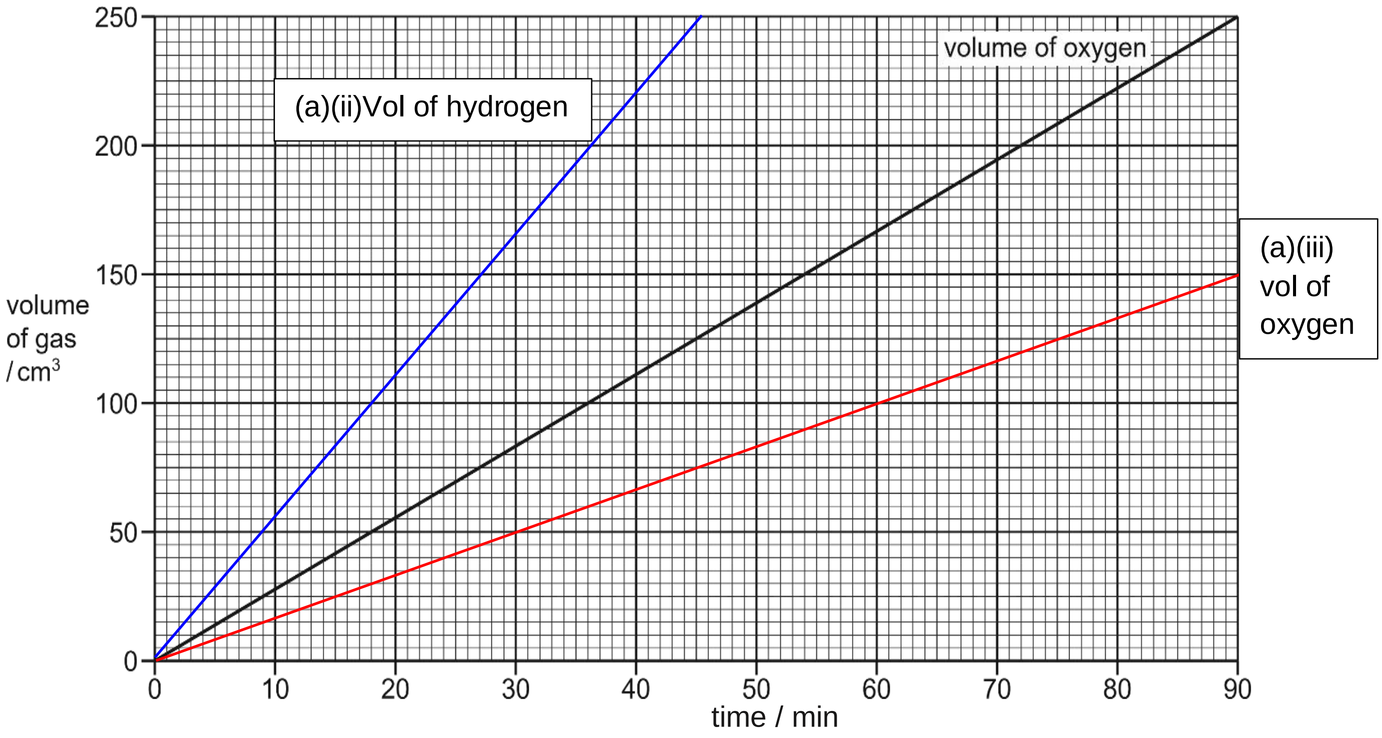
	Test	*Observations*
(i)	**To a 1 cm depth of FA 8, add 1 cm^3 of aqueous silver nitrate.**	**No ppt formed**
(ii)	**To a 1 cm depth of FA 8, add 1 cm^3 of √ aqueous barium nitrate, √ followed by nitric acid.** *[Note: cannot use sulfuric acid. Hydrochloric acid is acceptable]*	**√ White ppt formed,** **√ insoluble in HNO_3.**

Suggest the identity of the anion present in **FA 8**.

●sulfate / SO_4^{2-}

[3]
[Total:15]

4 (a) This question is about the electrolysis of different compounds.
During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 minutes, the volume of oxygen gas collected was recorded and is shown in the graph below.



(i) Table 1 below gives some standard electrode potential values

Electrode reaction	**$E^\ominus$ / V**
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Table 1

With reference to the values in the Table 1, write equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid.

[2]

- **Cathode :** $2H^+(aq) + 2e \longrightarrow H_2(g)$
- **Anode :** $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e$

On the graph on page 14,

(ii) Draw a straight line to show the volume of hydrogen evolved in the same experiment. Label the line as "hydrogen".

[1]

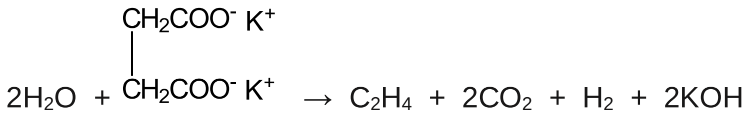
- **Straight line drawn from origin that has double the volume of oxygen at a given time.**

(iii) Draw a straight line to show the volume of oxygen evolved if a current of 0.45 A was used instead of the 0.75 A used in the original experiment. Label the line as "oxygen".

[1]

- **Straight line drawn from origin which has 0.45/0.75 x volume of oxygen at a given time.**

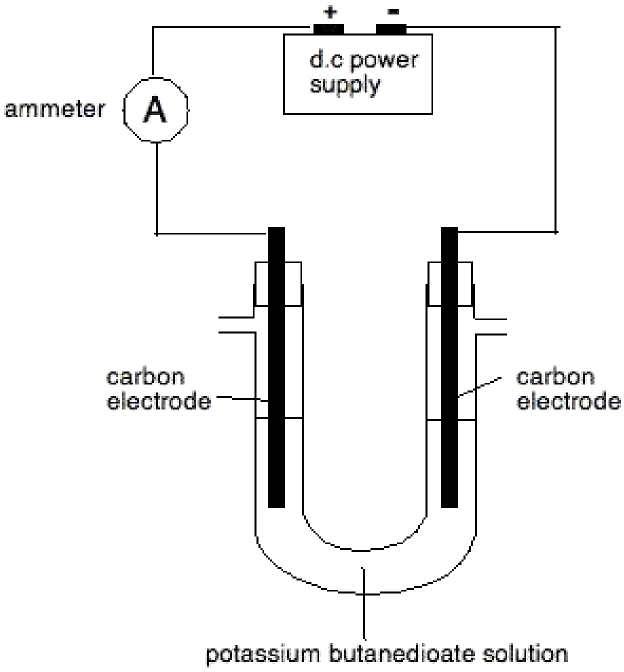
(b) During the electrolysis of potassium butanedioate, the following reaction occurs.



$$2H_2O + \begin{array}{l} CH_2COO^-\,K^+ \\ | \\ CH_2COO^-\,K^+ \end{array} \rightarrow C_2H_4 + 2CO_2 + H_2 + 2KOH$$

potassium
butanedioate

An experiment can be conducted to verify the stoichiometric ratio between hydrogen gas and ethene gas collected using the following set-up.



Hydrogen is produced at one electrode, ethene and carbon dioxide are produced at the other. The carbon dioxide can be separated from the ethene by absorbing it using a suitable reagent before the volume of ethene is measured.

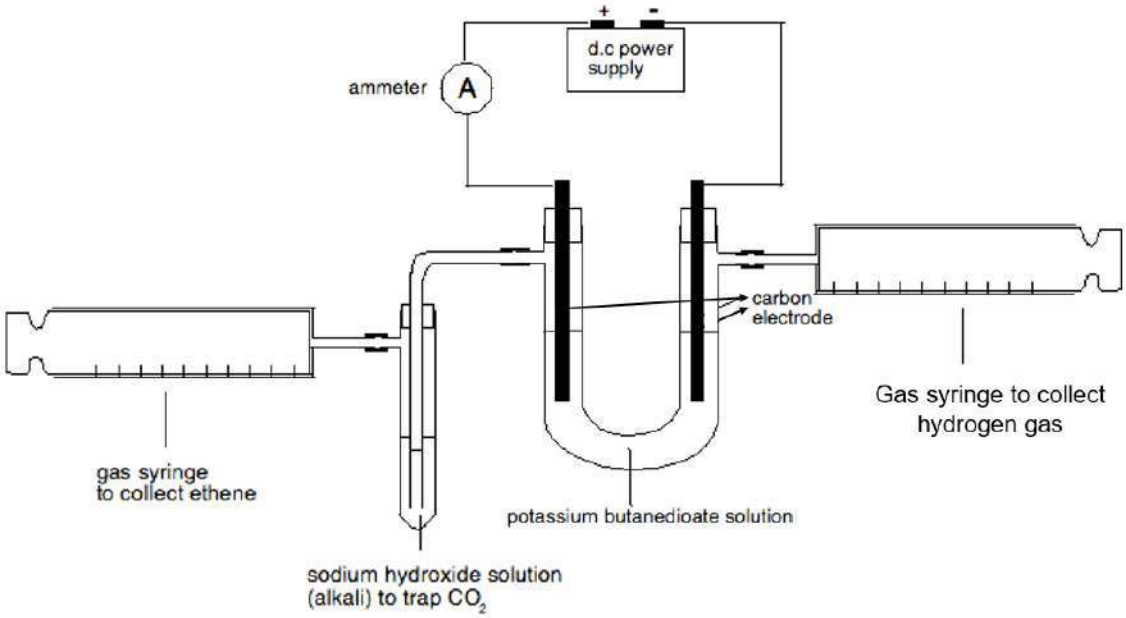
(i) Complete the diagram on page 15 to show how:

- the hydrogen could be collected and its volume measured,
- the carbon dioxide could be removed,
- the volume of ethene could be measured.

Your diagram should include appropriate apparatus and the identity of the suitable reagent used to remove carbon dioxide.

[3]

Answers:



√ Gases are released at the correct electrode (polarity)
√ Diagram shows collection of hydrogen using a means of measuring the volume of the gas
√ Diagram shows carbon dioxide from the anode being absorbed using an alkaline solution
√ Diagram shows ethene being collected using a means of measuring the volume of the gas

4√ : 3 m
2-3√ : 2m
1√ : 1 m
If use limewater not penalised here.

(ii) Calculate the number of coulombs, **N**, that would be required to produce **V** cm^3 of hydrogen at room temperature and pressure.

[1]

Amount of hydrogen = V/24000 mol

$2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Amount of electrons required = 2 x V/24000

● N = 2 x V/24000 x 96500 C
= 8.04V C

(iv) Write the equation for the reaction that takes place for the removal of carbon dioxide.

[1]

- **$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$**

(vi) Predict the organic product that would be obtained at the electrode when a solution of potassium *hexanedioate* is electrolysed.

[1]

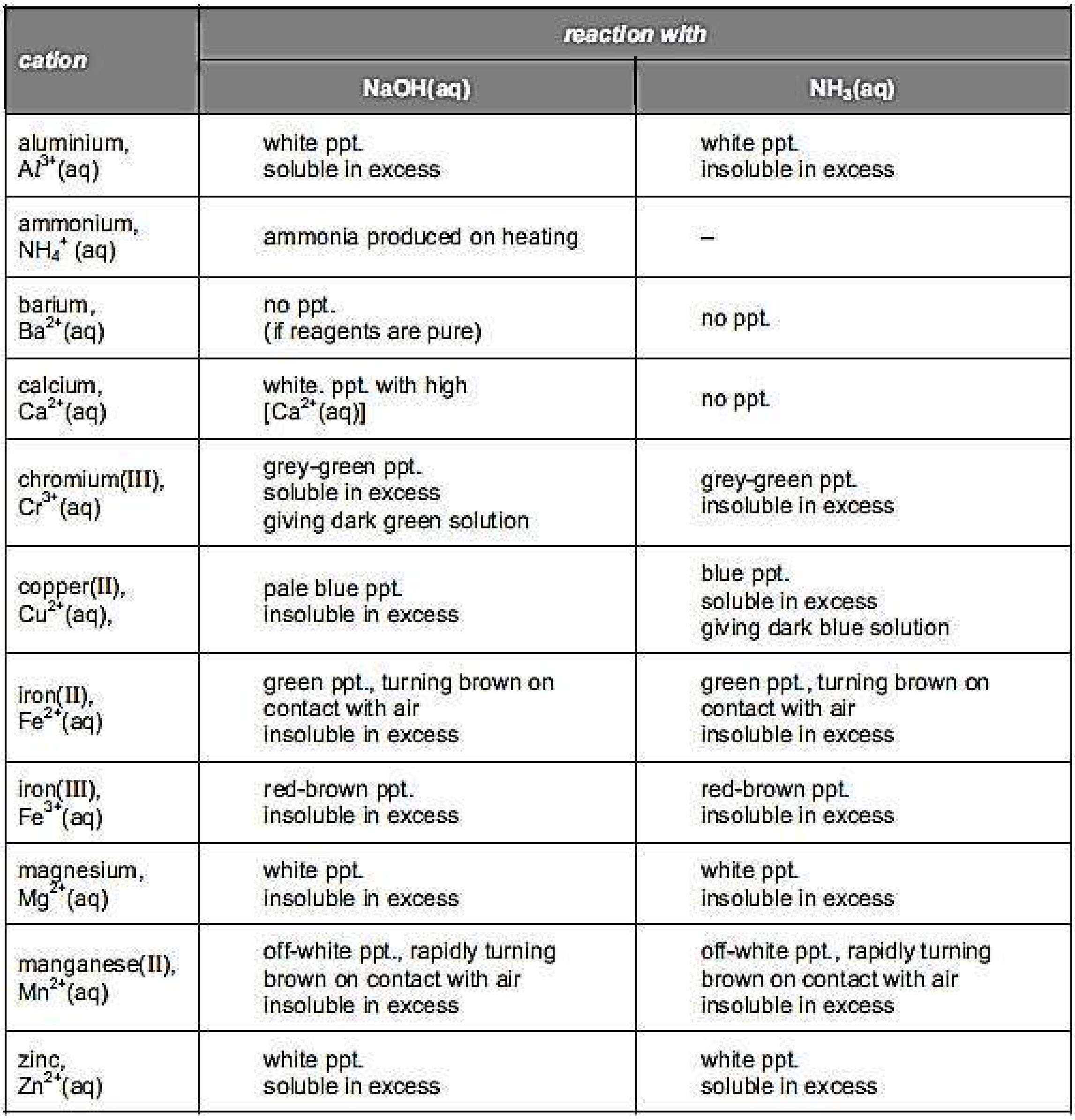
- **But-2-ene**

[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

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

Apparatus List

1. In addition to the fittings ordinarily contained in a chemical laboratory, the apparatus, and materials specified below will be necessary.

2. Pipette fillers (or equivalent safety devices), safety goggles and disposable plastic gloves should be used where necessary.

3. For each candidate

For each candidate

1 x burettes (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler;
1 x retort stands and burette clamps;
1 x 50 cm^3 measuring cylinder;
1 x funnels (for filling burette);
1 x 250cm^3 volumetric (graduated) flask
2 x 250 cm^3 conical flasks;
1 x 250cm^3 beaker
1 x white tile;
1 x thermometer with range -10 °C to +110 °C, graduated to 1 °C;
2 x styrofoam cup
4 plastic dropping pipettes;
5 test-tubes;
1 x test-tube rack;
1 x test-tube holder;
1 x delivery-tube (small one – for test-tube)
1 x small spatula
1 x wash bottle containing deionised water;
1 x Bunsen burner;
1 x lighter (per bench)
Water-soluble marker
wooden splinters
red and blue litmus paper
paper towels

Additional pipette filler, test-tubes and dropping pipettes should be available.

Chemicals Required

Question 1-3:

Label	**Per candidate**	**Identity**	**Notes (preparation)**
FA 1	70 cm^3	5 'vol' hydrogen peroxide	Dilute 50cm^3 of 100 'vol' hydrogen peroxide to 1 dm^3
FA 2	150 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	
FA 3	200 cm^3	1.0 mol dm^{-3} sulfuric acid	
FA 5	6.0 g – 7.0 g	Anhydrous sodium carbonate	Between 6.0 - 7.0 g of powdered Na_2CO_3 in a stoppered weighing bottle, labelled **FA 5.**
FA 6	6.0 g – 7.0 g	Sodium hydrogen carbonate	Place powdered $NaHCO_3$ beside weighing balance in lab (4 weighing balance in each lab). Each student would have 1 empty stoppered weighing bottle, labelled **FA6**.
2.0 mol dm^{-3} HCl	150 cm^3	2.0 mol dm^{-3} HC*l*	Bottled and labelled separately from QA reagents Labelled as '2.0 mol dm^{-3} HC*l*'.
FA 7	10 cm^3	0.2 mol dm^{-3} manganese (II) chloride	Dissolve 25.2 g of $MnCl_2$ (or 39.6g of $MnCl_2•4H_2O$) in each dm^3 of solution
FA 8	20 cm^3	0.1 mol dm^{-3} iron (II) ammonium sulfate	Dissolve 39.2 g of $Fe(NH_4)_2(SO_4)_2•6H_2O$ in acid Note: Cannot not prepare in acid as the solution gets oxidized quickly. If dissolve in acid, the solution is colourless.
FA 9	10 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	Labelled separately as '**FA 9**'. Different from **FA 2** labels.
Aqueous Starch	5 cm^3	Starch solution	
Potassium iodide	5 cm^3	0.1 mol dm^{-3} potassium iodide	

QA reagents required:

1. Dilute HC*l*
2. Dilute HNO_3
3. Dilute H_2SO_4
4. Aqueous NH_3
5. Aqueous NaOH
6. 0.1 mol dm^{-3} of Aqueous $Ba(NO_3)_2$
7. 0.05 mol dm^{-3} of aqueous silver nitrate ($AgNO_3$)
8. Limewater

2019 VJC H2 Chem Prelim P1
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.*

Which of the following statements are **incorrect**?

1 Both isotopes of $^{56}_{22}Ti$ and $^{58}_{22}Ti$ have more neutrons than electrons.

2 The first ionisation energy increases continuously from sodium to phosphorus as the number of protons increases but number of inner quantum shells remains the same.

3 The second ionisation energy of chromium is lower than the second ionisation energy of manganese as manganese has one more proton than chromium.

A **1, 2** and **3**

B **2** and **3** only

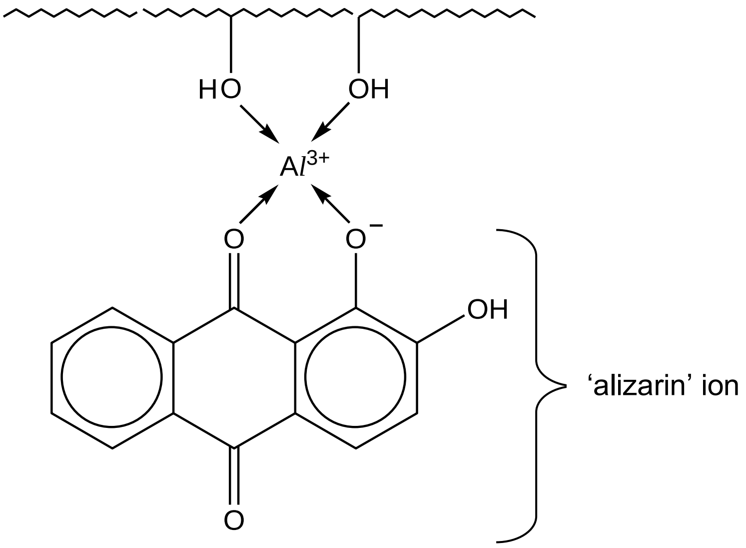
C **2** only

D **3** only

2 In which of the following pairs does the first substance have a higher melting point than the second substance?

	first substance	second substance
A	$CH_3CH_2OCH_3$	$CH_3CH_2NHCH_3$
B	$CH_3CH_2CH_2CH_2OH$	$CH_3CHClCH_2CH_2OH$
C	RbC*l*	KC*l*
D	$H_2NCH_2COCO_2H$	$H_2NCH_2CH_2CO_2H$

3 The dye 'alizarin' sticks fast to cotton when a 'mordant' containing aluminium ion is used. Under alkaline conditions, the aluminium ions become bonded to the hydroxyl groups of cotton. The dye 'alizarin' can then bond with the aluminium ions, giving the structure below which dyes cotton red.



Which statement is correct?

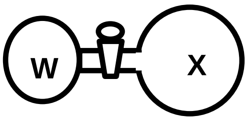
A The formula for 'alizarin' ion is $C_{14}H_9O_4^-$.

B There are 12 carbon atoms in the 'alizarin' ion that are sp^2 hybridised.

C In the absence of a mordant, alizarin can bind to cotton via hydrogen bonding.

D There is a decrease in the bond angles about the oxygen atoms of the cotton hydroxyl groups upon binding to aluminium ions.

4 Two vessels **W** and **X** are connected by a closed valve. Vessel **X** contains three times the volume of **W**.



W contains argon gas at 20 °C at a pressure of 1.00×10^5 Pa while **X** has been evacuated. In an experiment, the valve is opened and the temperature of the whole system is raised to T °C. The final pressure in the system decreases by 6.82×10^4 Pa.

What is the final temperature in the system?

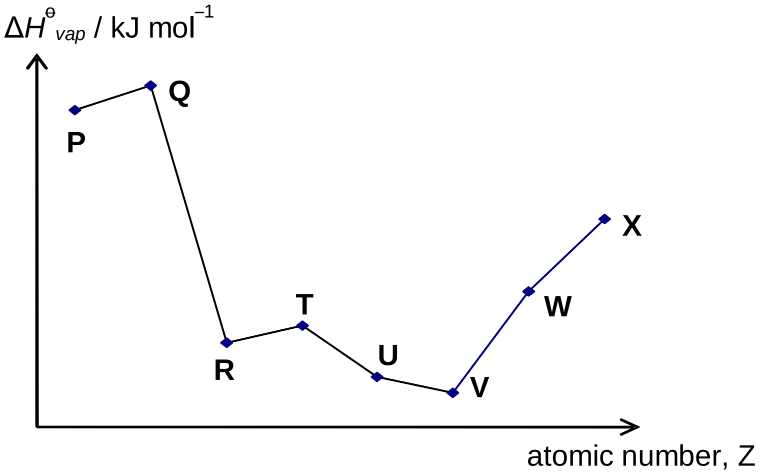
A 99.7 °C

B 373 °C

C 526 °C

D 799 °C

5 The graph below shows the variation in the standard enthalpy change of vaporisation, $\Delta H^{\ominus}_{vap}$, for eight consecutive elements in the Periodic Table, all with atomic number, $10 \le Z \le 20$.



Which one of the following statements is **incorrect**?

A Effervescence of hydrogen gas is observed when sodium is added to the solution containing chloride of element **P**.

B Element **U** is the most electronegative element among all the eight elements.

C When a mixture of the oxides of element **R** and element **W** is dissolved in water, the solution is approximately neutral.

D The oxide of element **Q** has a lower melting point than the oxide of element **T**.

6 Given a sample of strontium carbonate that was mixed with strontium nitrate, two separate experiments using the same mass of the solid mixture were conducted.

Experiment **1**: Excess dilute hydrochloric acid was added to the sample and volume of gas evolved was found to be 75 cm^3.

Experiment **2**: The sample was heated strongly to constant mass and the volume of gas evolved was found to be 200 cm^3.

All volumes were measured at the same temperature and pressure.

What is the mole ratio of strontium nitrate to strontium carbonate in the sample?

A 2 : 3

B 5 : 3

C 5 : 6

D 9 : 5

7 When H_2SO_4 is used to make an aqueous solution, the solution is found to contain H_2SO_4 molecules, H^+ ions, HSO_4^- ions and SO_4^{2-} ions.

Which one of the following statements best describes the system?

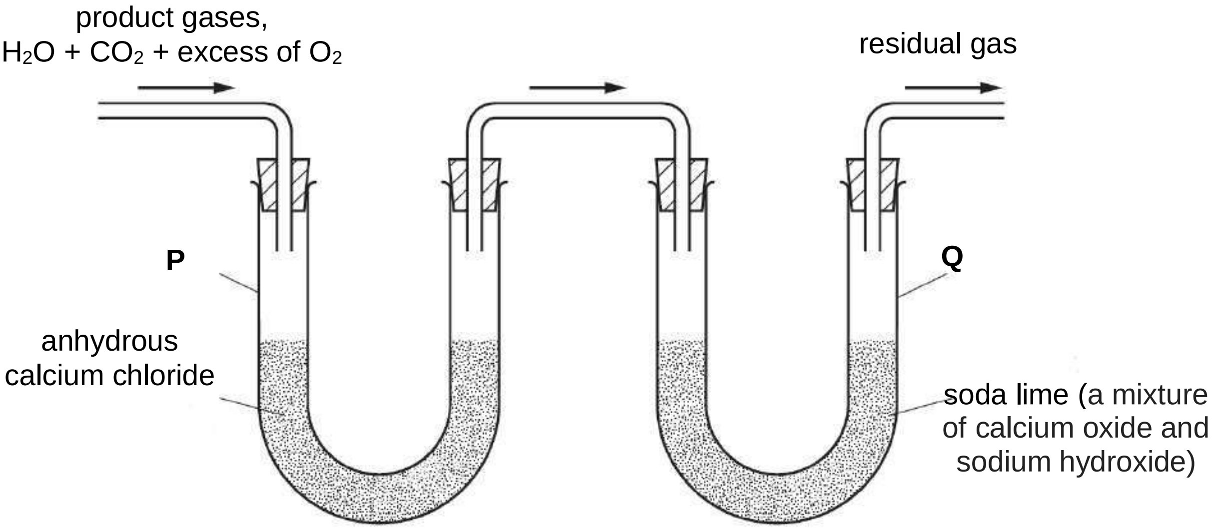
A The solution contains equal number of moles of H^+ ions and HSO_4^- ions.

B The solution contains equal number of moles of HSO_4^- ions and SO_4^{2-} ions.

C The number of moles of H_2SO_4 dissociated is equal to the sum of the number of moles of H^+ ions and HSO_4^- ions.

D The number of moles of H_2SO_4 dissociated is equal to the sum of the number of moles of HSO_4^- ions and SO_4^{2-} ions.

8 A 10 cm^3 sample of the hydrocarbon C_3H_8 is burned in excess oxygen and the product gases are collected as follows.



The increase in mass of the collecting vessels **P** and **Q** are M_P and M_Q respectively and the volume of the residual gas is V_R.

Which one of the following statements is **incorrect**?

A The ratio $\frac{V_R}{10}$ is equal to 5.

B The ratio $\frac{M_Q}{M_P}$ is equal to 1.8.

C The volume of residual gas, V_R, only contains excess O_2.

D The increase in mass in vessel **P**, M_P, is smaller than the increase in vessel **Q**, M_Q.

9 Which one of the following pairs contains identical enthalpy change values?

A	first ionisation energy of oxygen	–1 x first electron affinity of oxygen
B	standard enthalpy change of combustion of C(graphite)	standard enthalpy change of formation of $CO_2(g)$
C	standard enthalpy change of neutralization between $H_2SO_4(aq)$ and NaOH(aq)	standard enthalpy change of neutralization between $H_2SO_4(aq)$ and $NH_3(aq)$
D	bond energy of $F_2(g)$	standard enthalpy change of atomisation of $F_2(g)$

10 The table below gives the enthalpy changes and entropy changes for the dissolution of sodium chloride and magnesium chloride.

		$\Delta H^\ominus_{sol}$, kJ mol^{-1}	$\Delta S^\ominus_{sol}$, J mol^{-1} K^{-1}
I	$NaCl(s) + (aq) \rightarrow Na^+(aq) + Cl^-(aq)$	+3.87	+43.0
II	$MgCl_2(s) + (aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$	–155	–97.1

Which one of the following statements can be supported by the information given?

A Reaction **II** is more spontaneous than reaction **I** at higher temperatures.

B The hydration energy of Mg^{2+} is more exothermic than the hydration energy of Na^+.

C The system becomes more disordered when there is greater number of product particles.

D The lattice energy of $MgCl_2$ is more exothermic than the sum of the hydration energies of its ions.

11 When 10 g of calcium carbonate was added to 100 cm^3 of 0.10 mol dm^{-3} hydrochloric acid, the volume of CO_2 produced was recorded as follows:

time / s	0	50	75	100	125	150	175	200	225	250
total volume of CO_2 given off / cm^3	0	60	78	90	99	105	108	114	120	120

Which one of the following statements **cannot** be deduced from these results?

A The rate constant is around 0.02 s^{-1}.

B The rate of the reaction decreases with time

C The half-life of the reaction is around 50 seconds.

D The reaction is first order with respect to hydrochloric acid.

12 In the upper atmosphere, nitrogen oxides participate in the decomposition of ozone, O_3, via the following elementary steps:

reaction **I** : $O_3 \rightarrow O_2 + O$
reaction **II** : $O + NO_2 \rightarrow O_2 + NO$
reaction **III** : $O_3 + NO \rightarrow O_2 + NO_2$

Which of the following statements can be deduced from the information given?

1 The overall equation for the decomposition of ozone is $2O_3 \rightarrow 3O_2$.

2 Reaction **II** must take place before reaction **III** can occur.

3 Both NO and NO_2 can behave as a catalyst for the decomposition of ozone.

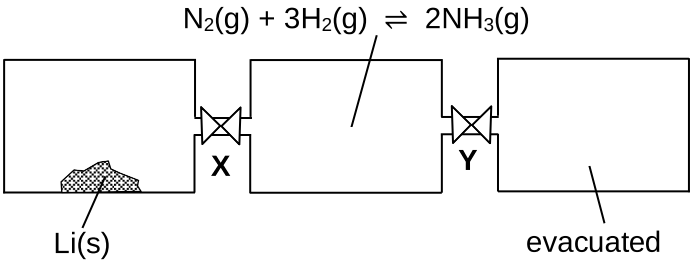
A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** and **3** only

13 Three vessels of equal volume are connected by taps, **X** and **Y**, as shown:



At the start, both taps are closed. The left-hand vessel contains lithium only, the middle vessel has the indicated reaction at equilibrium and the right-hand vessel is evacuated.

Lithium reacts with nitrogen at room temperature to form solid Li_3N.

Which one of the following actions will result in the most ammonia in the equilibrium mixture?

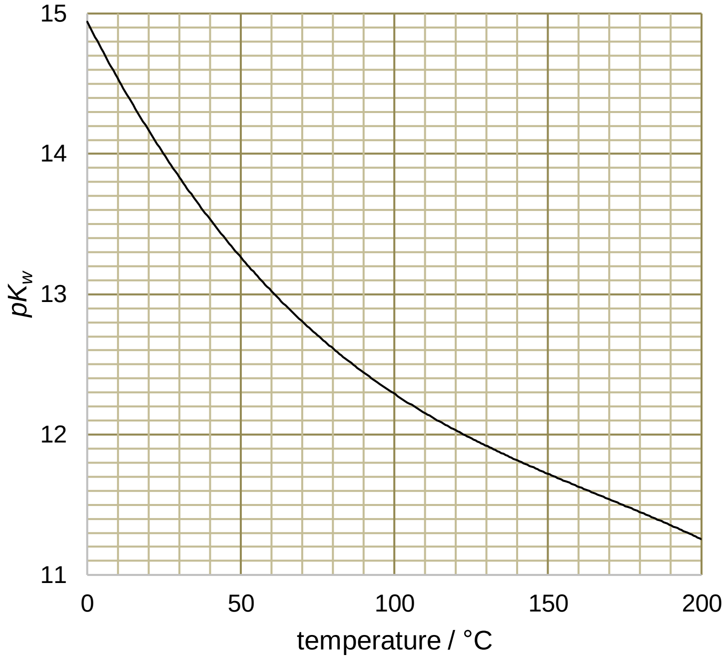
A open **X** only

B open **Y** only

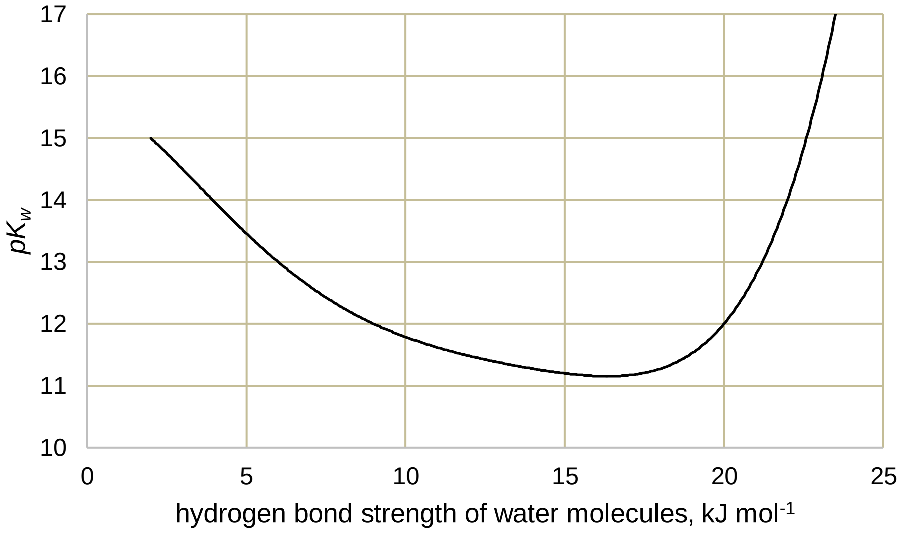
C open **X** and **Y**

D keep both **X** and **Y** closed

14 The graphs of pK_w against temperature and pK_w against strength of hydrogen bond of water molecules are given below.



graph 1: pK_w against temperature



graph 2: pK_w against hydrogen bond strength of water molecules

Which one of the following statements can be deduced from the graphs?

A The formation of extremely strong hydrogen bonds favours the dissociation of water molecules.

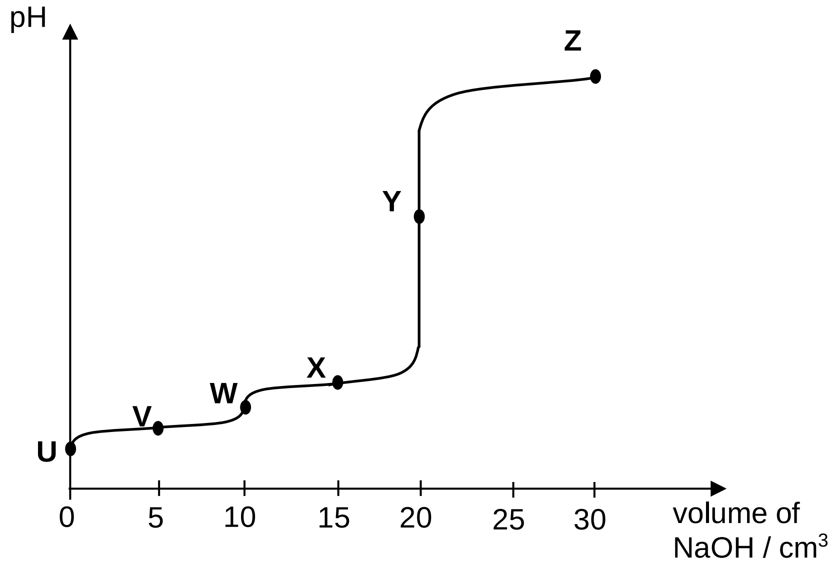
B There is more H^+ than OH^- present with increasing temperature.

C The pH of water increases with increasing temperature.

D The pH of water at 100 °C is 6.2.

15 Oxalic acid, $H_2C_2O_4$, is a relatively strong acid despite being an organic acid. The two pK_a values for oxalic acid is 1.23 and 4.19.

The titration curve between 0.10 mol dm^{-3} $H_2C_2O_4$ and 0.20 mol dm^{-3} NaOH is given below.



Which of the following statements are correct?

1 The volume of $H_2C_2O_4$ used in the titration is 20.0 cm^3.

2 The initial pH of $H_2C_2O_4$ is 1.1 [Ignore the effects of the second pK_a].

3 The points **V**, **X** and **Z** are made up of conjugate acid–base pairs.

4 The first end-point can be followed by using methyl orange indicator and the second end-point can be followed by using phenolphthalein indicator.

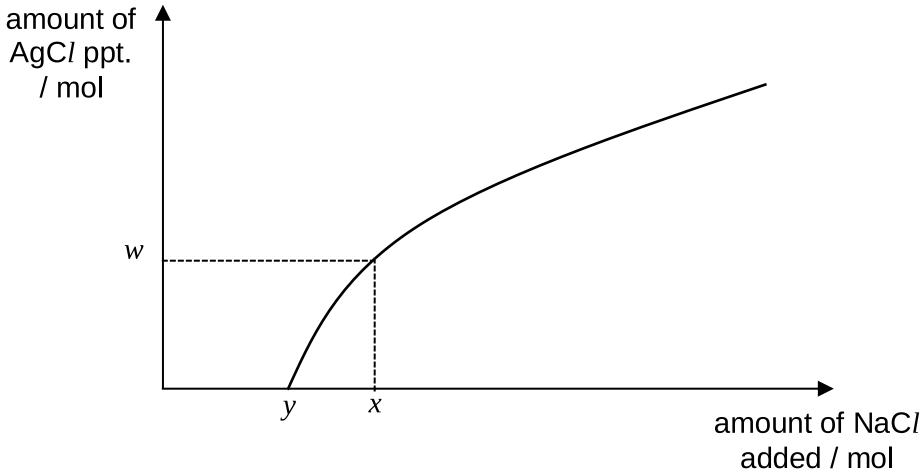
A **1**, **2** and **3** only

B **1**, **2** and **4** only

C **1** and **2** only

D **2** and **4** only

16 When solid NaCl was added to a 1 dm^3 solution containing z mol of Ag^+ ions, the amount of AgCl precipitated was found to change as follows:



Which one of the following gives the correct expression for the solubility product of AgCl?

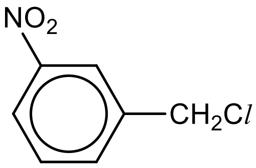
A $(z–w).(x–w)$

B $(w).(x–y)$

C $(z).(x)$

D $(y).(y)$

17 Which one of the following types of reaction is compound **K** **not** likely to undergo?



compound **K**

A electrophilic addition

B electrophilic substitution

C nucleophilic substitution

D reduction

18 The hydride ion, H^-, is a strong reducing agent, a good nucleophile and a good base.

Which one of the following conversions would the hydride ion **not** be expected to bring about?

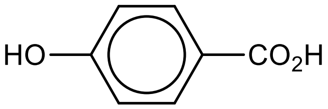
A C_2H_5Br to C_2H_6

B CH_3CH_3 to $CH_2=CH_2$

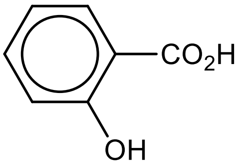
C CH_3CHO to CH_3CH_2OH

D CH_3CO_2H to $CH_3CO_2^-$

19 Which option correctly describes the comparison of the melting point and the first pK_a between 4–hydroxybenzoic acid and 2–hydroxybenzoic acid?



4–hydroxybenzoic acid



2–hydroxybenzoic acid

	melting point of 4–hydroxybenzoic acid	first pK_a of 4–hydroxybenzoic acid
A	lower	lower
B	lower	higher
C	higher	higher
D	higher	lower

20 In which one of the following processes is the organic product a gas at room temperature and pressure?

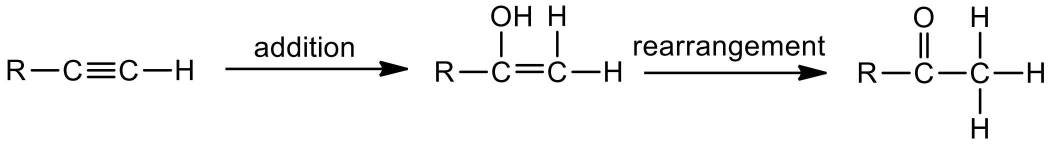
A substitution of ethanol by hydrogen bromide

B dehydration of ethanol

C esterification of ethanoic acid by ethanol

D oxidation of ethanal by acidified potassium dichromate(VI)

21 An alkyne (C≡C) undergoes addition of water in a similar mechanism as an alkene. However, the enol (C=C-OH) that is formed is unstable and would undergo rearrangement to form a carbonyl compound.

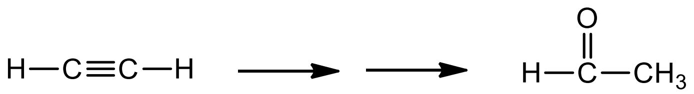


$$R-C\equiv C-H \xrightarrow{\text{addition}} R-C(OH)=C(H)-H \xrightarrow{\text{rearrangement}} R-C(=O)-CH_2-H$$

alkyne enol carbonyl

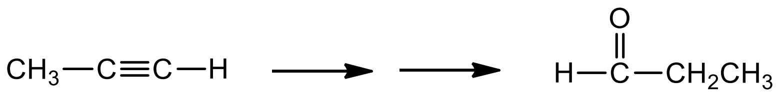
Which compound is **unlikely** to be formed when the following alkynes undergo addition of water?

A



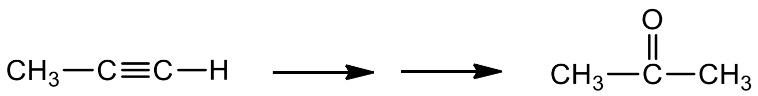
$$H-C\equiv C-H \longrightarrow \longrightarrow H-C(=O)-CH_3$$

B



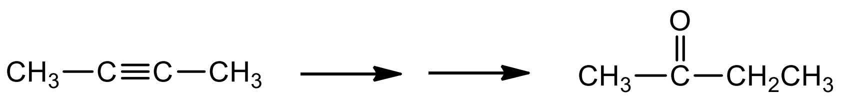
$$CH_3-C\equiv C-H \longrightarrow \longrightarrow H-C(=O)-CH_2CH_3$$

C



$$CH_3-C\equiv C-H \longrightarrow \longrightarrow CH_3-C(=O)-CH_3$$

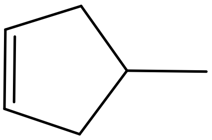
D



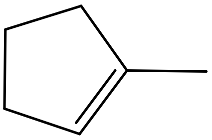
$$CH_3-C\equiv C-CH_3 \longrightarrow \longrightarrow CH_3-C(=O)-CH_2CH_3$$

22 Which one of the following compounds react with hot acidified $KMnO_4$ and the resultant product formed will give a positive test with **both** 2,4–dinitrophenylhydrazine and PCl_5?

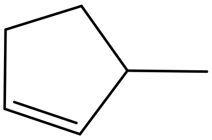
A



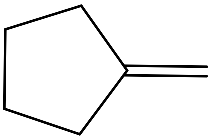
B



C

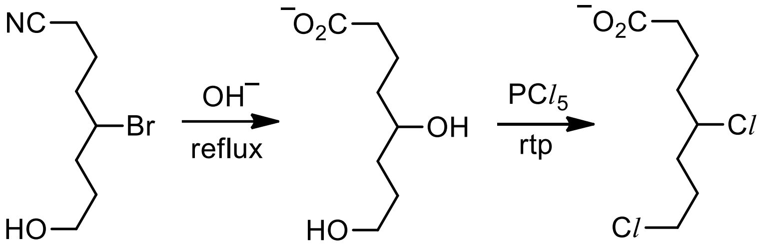


D

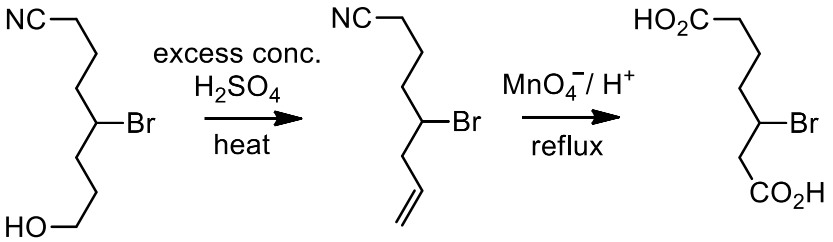


23 Which one of the following 2-stage processes will **not** yield the final product as shown?

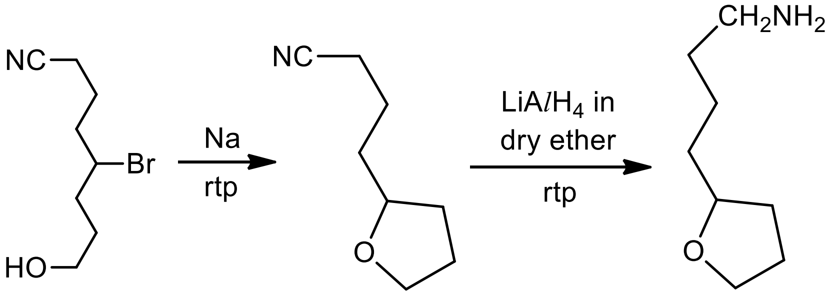
A



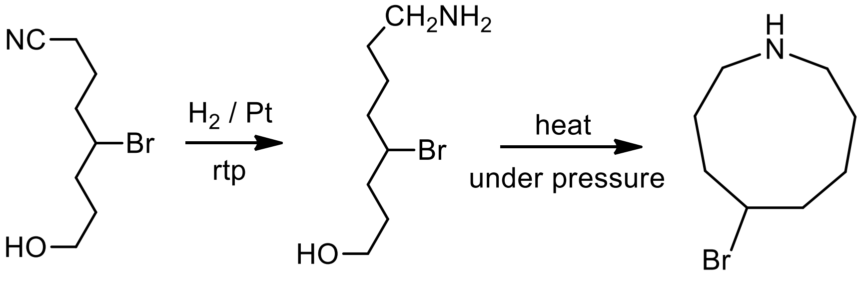
B



C



D



24 Compound **Z** releases a gas that turns damp red litmus paper blue upon addition of hot aqueous NaOH. Which compounds could be **Z**?

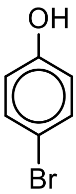
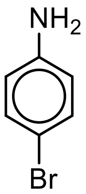
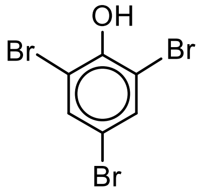
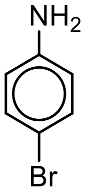
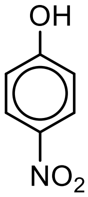
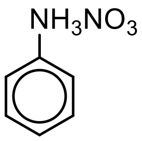
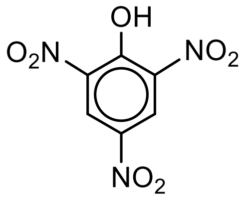
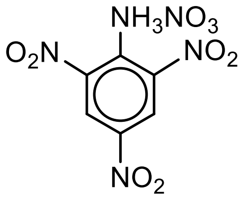
1 $CH_3CH_2CH_2CN$

2 $CH_3CH_2CONHCH_3$

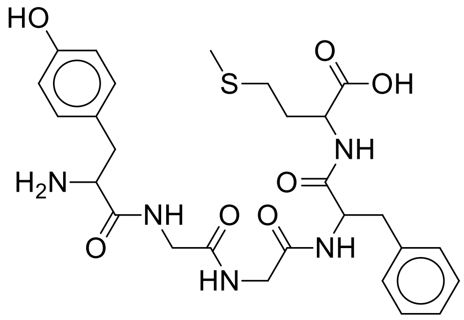
3 $CH_3CH_2CO_2NH_4$

A	**1**, **2** and **3**	**C**	**1** only
B	**1** and **3** only	**D**	**2** and **3** only

25 Which one of the following options shows the correct products when phenol and phenylamine react with the reagents and conditions indicated?

	reagents and conditions	product of phenol	product of phenylamine
A	$Br_2(aq)$ room temperature		
B	Br_2 in CCl_4 room temperature		
C	$HNO_3(aq)$ room temperature		
D	HNO_3(concentrated) room temperature		

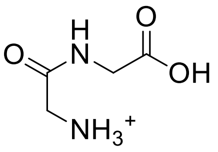
26 To reduce pain during stress, animals generate their own opiates. One such opiate is called *encephalin*, a pentapeptide as shown below:



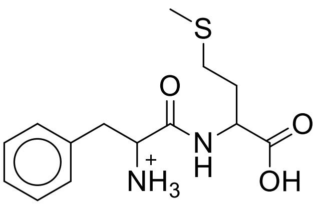
encephalin

Which one of the following dipeptides is **not** a product of the partial hydrolysis of *encephalin* with 6 mol dm^{-3} HC*l*?

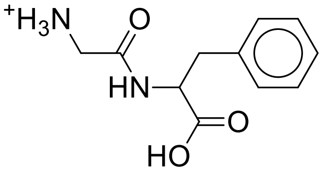
A



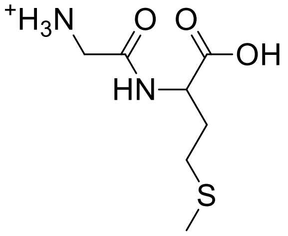
C



B



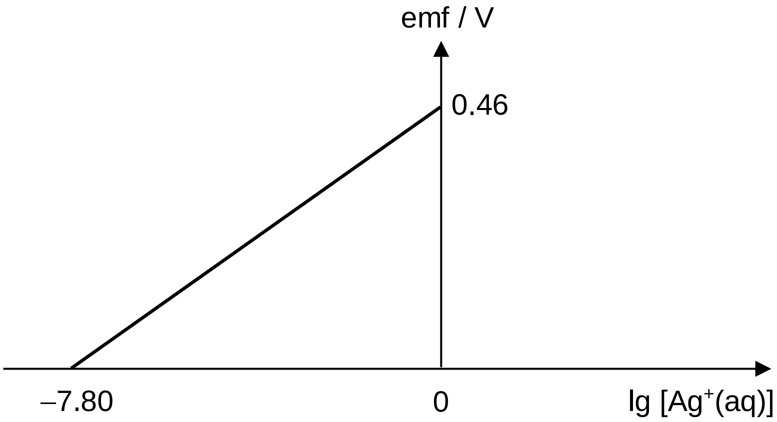
D



27 *Use of the Data Booklet is relevant to this question.*

An electrochemical cell is made up of **X**$^{2+}$(aq)|**X**(s) and Ag^{+}(aq)|Ag(s) half-cells. **X**(s) is the negative electrode and the concentration of **X**$^{2+}$(aq) is kept at 1.00 mol dm^{-3} throughout.

The graph below shows the variation in electromotive force (emf) of the above electrochemical cell with lg [Ag^{+}(aq)] at 298 K.



Which of the following statements are correct?

1 The direction of electron flow in the external circuit will be reversed when the concentration of Ag^{+}(aq) is 1.00 x 10^{-6} mol dm^{-3}.

2 The standard electrode potential of the **X**$^{2+}$(aq)|**X**(s) half-cell is +0.34 V.

3 The emf of the given cell under standard conditions will be +0.46 V.

A **2** and **3** only

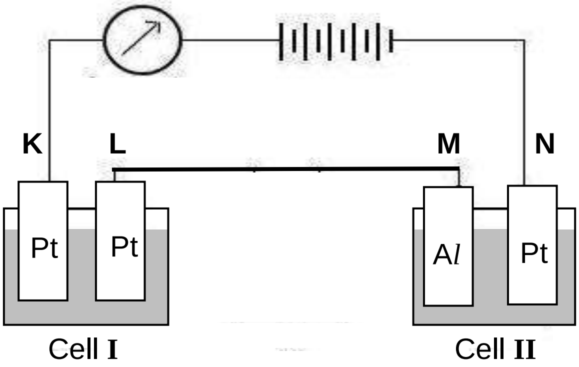
B **1** and **3** only

C **1** and **2** only

D **2** only

28 *Use of the Data Booklet is relevant to this question.*

An experiment involving the electrolysis of aqueous copper(II) sulfate in Cell **I** and aqueous sulfuric acid in Cell **II** was carried out.



Given that relative formula mass of Al_2O_3 is 102.0 and the mass of Al_2O_3 formed at electrode **M** is 0.142 g.

What is the maximum mass of copper deposited at electrode **L** after complete electrolysis?

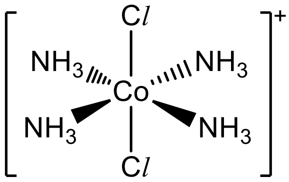
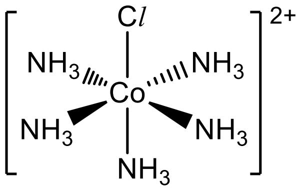
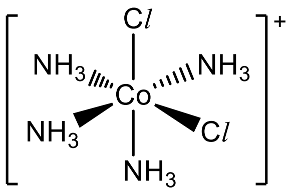
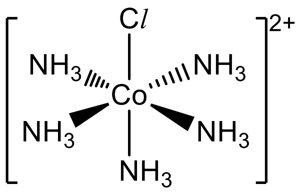
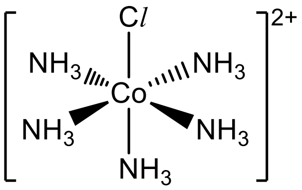
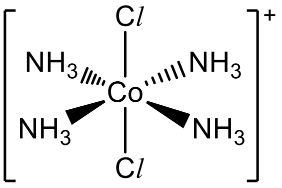
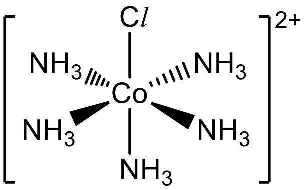
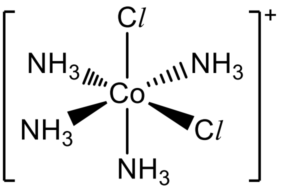
[Note: Assume that all the O_2 produced at electrode **M** completely reacted to form Al_2O_3.]

A	0.133 g	**C**	0.265 g
B	0.236 g	**D**	0.530 g

29 Two different complexes, **K** and **L**, can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Different proportions of chloride are precipitated when each of the complexes is treated with aqueous silver nitrate.

	Formula	Number of moles of $AgCl$ precipitated per mole of complex	Does the complex have a dipole moment?
K	$CoCl_3(NH_3)_5$	2	yes
L	$CoCl_3(NH_3)_4$	1	no

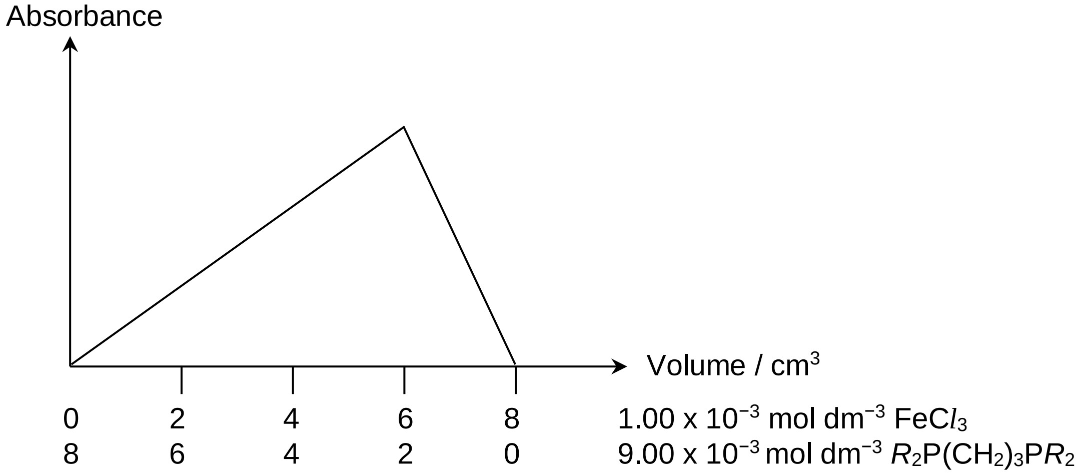
Which one of the following options shows the correct structures of **K** and **L**?

	K	**L**
A		
B		
C		
D		

30 In this question, ‘*R*’ represents a phenyl group.

2-bis(diphenylphosphino)propane, $R_2P(CH_2)_3PR_2$, is a commonly used ligand which forms a complex ion with many metal ions.

In the graph below, the intensity of visible light absorbance for different mixtures containing 1.00 x 10^{-3} mol dm^{-3} $FeCl_3(aq)$ and 9.00 x 10^{-3} mol dm^{-3} $R_2P(CH_2)_3PR_2$ are shown.



Which one of the following statements is **not** true?

A The formula of the complex ion formed is $[Fe(R_2P(CH_2)_3PR_2)_3]^{3+}$.

B Each $R_2P(CH_2)_3PR_2$ can form three dative covalent bonds with Fe^{3+} ion

C The coordination number of the complex ion formed is 6.

D H_2O molecule is a weaker ligand than $R_2P(CH_2)_3PR_2$.

1 **(a)** An unknown solid sample, with a mass of 1.50 g, contains three sodium salts, $NaCl$, $NaClO_3$ and $NaNO_3$. The sample was completely dissolved in water and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In one experiment, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The $AgCl$ precipitate formed was removed by filtration, dried and weighed. The $AgCl$ precipitate was found to have a mass of 0.240 g.

In another experiment, a gas was bubbled into a new 50.0 cm^3 portion of solution **L** to convert ClO_3^- to Cl^-. Excess silver nitrate was then added to the resulting mixture. The $AgCl$ precipitated formed was treated similarly as before and found to have a mass of 0.285 g.

(i) Determine the amount of ClO_3^- ions present in 50 cm^3 of solution **L**.

[2]

(ii) Hence, determine the percentage by mass of $NaClO_3$ present in the original solid sample.

[2]

(b) Suggest whether $NaCl$ or $NaClO_3$ has a lower melting point. Explain your answer.

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[2]

(c) **(i)** Draw a dot-and-cross diagram of the ClO_3^- anion.

[1]

(ii) Chlorine forms a number of oxides, one of which is Cl_2O_7. Cl_2O_7 is a symmetrical molecule, with a central oxygen atom bonded to two chlorine atoms.

Draw the structure of Cl_2O_7.

[1]

(iii) The bonds in Cl_2O_7 exhibit two different bond lengths, namely, 0.141 nm and 0.171 nm. However, all the bonds in the ClO_3^- ion have the same bond length of 0.149 nm.

Suggest why the bond length in ClO_3^- is intermediate between those present in Cl_2O_7.

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....
[2]

(iv) The bond angle formed between the central oxygen atom and its two surrounding chlorine atoms is larger than expected with a value of 118.6°.

Suggest a possible reason why.

....

....

[1]

[Total: 11]

2 **(a)** Use of the *Data Booklet* is necessary for this part of the question.

The sub–atomic makeup of certain ions formed from isotopes of cobalt and lead is given below:

	number of neutrons	number of electrons
Co ion	33	25
Pb ion	122	▨

In a particular experimental set–up, a beam containing the above ions of cobalt was passed through an electric field and was deflected by an angle of +10.2°.

Under identical conditions, another beam containing the above ions of lead was deflected by an angle of +6.0°.

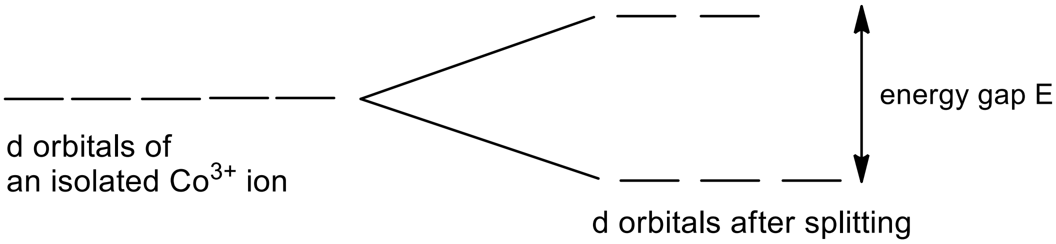
What is the overall charge of the lead ions?

[2]

(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.

CoF_6^{3-} and $[Co(NH_3)_6]^{3+}$ are both complexes with cobalt in the +3 oxidation state. However, only CoF_6^{3-} displays paramagnetism while $[Co(NH_3)_6]^{3+}$ does not. This is determined by whether the electronic configuration of the Co^{3+} ion in the complex displays a "high spin" or a "low spin" state.

The following diagram shows how the d–orbitals are split in an octahedral environment.



In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

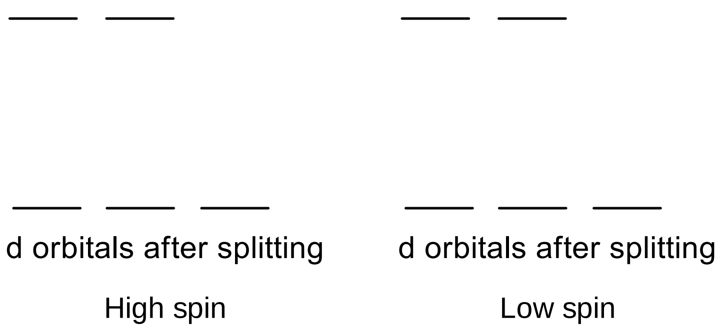
In a 'low spin' state, the lower energy d–orbitals are filled first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Draw the shapes of the d_{xy} and d_{z^2} orbitals. Label your drawings clearly.

[2]

(ii) Using ↑ or ↓ to represent electrons, show, on the two diagrams below, the electronic distribution of a Co^{3+} ion in a high spin state, and in a low spin state.

Hence, identify the cobalt complex that corresponds to each particular spin state.



Complex: ....

[2]

(iii) Suggest why electrons usually prefer to occupy orbitals singly rather than in pairs.

....

....

[1]

(iv) Using the explanation in **(b)(iii)**, together with the information given above, state and explain which of the two cobalt complexes contains the larger energy gap, E, between its d orbitals.

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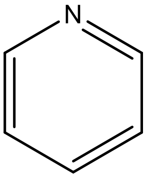
[1]

[Total: 8]

3 Frederick Thomas Trouton was an Irish physicist who observed a relationship between boiling points and enthalpy changes of vaporisation after studying many liquids. He published his findings and formulated Trouton's rule which states that the molar *entropy* of vaporisation, ΔS_{vap}, for most liquids is about 85 J K^{-1} mol^{-1}.

The boiling points and enthalpy changes of vaporisation of several organic liquids are as follows:

substance	boiling point / °C	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J K^{-1} mol^{-1}
propanone, $(CH_3)_2CO$	56.1	29.1	
dimethyl ether, $(CH_3)_2O$	–24.8	21.5	86.6
ethanol, CH_3CH_2OH	78.4	38.6	
octane, $CH_3(CH_2)_6CH_3$	125.6	34.4	86.3
pyridine, 	115.3	35.1	90.4

(a) Explain the term *entropy* and why ΔS_{vap} at constant pressure is positive.

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.... [2]

(b) Complete the above table by calculating the ΔS_{vap} for propanone and ethanol. Show your working for the calculation of ΔS_{vap} for propanone.

[2]

(c) By considering the structure and bonding of the various substances in this question, state and explain the relationship between strength of intermolecular forces of attraction and the entropy of a substance in the liquid state.

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[2]

(d) **(i)** With the aid of a diagram, show and label the bonding between two methanoic acid molecules in the **gaseous** phase.

[1]

(ii) Hence, predict if ΔS_{vap} for methanoic acid is more or less positive than predicted by Trouton's rule. Explain your reasoning.

[No marks will be awarded if a prediction has no reasoning.]

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[2]

[Total: 9]

4 Ozone, O_3, is fairly stable but rapidly decomposes, with the release of heat, to form oxygen in the presence of silver catalyst. A silver catalyst was added to 800 cm^3 of a mixture of oxygen and ozone. The volume increased as follows and the reaction is complete at 1800 s.

total volume of gas mixture, V_{total} / cm^3	800	805	810	815	818	819
volume of O_3(g) /cm^3						0
time, t / s	0	210	420	860	1350	1800

(a) **(i)** Write a chemical equation to represent the overall process of the decomposition of ozone to form oxygen.

.... [1]

(ii) By considering the stoichiometry of the reaction, calculate the initial volume of ozone and initial volume of oxygen in the mixture.

[1]

(iii) Given that volume of O_3 reacted = 2 (V_{total} – 800), complete the above table by calculating the volume of ozone in the mixture at the various times stated. Fill in the volume of O_3 at t = 0 s using your answer in **a(ii)**.

[1]

(iv) The decomposition of ozone is a *first order* reaction.

Write down the rate equation and explain the term *first order*.

[2]

(v) Show, by means of a suitable graph, that these data are consistent with a first order reaction.

[If you are unable to solve **(iii)**, sketch the graph without data points and indicate clearly how it can be used to verify the order of reaction.]

[2]

(b) **(i)** Silver is a heterogeneous catalyst in this reaction. Outline how a heterogeneous catalyst works.

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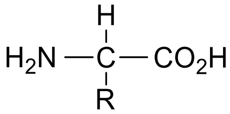
....

....
[2]

(ii) Draw a labelled energy profile diagram for the decomposition of ozone, with and without the use of a catalyst.

[2]
[Total: 11]

5 **(a)** Nitrogen is one of the key elements present in α-amino acids, the building block of proteins. α-amino acids have the following general formula.



$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-CO_2H$$

The table below shows the R groups of the α-amino acids present in a polypeptide, **J**.

α–amino acid	M_r	R group
asp	133.0	$-CH_2CO_2H$
lys	146.0	$-CH_2CH_2CH_2CH_2NH_2$
gln	146.0	$-CH_2CH_2CONH_2$

You have to refer to the table above when answering **a(i)** and **a(ii)**.

(i) When polypeptide **J** undergoes hydrolysis, three aspartic acid, two lysine and one glutamine molecules were formed as shown in the following reaction:

$$\mathbf{J} \longrightarrow 3\text{ asp} + 2\text{ lys} + 1\text{ gln}$$

Calculate the M_r of polypeptide **J**.

[1]

(ii) A dipeptide, *gln–lys*, is obtained upon hydrolysis of polypeptide **J** by an enzyme. Draw the structural formula of this dipeptide at pH 1.

[1]

(iii) A sample of lysine, extracted from the hydrolysis of polypeptide **J** rotated plane polarised light anticlockwise. However, a second sample of lysine obtained from laboratory synthesis had no effect on plane polarised light.

Suggest an explanation for these observations.

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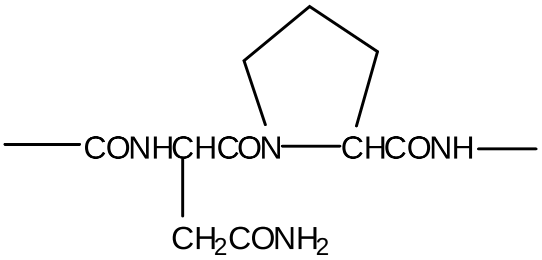
[2]

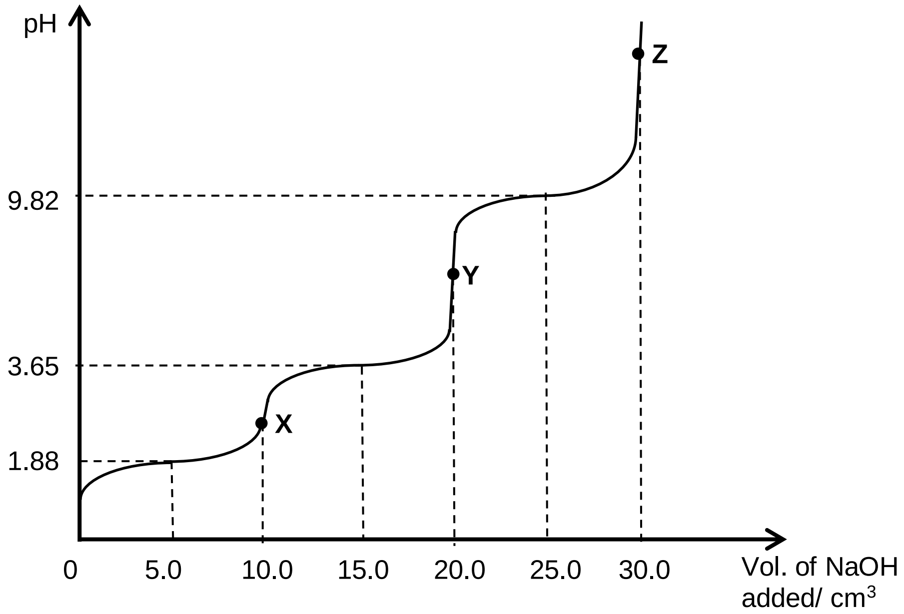
(iv) Part of the chain of another polypeptide **K** is shown below.



Draw the structure of the organic products formed when polypeptide **K** is treated with excess aqueous KOH under prolonged heating.

[2]

(b) The following titration curve is obtained when a solution of fully protonated aspartic acid, $H_3N^+CH(CH_2CO_2H)CO_2H$ is titrated with NaOH(aq). **X**, **Y** and **Z** denote the first, second and third equivalence point respectively.



(i) Identify the species present at **X** and **Z**.

[1]

(ii) Hence, explain why there is a sharp increase in pH when a small amount of NaOH(aq) is added to solution at **Z**.

……………………………………………………………………………………………..

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……………………………………………………………………………………………..

[1]

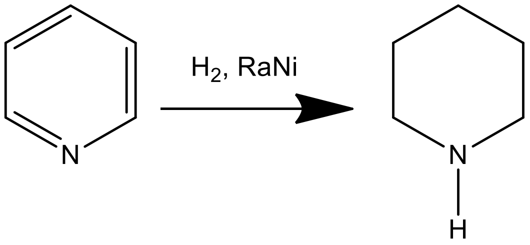
(iii) At pH 10.0, the mixture can act as a buffer. Identify the two species present in this buffer. With the aid of an equation, show how the buffer works when a small amount of acid is added to it.

[2]

(iv) Calculate the ratio of the concentrations of the two species in the buffer required to maintain the pH in **(b)(iii)**.

[2]

(c) Pyridine is a cyclic structure containing nitrogen and is analogous to that of benzene. It can be reduced to piperidine with Raney nickel (RaNi) as shown in the following reaction:



(i) State the type of hybrid orbital occupied by the lone pair of electrons on the N atom in pyridine and piperidine.

Pyridine: ……………………………

Piperidine: …………………………

[1]

(ii) Hence, suggest how the basicity of pyridine might compare to that of piperidine. Give reasons for your answers.

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[2]

(iii) In an attempt to form a quaternary amine salt, a student treated piperidine with excess iodomethane under acidic condition. Explain why this synthesis will **not** be successful.

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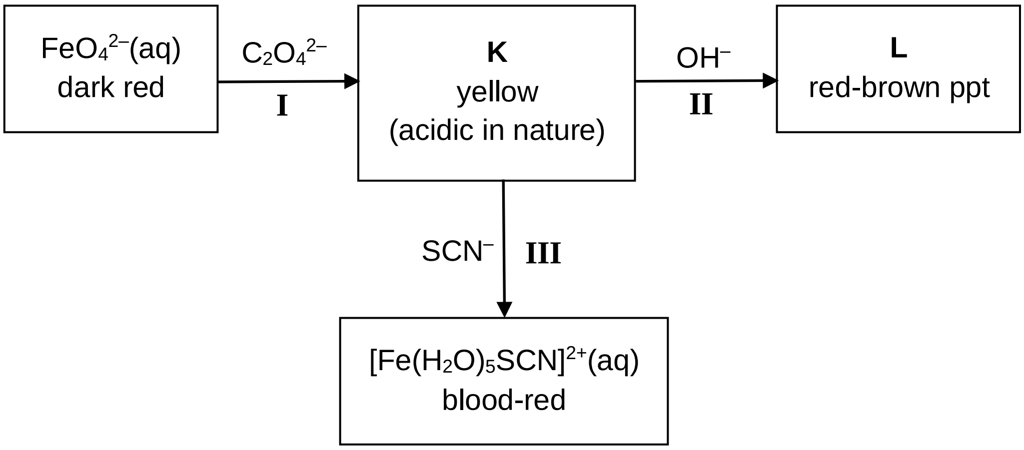
………………………………………………………………………………………………..

[2]

[Total: 17]

6 **(a)** In most of its compounds, iron has the oxidation state +2 or +3. However, other oxidation states of iron are possible. For example, potassium ferrate(VI), K_2FeO_4, contains iron in the +6 oxidation state. Reflecting its high oxidation state, FeO_4^{2-} is a powerful oxidising agent.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Iron is considered to be a transition metal. Justify the statement.

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………………………………………………………………………………………………

[1]

(ii) Explain why FeO_4^{2-}(aq) is coloured.

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………………………………………………………………………………………………

[2]

(iii) State the type of reaction that occurred in reactions **I** to **III**.

I ……………………………………………

II ……………………………………………

III ……………………………………………

[3]

(iv) Write an equation to illustrate the acidic nature of **K**.

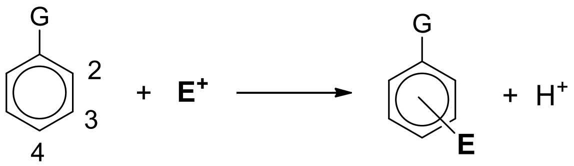
……………………………………………………………………………………………..

[1]

(v) Using relevant data from the *Data Booklet,* predict whether a reaction will occur when iodide ions are mixed with **K** and **L** separately. Write an equation for any reaction that occurs.

[2]

(b) In an aromatic substitution reaction, 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**.



(i) Name the type of reaction mechanism between phenol and the incoming group, **E**.

……………………………………………………………………………………………..

[1]

(ii) Both phenylamine, $C_6H_5NH_2$, and phenol, activate the benzene ring in a similar manner so that the ring becomes highly susceptible to the incoming group, **E**. Comparing the difference in electronegativity between oxygen in phenol and nitrogen in phenylamine, explain the relative rate of phenol and phenylamine with the incoming group, **E**.

....

....

....

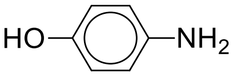
....

....

....

.... [2]

(iii) From your answers in **(b)(ii)**, outline the reaction mechanism for the mono-substitution of 4-aminophenol with the incoming group, $\mathbf{E}^+$.



4-aminophenol

[3]

(c) The choice of solvent used in the bromination of phenol can greatly affect the type of product formed.

(i) Draw the structure of the product formed when phenol undergoes reaction with Br_2 in water and with Br_2 in a non-polar organic solvent like CS_2 separately.

[1]

(ii) By considering the nature of the incoming group, **E**, suggest an explanation for the difference in the reaction between phenol and bromine dissolved in the two different types of solvent mentioned in **(c)(i)**.

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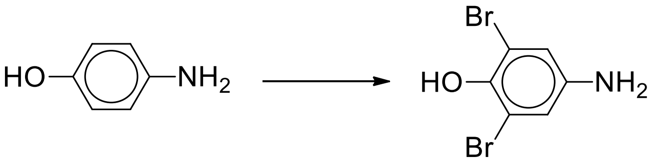
…………………………………………………………………………………………… [1]

(d) Suggest the reagents and conditions required to carry out the following transformation and explain the rationale for the choice.



Reagents and conditions: ………………………………………………………………………

Explanation: ………………………………………………………………………………

…………………………………………………………………………………………… [2]

[Total: 19]

Section A

Answer **all** the questions in this section.

1 **(a)** Account for the reactions that occur when $MgCl_2$ and PCl_5 are separately dissolved in water. Predict the pH of the resulting solutions formed and write equations for the reactions that occur. [4]

(b) A sample consists of a solid mixture of MgO and Al_2O_3. Describe briefly an experimental procedure that will enable you to separate the mixture and recover each of the oxides in its pure form. [3]

(c) The highest fluoride of xenon, XeF_6, can be obtained by heating the octafluoroxenates of the Group 1 metals, M_2XeF_8, where M represents the Group 1 metal.

$$M_2XeF_8 \rightarrow 2MF + XeF_6$$

Suggest reasons why the sodium salt (M = Na) decomposes below 100 °C, whereas the caesium salt (M = Cs) requires a temperature of 400 °C. Hence explain why $MgXeF_8$ is not known to exist. [3]

(d) Suggest identities for the following substances **A** to **D**, writing equations where appropriate.

When magnesium is heated with nitrogen under inert conditions, an ionic compound, **A** is produced. When water is added to **A**, a colourless gas **B** which turns damp red litmus paper blue is produced. **B** reacts with chlorate(I) ion, ClO^- in a 2 : 1 mole ratio to form a colourless liquid **C** with empirical formula NH_2. The reaction of **C** with sulfuric acid in a 1:1 mole ratio produces a salt **D**, $N_2H_6SO_4$, which contains one cation and one anion per formula unit. [4]

(e) Real gases do not obey the ideal gas equation exactly. Many chemists have tried to come up with gas equations that describe the behaviour of real gases. In 1873 J D van der Waals introduced an approximate gas equation that is applicable for all real gases. The van der Waals equation is

$$P = \frac{nRT}{V-n\mathbf{b}} - \mathbf{a}\frac{n^2}{V^2}$$

where **a** and **b** are constants which are characteristic of each gas. The other symbols carry their usual meaning and units as in the ideal gas equation.

(i) Using what you have learnt about the differences between ideal and real gases, suggest what the constants **a** and **b** represent. [2]

(ii) The values of the constants **a** and **b** for CO_2 are $\mathbf{a} = 0.3658$ Pa m^6 mol^{-2} and $\mathbf{b} = 4.29 \times 10^{-5}$ m^3 mol^{-1}.

Use your answer in **(e)(i)** to suggest how the value of the constant **a** for xenon (Xe) will compare with CO_2. Explain your answer briefly. [1]

(iii) Use the

- ideal gas equation and
- van der Waals equation

to calculate the pressure exerted by 1 mol of CO_2 at a temperature of 30 °C and volume of 1 dm^3.

[3]

[Total: 20]

2 **(a)** Malonic acid, $CH_2(CO_2H)_2$ is an organic *weak dibasic acid*. It is a building block chemical to produce numerous valuable compounds, including the flavour and fragrance compound, cinnamic acid, and the pharmaceutical compound, valproate. The two pK_a values of $CH_2(CO_2H)_2$ are 2.83 and 5.69.

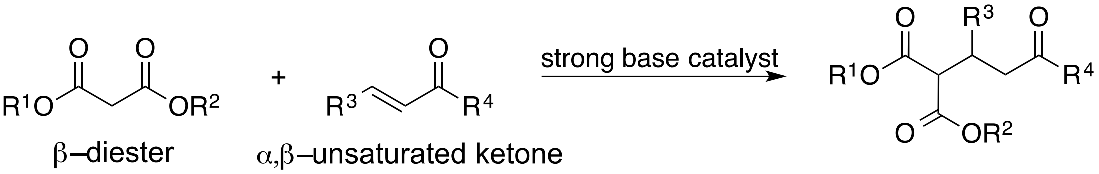
(i) Define the term *weak acid*. [1]

(ii) Calculate the pH of 25.0 cm^3 solution of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. [1]

(iii) Calculate pH of the resulting solution when 50 cm^3 of 0.100 mol dm^{-3} NaOH was added to the solution in **(a)(ii)**. [2]

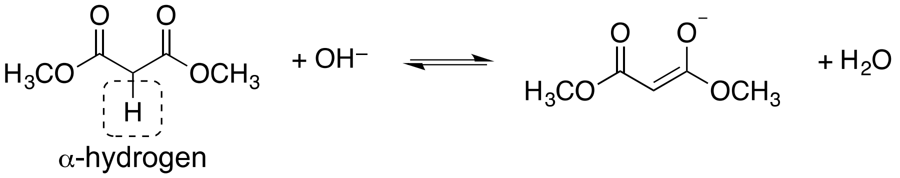
(iv) Using your answers in **(a)(ii)** and **(a)(iii)**, as well as the pK_a values provided, sketch a graph to show how the pH of the solution changes as 50 cm^3 of 0.100 mol dm^{-3} NaOH is gradually added to 25.0 cm^3 of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. Clearly indicate the corresponding volumes of NaOH in your graph. [2]

(b) Malonic acid can be converted to its corresponding β–diester. β–diesters are commonly used as starting compounds in the Michael addition reaction, where they react with α,β-unsaturated ketones. It is one of the most useful methods for the formation of C–C bonds.



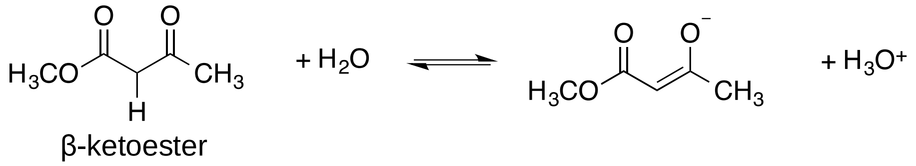
(i) Suggest reagents and conditions to convert malonic acid to dimethyl malonate, $CH_2(COOCH_3)_2$. State the type of reaction. [2]

(ii) The first step in the mechanism of Michael addition involves an acid–base reaction where the strong base catalyst extracts an α-hydrogen from the β–diester.

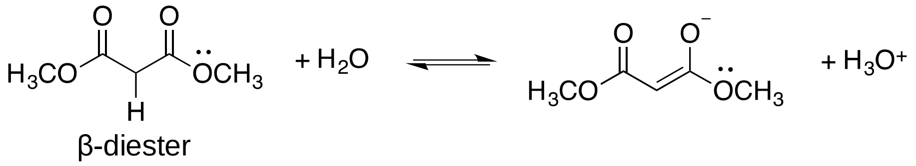


Reagents similar to the malonate ester can undergo the same type of reaction. The pK_a values of malonate ester and another similar reagent are as follows:

pKa



11



13

Explain the difference in pK_a values between the two compounds. [2]

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(iii) Compound **A**, C_8H_9ClO, contains a non-aromatic six-membered ring. **A** reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent. 1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum. When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed. **B** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. When **B** is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed. **D** also gives a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.

Deduce the structural formulae of compounds **A**, **B**, **C**, **D** and **E**, explaining clearly your reasoning for all reactions described.

[10]
[Total: 20]

3 **(a)** A Latimer diagram provides a concise way of representing large amount of information about the different oxidation states of an element. In a Latimer diagram, the most highly oxidised form of an element is written on the left, with successively lower oxidation states to the right. The different species are connected by arrows, and the standard electrode potential in volts is written above each arrow.

The Latimer diagrams for chlorine in acidic and alkaline medium are shown below.

In acidic medium:

$$ClO_4^- \xrightarrow{+1.19\text{ V}} ClO_3^- \xrightarrow{+1.21\text{ V}} ClO_2^- \xrightarrow{+1.66\text{ V}} ClO^- \xrightarrow{+1.64\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

In alkaline medium:

$$ClO_4^- \xrightarrow{+0.36\text{ V}} ClO_3^- \xrightarrow{+0.35\text{ V}} ClO_2^- \xrightarrow{+0.65\text{ V}} ClO^- \xrightarrow{+0.40\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

(i) Define the term *standard electrode potential*. [1]

(ii) The standard electrode potentials in a Latimer diagram are not additive. For example, the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is **not** the sum of +1.19 V and +1.21 V and +1.66 V. However, their respective standard Gibbs' free energy changes are additive.

Using relevant data given below, show that the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is 1.34 V.

electrode reaction	$E^\ominus$ / V	$\Delta G^\ominus$ / kJ mol^{-1}
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–220.7
$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$	+1.21	–233.5
$ClO_2^- + 2H^+ + 2e^- \rightleftharpoons ClO^- + H_2O$	+1.66	–320.4
$ClO^- + 2H^+ + e^- \rightleftharpoons \frac{1}{2}Cl_2 + H_2O$	+1.64	–158.3
$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36	–131.2

[2]

(iii) With the exception of the conversion of Cl_2 to Cl^-, the standard electrode potentials in alkaline medium are less positive than their corresponding conversions in the acidic medium.

Suggest why this is so. [2]

(iv) A disproportionation reaction is a redox reaction in which a chemical species undergo reduction and oxidation simultaneously.

In hot alkaline medium, Cl_2 undergoes disproportionation to form two chlorine-containing species according to the following equation.

$$3Cl_2(g) + xOH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_y^-(aq) + zH_2O(l)$$

By considering the number of moles of electrons transferred and using the Latimer diagram for chlorine in alkaline medium, first solve for y. Then, use it to solve for x and z. [2]

(b) Besides the standard hydrogen electrode, other reference electrodes have also been employed in electrochemistry. An example is the silver chloride electrode, which involves dipping silver metal coated with solid silver chloride into a solution of sodium chloride. The solubility product for $AgCl$ is 2.0×10^{-10} mol^2 dm^{-6}.

(i) The standard electrode potential of a silver chloride electrode is +0.230 V. However, when 1.0 mol dm^{-3} sodium chloride is used to set up the silver chloride electrode, this value cannot be achieved.

Explain why this is so. [1]

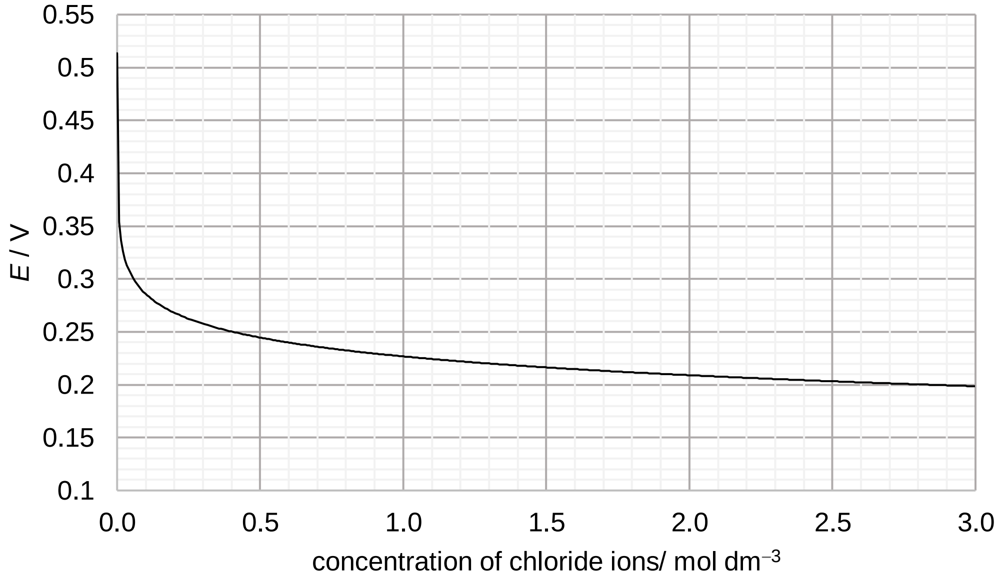
At 298 K, the electrode potential of the silver chloride electrode, E, can be estimated from the concentration of silver ions present using formula (1):

$$E = 0.80 - 0.0591 \log \frac{1}{[\mathrm{Ag}^+]} \text{ .....formula (1)}$$

(ii) Using the expression given, calculate the value of E in each of the following cases:

- in pure water and
- when the addition of sodium chloride results in a chloride ion concentration of 2.5 mol dm^{-3}. [3]

(iii) Using the graph given below, suggest why sodium chloride solution ranging from 1.0 mol dm^{-3} to 3.0 mol dm^{-3} is typically used in the setting up of a silver chloride electrode rather than pure water.



[1]

(iv) A student attempted to study the validity of formula (1) by adding aqueous ammonia to vary the concentration of silver ions in solution. This is due to the ability of ammonia to form a complex with the silver ions, thus decreasing its concentration in solution.

Explain a potential problem that may arise with this method of analysis. [1]

(v) The silver chloride electrode is used in many medical equipment. In a particular device used for electrocardiography, a layer of silver metal with a thickness of 1mm is plated onto an electrode with a surface area of 0.12 cm^2 before coating it with solid silver chloride.

If a current of 15.0 mA is used for the electroplating process, calculate the time required to completely plate the silver metal onto the electrode from a solution containing $Ag^+(aq)$.

[The density of silver metal is 10.5 g cm^{-3}]

[2]

(c) When sodium halides react with concentrated sulfuric acid, an acid-base reaction takes place resulting in the formation of white fumes of hydrogen halides.

$$\mathrm{Na\mathbf{X}(s) + H_2SO_4(\mathit{l}) \longrightarrow H\mathbf{X}(g) + NaHSO_4(s)}, \text{ where } \mathbf{X} = \mathrm{C\mathit{l}, Br \text{ or } I}$$

Subsequently, depending on the reducing strength of the hydrogen halides, a further reaction might take place with concentrated sulfuric acid, resulting in the formation of halogens, a sulfur-containing product and water.

The observations for the reaction of the different sodium halides with concentrated sulfuric acid are shown below:

sodium halide	observations
NaC*l*	white fumes of HC*l*
NaBr	white fumes of HBr red-brown Br_2 gas which condenses to form a red-brown liquid colourless and pungent SO_2 gas
NaI	white fumes of HI violet I_2 gas which condenses to form a black solid colourless and pungent H_2S gas

(i) Write a balanced molecular equation for each of the following reactions:

- between gaseous HBr and concentrated H_2SO_4
- between gaseous HI and concentrated H_2SO_4 [2]

(ii) Arrange the hydrogen halides in order of increasing reducing strength. Explain your answer, using relevant information from the *Data Booklet* to support the difference in observations. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When a 1.00 g sample of sulfur was dissolved in 1 dm^3 of an organic solvent, the following equilibrium was established:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

The percentages by mass of S_7 and S_8 at equilibrium are:

ring size	S_7	S_8
percentage by mass	0.76	98.92

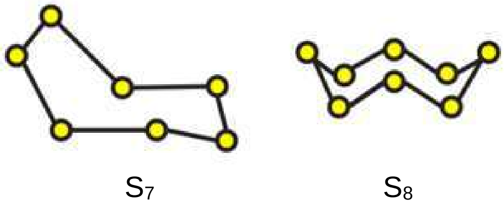
(a) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium. [2]

(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

(iii) The amount of S_8 is increased by 0.01 mol at time t_1. Sketch, on the same axes, two graphs to show how $[S_7]$ and $[S_8]$ vary from t_1 to t_2, the time when equilibrium is re-established at the same temperature.
[You are only required to label the concentrations at t_1.] [2]

(iv) An inert gas is then added at constant pressure. State and explain how the position of equilibrium would change. [2]

The shape of the S_7 and S_8 molecules are as follows.



(b) **(i)** Define the term bond energy with reference to the S–S bonds in S_8. [1]

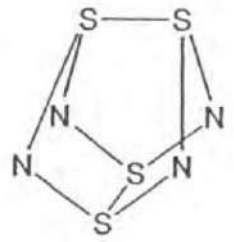
(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction between S_7 and S_8. [1]

(iii) Using your answers in **(a)(ii)** and **(b)(ii)**, and given that:

$$\Delta G^\ominus = -RT \ln K_c$$

where T is in Kelvins and ΔG is in J mol^{-1}, calculate the standard entropy change of the reaction. [2]

(c) Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4. In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The four nitrogen atoms are arranged in a plane, with two sulfur atoms above the plane, and two sulfur atoms below the plane. The shape of a molecule of S_4N_4 is as shown.



S_4N_4

Using the data provided below, construct an energy cycle to calculate the average S–N bond energy in S_4N_4.

enthalpy change of formation of S_4N_4	+460 kJ mol^{-1}
enthalpy change of atomisation of sulfur	+297 kJ mol^{-1}
enthalpy change of atomisation of nitrogen	+497 kJ mol^{-1}
S–S bond energy in S_4N_4	+204 kJ mol^{-1}

[3]

(d) Sulfur and tungsten has certain similarities since both atoms have a total of six valence electrons, even though sulfur is a main group element and tungsten is a transition metal. Both elements reach their maximum +6 oxidation state when combined with electronegative elements such as fluorine and oxygen.

(i) Sulfur trioxide, SO_3 and tungsten(VI) oxide, WO_3 differ markedly in their physical properties. While SO_3 is a gaseous pollutant used in industrial preparation of sulfuric acid, WO_3 is used in electrochromic windows, allowing the windows to change colour when an electrical voltage is applied. Their boiling points are 44.9 ^{o}C and 1700 ^{o}C respectively.

With reference to the structure and type of bonding, account for the difference in boiling points. [3]

(ii) Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}.

Draw the structure of WO_4^{2-}. State the shape and bond angle of the O–W–O bond. [2]

[Total: 20]

5 **(a)** The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

N_2H_4 has a boiling point of 114 °C and decomposes to its elements when passed over a suitable catalyst. The rapid production of hot gaseous products is what provides the thrust.

(i) With the aid of a balanced equation, define the term standard enthalpy change of formation for hydrazine. [2]

(ii) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_r^\ominus = -241.0 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change for the decomposition of 1 mol of hydrazine to its elements using data below.

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
NH_3	–46.1
H_2O_2	–187.8
H_2O	–285.8

[2]

(b) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as 'C-Stoff', and hydrogen peroxide ('T-Stoff'). The standard enthalpy change of combustion of hydrazine and methanol are −622.2 kJ mol^{-1} and −726.0 kJ mol^{-1}.

The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol. The densities of hydrazine and methanol are 1.021 g cm^{-3} and 0.7918 g cm^{-3} respectively.

Calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel, assuming that all the hydrazine and methanol are fully combusted.

[2]

(c) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, that is, the reactants ignite spontaneously on contact.

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4. Briefly explain why. [2]

(ii) Draw the structure of N_2O_4, indicating clearly the shape and bond angle around each nitrogen atom. [2]

(iii) At room temperature, N_2O_4 exists as a gas while N_2H_4 is a liquid. With reference to their structure and bonding, account for this difference. [3]

(d) At 46 °C, N_2O_4 (colourless gas) exists in equilibrium with nitrogen dioxide, NO_2 (brown gas) with an equilibrium constant, K_p of 0.66 atm. The equation for the equilibrium is

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(i) Write an expression for the equilibrium constant, K_p. [1]

(ii) A certain amount of N_2O_4 is allowed to dissociate in a vessel. At equilibrium, the partial pressure of NO_2 is found to be 0.332 atm.

Calculate the partial pressure of N_2O_4 and total pressure at equilibrium. [2]

(iii) Hence, determine the percent dissociation of N_2O_4 at 46 °C. [2]

(iv) State and explain what may be observed when the vessel containing the gases is expanded. [2]

[Total: 20]

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

1 Determination of the dependence of the rate of reaction between glucose and acidified potassium manganate(VII) on temperature

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Glucose, $C_6H_{12}O_6$, is a sugar that can act as a reducing agent. You will investigate how an increase in temperature affects the rate of the redox reaction between glucose and acidified potassium manganate(VII).

FA 1 is 0.020 mol dm^{-3} acidified potassium manganate(VII), $KMnO_4$.
FA 2 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is an aqueous solution containing 32.8 g dm^{-3} glucose, $C_6H_{12}O_6$.
FA 4 is a solid mixture containing an unknown percentage of glucose.

You will measure the time it takes for the purple colour to disappear. Your table of results on the following page should include the rate of reaction for each experiment.

(a) Method

Experiment 1

1. Fill the burette with **FA 1**.
2. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
3. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
4. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
5. Place the beaker on the tripod and heat its contents to between 75 °C and 80 °C.
6. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
7. When the temperature of the contents of the beaker has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with a paper towel and place it onto the white tile.
8. Record the temperature of the solution in the beaker.
9. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
10. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
11. Record the temperature of the solution as soon as it is colourless.
12. Calculate and record the average temperature of the reaction mixture to one decimal place.
13. Empty, rinse and dry the beaker so it is ready for use in **Experiment 2**.

Experiment 2

1. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
2. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
3. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
4. Place the beaker on the tripod and heat its contents to between 35 °C and 40 °C.
5. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
6. When the temperature of the contents of the beaker has reached between 35 °C and 40 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with a paper towel and place it onto the white tile.
7. Record the temperature of the solution in the beaker.
8. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
9. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
10. Record the temperature of the solution as soon as it is colourless.
11. Calculate and record the average temperature of the reaction mixture to one decimal place.
12. Empty, rinse and dry the beaker so it is ready for use in **Experiment 3**.

Experiments 3, 4 and 5

1. Repeat the method for **Experiment 2** at three different temperatures.
2. Keep the temperature of the contents of the beaker between room temperature and 80 °C.
3. Record all your results in your table.

Results:

The rate of reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

Calculate the rate of reaction for each experiment and include this in your table.

[5]

(b) Plot a graph of rate (*y*-axis) against average temperature (*x*-axis) on the grid below. Select a scale on the *x*-axis to include an average temperature of 30.0 °C. Label any points you consider anomalous.

Draw the most appropriate best-fit curve taking into account all of your plotted points and extrapolate it to 30.0 °C.

[3]

(c) **Use your graph** to calculate the **time** to the nearest second that the reaction would have taken if the average temperature had been 52.5°C.
Show **on the grid** how you obtained your answer.

time =……………… [2]

(d) Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in temperature.

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(e) **(i)** Calculate the maximum percentage error in the reaction time recorded for **Experiment 1**. Assume the error of the timer is ±1 s.

maximum percentage error in **Experiment 1** =……………… [1]

(ii) You have carried out experiments at five different temperatures.

Identify an experiment, if any, you should have repeated. Give a reason for your answer.

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(iii) Suggest one way to improve the accuracy of the results for this investigation.

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(f) **(i)** Calculate the concentration of glucose in **FA 3** in mol dm^{-3}.

concentration of glucose in **FA 3** =……………… [1]

(ii) Calculate the volume of 0.020 mol dm^{-3} acidified $KMnO_4$ that would react with **all** the glucose present in 25.0 cm^3 of **FA 3**.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Volume of acidified $KMnO_4$ required =……………… [2]

(iii) Comment on the feasibility of conducting a redox titration between the given concentration of glucose and acidified $KMnO_4$.

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(g) **Determination of the percentage of glucose in FA 4 by titration**

1. Weigh accurately 1.5 g of **FA 4** in a weighing bottle. Record your weighing appropriately in the space below. If you use **TARE** facility of the balance, please indicate clearly in your recording.
2. Dissolve the solid in a beaker and quantitatively transfer into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Label this **FA 4 solution**.
3. Pipette 25.0 cm^3 of **FA 4 solution** into a conical flask.
4. Using a measuring cylinder add 50.0 cm^3 of **FA 2** into the conical flask.
5. Place the conical flask on the tripod and heat its contents to between 75 °C and 80 °C.
6. When the temperature of the contents of the conical flask has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the <u>neck of the conical flask with a paper towel</u>.
7. Titrate with **FA 1** until a permanent colour change is observed.
8. Record the burette readings in the suitable format. Repeat titration to achieve consistent results.

Results:

*Weighing of **FA 4***

Titration

[5]

(h) **(i)** 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]

(ii) Calculate the amount of **FA 1** required for titration.

$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$

amount of **FA 1** = ………………….. [1]

(iii) Hence, calculate the amount of glucose in **FA 4**.

amount of glucose in **FA 4** = ………………….. [1]

(iv) Use your answer in **(h)(iii)** to determine the percentage of glucose in the mixture. [A_r: C, 12.0; O, 16.0; H, 1.0]

percentage of glucose in the mixture = ………………….. [1]

[Total: 27]

2 Planning

An electroplating process uses an electric current to coat an object with a thin layer of metal. An example is *copper plating*. In this process, copper metal is made the anode and is allowed to undergo oxidation. The copper is then reformed at the cathode, coating the object to the plated. The mass of copper plated at the end of the process can be calculated by taking relevant mass measurements.

In the following, you will use the *copper plating* process to determine the Faraday constant, which is the charge in coulombs, C, carried by 1 mole of electrons.

(a) Show that the mass of copper plated onto an object is related to the duration of the *copper plating* process by the following expression:

$$m_{Cu} = \frac{I \times M_{Cu}}{2F} t$$

where

m_{Cu} : mass of copper plated onto an object in grams, g

M_{Cu} : molar mass of copper, g mol^{-1}

I : current in amperes, A

F : Faraday constant

t : duration of the *copper plating* process in seconds, s

[2]

(b) A series of experiments can be carried out, in which the duration of each experiment is varied and the corresponding mass of copper plated onto the object is determined. The data obtained is then to be used for plotting a suitable graph to determine the value of the Faraday constant.

You are required to write a plan, describing how such a series of experiments can be carried out for an appreciable mass of copper to be plated. The duration of each experiment should be at least 5 min but not exceeding 50 min.

You may assume that you are provided with:

- 1.0 mol dm^{-3} copper(II) sulfate solution;
- five equal pieces of clean, dry copper metals;
- five equal pieces of clean, dry objects to be plated (the object is electrically conductive but is inert during the *copper plating* process);
- an electrical power source that supplies a constant current of 0.50 A (the electrical power source can be switched on and off);
- connecting wires;
- stopwatch;
- the apparatus and chemicals normally found in a school laboratory.

Your plan should include the following:

- a clearly labelled diagram of the *copper plating* setup, including the direction of electron flow;
- the procedure you would follow;
- the measurements you would make and how you would determine the mass of copper plated accurately and reliably to allow a suitable graph to be drawn.

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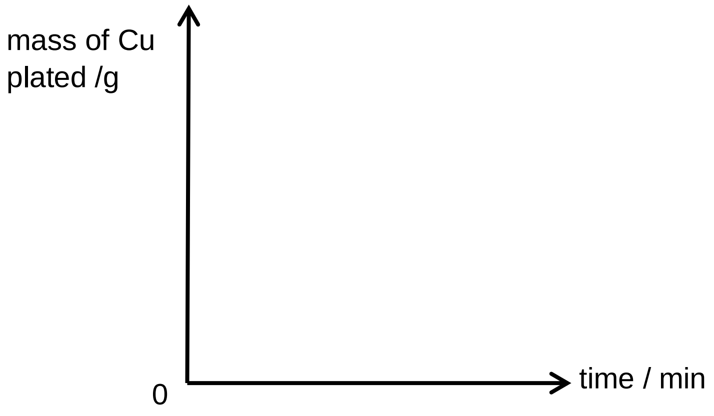
(c) Sketch, on the axes below, the graph you would expect and describe how it could be used to determine the value of Faraday constant.



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(d) During the *copper plating* process, the mass lost at the anode should ideally be the same as the mass gained at the cathode. However, the presence of impurities can cause the mass change at one electrode to be numerically larger than the other electrode.

For each of the following, deduce, with explanation, the electrode that will have a numerically larger mass change.

You may find the following information useful:

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $\quad E^\ominus = -0.13$ V

[A_r: Ag, 107.9; Cu, 63.5; Pb, 207.2]

(i) Presence of Pb impurity at the anode.

Electrode with numerically larger mass change: ………………..

Explanation:

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(ii) Presence of Ag^+ impurity in the electrolyte.

Electrode with numerically larger mass change: ………………..

Explanation:

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……………………………………………………………………………………………[1]

(e) It is important to ensure that the cathode is dry at the start and at the end of each experiment.

Explain the effect, if any, on the calculated value of the Faraday constant if the cathode is dry at the beginning but wet at the end of each experiment.

Effect on calculated value of the Faraday constant: ………………..

Explanation:

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………………………………………………………………………………………………[1]

(f) The Faraday constant obtained from the *copper plating* process can be used to provide an estimate for Avogadro's constant.

A student who conducted the *copper plating* process obtained a value of 96480 C mol^{-1} for the Faraday constant. Using this value, calculate Avogadro's constant.

[Note: The charge of an electron has a numerical value of 1.60×10^{-19} C.]

[1]

[Total: 14]

3 (a) Investigation of some inorganic reactions

FA 5 is an aqueous solution of $CuSO_4$.

FA 6 is a reducing agent.

FA 7 is a solution of ammonium vanadate(V), NH_4VO_3.

You will also need access to the **FA 2** solution you used earlier.

You are to perform the tests described in **Table 3.1** and record your observations in the table.

Test and identify any gases evolved. If there is no observable change, write **no observable change.**

Table 3.1

tests		observations
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 5** into a boiling tube. Add 4 spatulas of **FA 6**. 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 from **(i)**, add aqueous ammonia.	
(iii)	To another 1 cm depth of the filtrate from **(i)**, add 1 spatula of solid ammonium chloride. Stir to ensure all the solid ammonium chloride dissolves. Then add aqueous ammonia.	

Table 3.1

tests		observations
(iv)	Using a measuring cylinder, transfer 2 cm^3 of **FA 7** and 10 cm^3 of **FA 2** into a boiling tube. Swirl the mixture gently. The resultant yellow solution is **FA 8**, which is an acidified solution of VO_2^+.	
(v)	Transfer about 2 spatulas of **FA 6** into a **dry** weighing bottle. From this sample in the weighing bottle, add a **very small** quantity of **FA 6** to the boiling tube containing **FA 8** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 6** in **small** quantities with swirling, until all the **FA 6** in the weighing bottle is used up. 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)** Suggest an identity for **FA 6**. Explain your answer with reference to evidence from relevant tests above.

identity of **FA 6**

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explanation

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(ii) Explain the difference in observations between tests **(a)(ii)** and **(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 obtained in test **(a)(v)**, a grey precipitate is observed.

Given that the $E^\ominus$ value for **FA 6** is between −1.00 V to –0.50 V, state the identity of the grey precipitate.

…………………………………………………………………………………………..[1]

(c) Planning

There are three unlabelled bottles of aqueous solutions. Each bottle contains a different solution from the other two.

The possible identities of the solutions are:

Na_2CO_3(aq) $Al_2(SO_4)_3$(aq) $Mg(NO_3)_2$(aq)

Plan an investigation, using test–tube reactions, which would allow you to identify each of these three solutions.

Other than the three solutions, the only reagent available is the **FA 5** solution used in **3(a)**, which contains $CuSO_4$.

Your plan should include:

- an outline of the sequence of steps you would follow,
- the expected observations at each step, and
- an explanation of how you would analyse your results in order to identify each solution.

You are **not** required to carry out the plan.

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[Total: 14]

H2 CHEMISTRY PAPER 1 ANSWERS

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

Victoria Junior College
2019 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

1 **(a)** An unknown solid sample, with a mass of 1.50 g, contains three sodium salts, $\mathrm{NaC}l$, $\mathrm{NaC}l\mathrm{O_3}$ and $\mathrm{NaNO_3}$. The sample was completely dissolved in water and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In one experiment, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The $\mathrm{AgC}l$ precipitate formed was removed by filtration, dried and weighed. The $\mathrm{AgC}l$ precipitate was found to have a mass of 0.240 g.

In another experiment, a gas was bubbled into a new 50.0 cm^3 portion of solution **L** to convert $\mathrm{C}l\mathrm{O_3}^-$ to $\mathrm{C}l^-$. Excess silver nitrate was then added to the resulting mixture. The $\mathrm{AgC}l$ precipitated formed was treated similarly as before and found to have a mass of 0.285 g.

(i) Determine the amount of $\mathrm{C}l\mathrm{O_3}^-$ ions present in 50 cm^3 of solution **L**.

From 1st experiment, $n_{\mathrm{AgC}l} = \dfrac{0.240}{107.9 + 35.5} = 1.674 \times 10^{-3}\ \text{mol} = n_{\mathrm{C}l^-}$

From 2nd experiment, $n_{\mathrm{AgC}l} = \dfrac{0.285}{107.9 + 35.5} = 1.987 \times 10^{-3}\ \text{mol} = n_{\mathrm{C}l^-} + n_{\mathrm{C}l\mathrm{O_3}^-}$

$n_{\mathrm{C}l\mathrm{O_3}^-}$ **in 50.0 cm^3 of L** $= 1.987 \times 10^{-3} - 1.674 \times 10^{-3}$
$= 3.13 \times 10^{-4}$ **mol** [2]

(ii) Hence, determine the percentage by mass of $\mathrm{NaC}l\mathrm{O_3}$ present in the original solid sample.

$n_{\mathrm{C}l\mathrm{O_3}^-}$ **in 250.0 cm^3 of L** $= (250 / 50) \times 3.13 \times 10^{-4}$
$= 1.565 \times 10^{-3}\ \text{mol} = n_{\mathrm{NaC}l\mathrm{O_3}}$

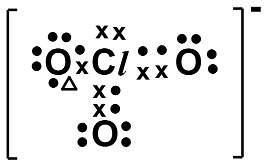
Percentage by mass of $\mathrm{NaC}l\mathrm{O_3}$

$= \dfrac{1.565 \times 10^{-3} \times (23.0 + 35.5 + 3 \times 16.0)}{1.50} \times 100\% = 11.1\%$ [2]

(b) Suggest whether $\mathrm{NaC}l$ or $\mathrm{NaC}l\mathrm{O_3}$ has a lower melting point. Explain your answer.

$\underline{\mathrm{NaC}l\mathrm{O_3}}$ has a lower melting point. Both $\mathrm{NaC}l$ and $\mathrm{NaC}l\mathrm{O_3}$ have <u>giant ionic structure</u> with electrostatic attraction between ions of opposite charges. $|\text{Lattice energy}| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$. Since <u>$\mathrm{C}l\mathrm{O_3}^-$ is larger than $\mathrm{C}l^-$</u>, $\mathrm{NaC}l\mathrm{O_3}$ has a <u>lower magnitude of lattice energy</u>. Hence, <u>less energy is required</u> to break the ionic bonds. [2]

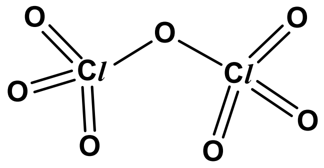
(c) **(i)** Draw a dot-and-cross diagram of the ClO_3^- anion.



[1]

(ii) Chlorine forms a number of oxides, one of which is Cl_2O_7. Cl_2O_7 is a symmetrical molecule, with a central oxygen atom bonded to two chlorine atoms.

Draw the structure of Cl_2O_7.



[1]

(iii) The bonds in Cl_2O_7 exhibit two different bond lengths, namely, 0.141 nm and 0.171 nm. However, all the bonds in the ClO_3^- ion have the same bond length of 0.149 nm.

Suggest why the bond length in ClO_3^- is intermediate between those present in Cl_2O_7.

Resonance arising from the overlapping of p orbitals of C*l* atom with those of the surrounding O atoms. This leads to delocalization of the lone pair on O^- into the C*l*=O double bonds, causing all bonds to have partial double bond character. [2]

(iv) The bond angle formed between the central oxygen atom and its two surrounding chlorine atoms is larger than expected with a value of 118.6°.

Suggest a possible reason why.

Repulsion between the electron clouds (or steric hindrance) of the two bulky –C*l* atoms [1]

[Total: 11]

2 **(a)** Use of the *Data Booklet* is necessary for this part of the question.

The sub–atomic makeup of certain ions formed from isotopes of cobalt and lead is given below:

	Number of neutrons	Number of electrons
Co ion	33	25
Pb ion	122	▨

In a particular experimental set–up, a beam containing the above ions of cobalt was passed through an electric field and was deflected by an angle of +10.2°.

Under identical conditions, another beam containing the above ions of lead was deflected by an angle of +6.0°.

What is the overall charge of the lead ions?

From the Data Booklet,
Proton number: Co = 27, Pb = 82

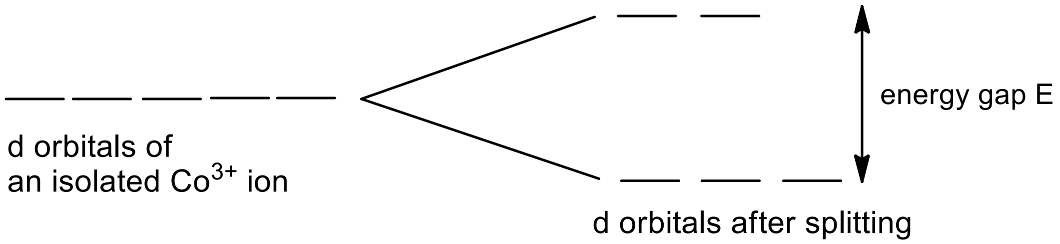
Charge of Co ion = +27 – 25 = +2
Nucleon number of Co = 33 + 27 = 60
Nucleon number of Pb = 122 + 82 = 204
Angle of deflection of Co ion = $+10.2 = k\left(\frac{2}{60}\right) \Rightarrow k = 306$
Let charge of Pb be x.
Angle of deflection of Pb ion = $+6.0 = 306\left(\frac{x}{204}\right)$
$x = +4$ ***(+ve sign must be included)***

[2]

(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.

CoF_6^{3-} and $[Co(NH_3)_6]^{3+}$ are both complexes with cobalt in the +3 oxidation state. However, only CoF_6^{3-} displays paramagnetism while $[Co(NH_3)_6]^{3+}$ does not. This is determined by whether the electronic configuration of the Co^{3+} ion in the complex displays a "high spin" or a "low spin" state.

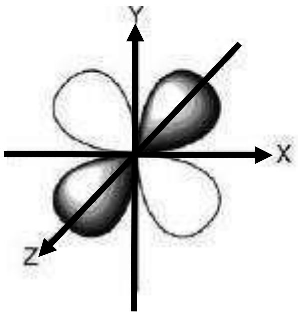
The following diagram shows how the d–orbitals are split in an octahedral environment.



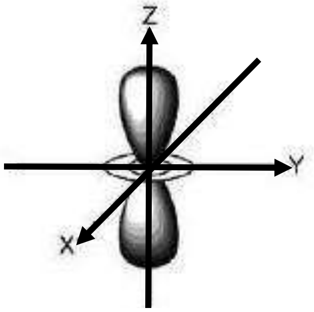
In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

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.

(i) Draw the shapes of the d_{xy} and d_{z^2} orbitals. Label your drawings clearly.



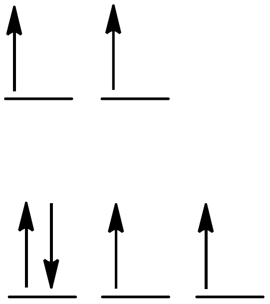
d_{xy}



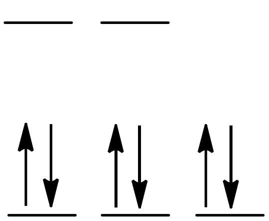
d_{z^2}

[2]

(ii) Using ↑ or ↓ to represent electrons, show, on the two diagrams below, the electronic distribution of a Co^{3+} ion in a high spin state, and in a low spin state. Hence, identify the cobalt complex that corresponds to each particular spin state.



d orbitals after splitting



d orbitals after splitting

Complex:	High spin	Low spin
	CoF_6^{3-}	**$[Co(NH_3)_6]^{3+}$**

[2]

(iii) Suggest why electrons usually prefer to occupy orbitals singly rather than in pairs.

To minimize repulsion between negatively (OR similarly) charged electrons. [1]

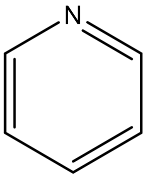
(iv) Using the explanation in **(b)(iii)**, together with the information given above, state and explain which of the two cobalt complexes contains the larger energy gap, E, between its d orbitals.

The low spin complex, $[Co(NH_3)_6]^{3+}$, contains the larger energy gap. Electrons pair up only if the energy gap is larger than the energy required to overcome the interelectronic repulsion. [1]

[Total: 8]

3 Frederick Thomas Trouton was an Irish physicist who observed a relationship between boiling points and enthalpy changes of vaporisation after studying many liquids. He published his findings and formulated Trouton's rule which states that the molar *entropy* of vaporisation, ΔS_{vap}, for most liquids is about 85 J K^{-1} mol^{-1}.

The boiling points and enthalpy changes of vaporisation of several organic liquids are as follows:

substance	boiling point / °C	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J K^{-1} mol^{-1}
propanone, $(CH_3)_2CO$	56.1	29.1	**88.4**
dimethyl ether, $(CH_3)_2O$	-24.8	21.5	86.6
ethanol, CH_3CH_2OH	78.4	38.6	**109.8**
octane, $CH_3(CH_2)_6CH_3$	125.6	34.4	86.3
pyridine, 	115.3	35.1	90.4

(a) Explain the term *entropy* and why ΔS_{vap} at constant pressure is positive.

Entropy is a measure of the dispersal of energy / disorderliness / randomness in a system.
Vapourisation involves the phase/state of a substance from liquid to gas at constant pressure, the same number of particles can move more freely and in greater volume in gaseous phase as compared to liquid phase resulting in greater entropy of a substance in gas phase as compared to liquid phase. [2]

(b) Complete the above table by calculating the ΔS_{vap} for two propanone and ethanol. Show your working for the calculation of ΔS_{vap} for propanone.

$$\Delta G = \Delta H - T\Delta S\text{; phase change } \therefore \Delta G = 0$$

$$\Delta S = \frac{\Delta H}{T} = \frac{29.1\times10^3}{56.1+273} = 88.4 \text{ J K}^{-1}\text{ mol}^{-1}$$

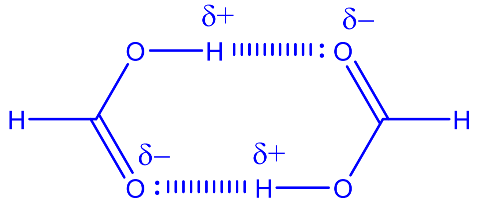
[2]

(c) By considering the structure and bonding of the various substances in this question, state and explain the relationship between strength of intermolecular forces of attraction and the entropy of a substance in the liquid state.

Octane is non-polar and has instantaneous dipole-induced dipole interactions between molecules.

Propanone, dimethyl ether and pyridine are polar and have stronger permanent dipole-permanent dipole attraction between molecules.
Ethanol is the most polar and has strongest hydrogen bonds between molecules.
The stronger the intermolecular forces of attraction between molecules, the lower the entropy of a substance in liquid state. [2]

(d) **(i)** With the aid of a diagram, show and label the bonding between two methanoic acid molecules in the **gaseous** phase.



[1]

(ii) Hence, predict if ΔS_{vap} for methanoic acid is more or less positive than predicted by Trouton's rule. Explain your reasoning carefully.

[No marks will be awarded if a prediction has no reasoning.]

ΔS_{vap} is less positive.
In gaseous phase, methanoic acid molecules exist as <u>dimers</u> which decrease the total number of molecules in the sample/show greater structure/lower randomness/reduce dispersal of energy leading to a smaller change in entropy during phase change. [2]

[Total: 9]

4 Ozone, O_3, is fairly stable but rapidly decomposes, with the release of heat, to form oxygen in the presence of silver catalyst. A silver catalyst was added to 800 cm^3 of a mixture of oxygen and ozone. The volume increased as follows and the reaction is complete at 1800 s.

Total volume of gas mixture, V_{total} / cm^3	800	805	810	815	818	819
volume of O_3(g) / cm^3	**38**	**28**	**18**	**8**	**2**	0
time, t / s	0	210	420	860	1350	1800

(a) **(i)** Write a chemical equation to represent the overall process of the decomposition of ozone to form oxygen.

$2O_3(g) \rightarrow 3O_2(g)$ [1]

(ii) By considering the stoichiometry of the reaction, calculate the initial volume of ozone and initial volume of oxygen in the mixture.

For every 2 mol of O_3 reacted, there is a net increase of 1 mol of gas particles. Since there is a net increase of 19 cm^3 of gas at the end of the reaction, by Avogadro's Law,
no. of moles of O_3(g) = 19.0 × 2 = 38.0 cm^3
no. of moles of O_2(g) = 800 – 38 = 762 cm^3 [1]

(iii) Given that volume of O_3 reacted = 2 (V_{total} – 800), complete the above table by calculating the volume of ozone in the mixture at the various times stated. Fill in the volume of O_3 at t = 0 s using your answer in **a(ii)**.

At 210 s, there is a net increase in gas volume of 5 cm^3. This means 10 cm^3 of O_3(g) has reacted.

Amount of O_3(g) left = 38 – 10 = 28 cm^3 [1]

(iv) The decomposition of ozone is a *first order* reaction.

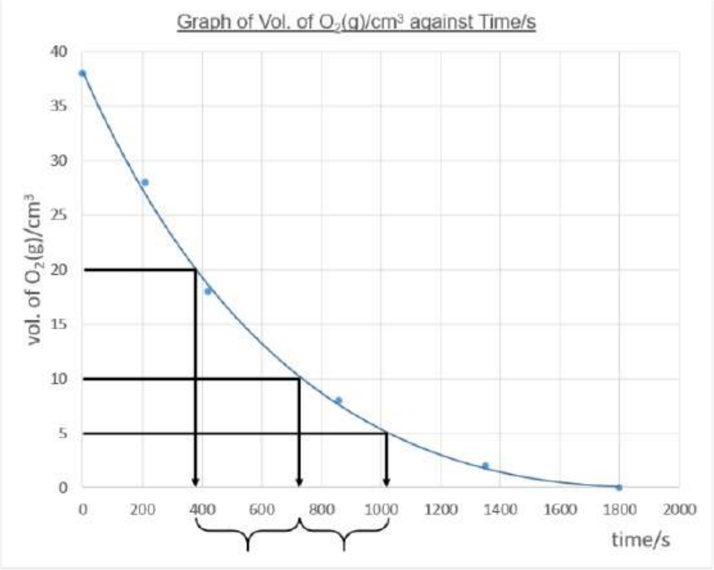
Write down the rate equation and explain the term *first order*.

rate = $k[O_3]$

The order of reaction refers to the power to which the O_3 concentration term is being raised in the rate equation. [2]

(v) Show, by means of a suitable graph, that these data are consistent with a first order reaction.

[If you are unable to solve (iii), sketch the graph without data points and indicate clearly how it can be used to verify the order of reaction.]



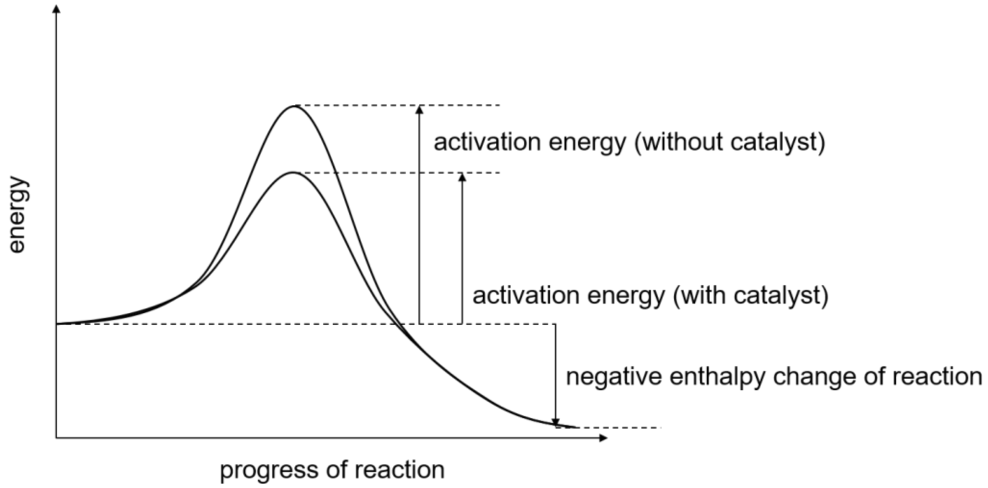
constant $t_{1/2}$ ≈ 300 s

[2]

(b) **(i)** Silver is a heterogeneous catalyst in this reaction. Outline how a heterogeneous catalyst work.

Reactant molecules are adsorbed on the surface of the catalyst. Concentration of reactants at the catalyst surface is increased and bonds in reactant molecules are weakened resulting in lowering of activation energy. Products formed subsequently desorb from the surface. [2]

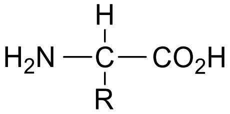
(ii) Draw a labelled energy profile diagram for the decomposition of ozone, with and without the use of a catalyst.



[2]

[Total: 11]

5 **(a)** Nitrogen is one of the key elements present in α-amino acids, the building block of proteins. α-amino acids have the following general formula.



$$H_2N-\underset{R}{\overset{H}{C}}-CO_2H$$

The table below shows the R groups of the α-amino acids present in a polypeptide, **J**.

α–amino acid	M_r	R group
asp	133.0	$-CH_2CO_2H$
lys	146.0	$-CH_2CH_2CH_2CH_2NH_2$
gln	146.0	$-CH_2CH_2CONH_2$

You have to refer to the table above when answering **a(i)** and **a(ii)**.

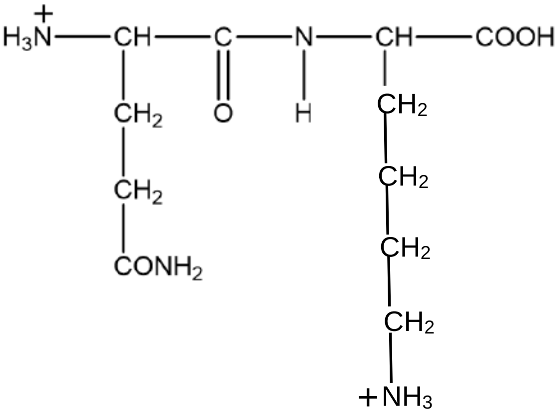
(i) When polypeptide **J** undergoes hydrolysis, three aspartic acid, two lysine and one glutamine molecules were formed as shown in the following reaction:

$$\textbf{J} \longrightarrow 3\text{ asp} + 2\text{ lys} + 1\text{ gln}$$

Calculate the M_r of polypeptide **J**.

M_r of J = 3(133.0) + 2(146.0) + 1(146.0) – 5(18.0) = 747.0 [1]

(ii) A dipeptide, *gln–lys*, is obtained upon hydrolysis of polypeptide **J** by an enzyme. Draw the structural formula of this dipeptide at pH 1.



[1]

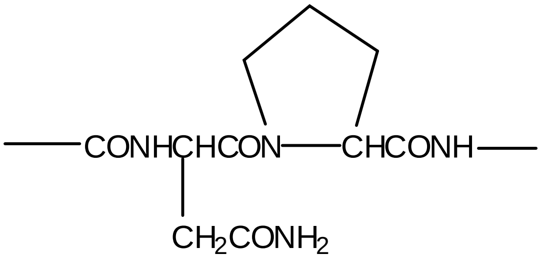
(iii) A sample of lysine, extracted from the hydrolysis of polypeptide **J** rotated plane polarised light anticlockwise. However, a second sample of lysine obtained from laboratory synthesis had no effect on plane polarised light.

Suggest an explanation for these observations.

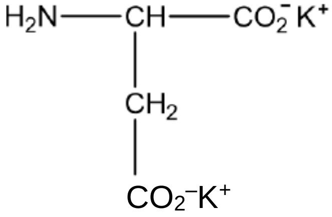
The sample of aspartic acid extracted from the hydrolysis of polypeptide J contains only one enantiomer. However, the one obtained from laboratory synthesis is a racemic mixture, in which each

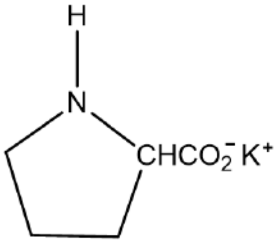
of the both enantiomers rotating plane polarised light by an equal angle but in opposite directions. [2]

(iv) Part of the chain of another polypeptide **K** is shown below.



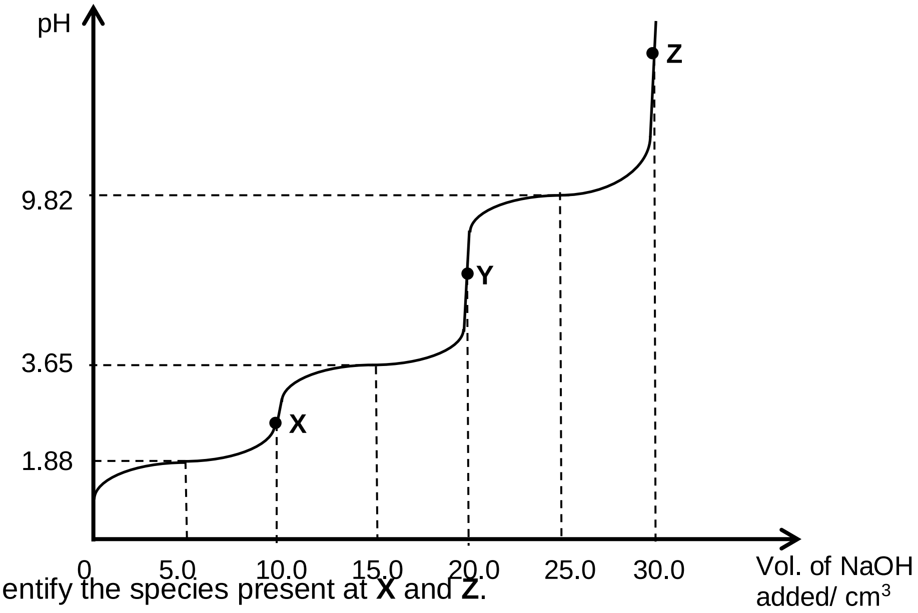
Draw the structure of the organic products formed when polypeptide **K** is treated with excess aqueous KOH under prolonged heating.





[2]

(b) The following titration curve is obtained when a solution of fully protonated aspartic acid, $H_3N^+CH(CH_2CO_2H)CO_2H$ is titrated with NaOH(aq). **X**, **Y** and **Z** denote the first, second and third equivalence point respectively.



(i) Identify the species present at **X** and **Z**.

X: $H_3N^+CH(CH_2CO_2H)CO_2^-$
Z: $H_2NCH(CH_2CO_2^-)CO_2^-$

[1]

(ii) Hence, explain why there is a sharp increase in pH when a small amount of NaOH(aq) is added to solution at **Z**.

The solution at Z is basic. It <u>does not have any H^+ to neutralise $OH^–$ from NaOH</u>. Hence, there is a large increase in pH with the addition of small amount of NaOH(aq). [1]

(iii) At pH 10.0, the mixture can act as a buffer. Identify the two species present in this buffer. With the aid of an equation, show how the buffer works when a small amount of acid is added to it.

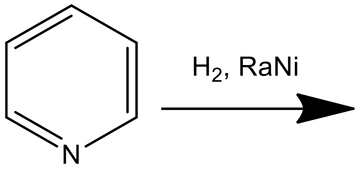
$H_3N^+CH(CH_2CO_2^-)CO_2^-$ and $H_2NCH(CH_2CO_2^-)CO_2^-$
$H^+ + H_2NCH(CH_2CO_2^-)CO_2^- \rightarrow H_3N^+CH(CH_2CO_2^-)CO_2^-$

[2]

(iv) Calculate the ratio of the concentrations of the two species in the buffer required to maintain the pH in **(b)(iii)**.

$\text{pH} = \text{p}K_{a3} + \lg([\text{salt}] / [\text{acid}])$
$10.0 = 9.82 + \lg([\text{salt}] / [\text{acid}])$
$[\text{salt}] / [\text{acid}] = 1.51$ [2]

(c) Pyridine is a cyclic structure containing nitrogen and is analogous to that of benzene. It can be reduced to piperidine with Raney nickel (RaNi) as shown in the following reaction:



(i) State the type of hybrid orbital occupied by the lone pair of electrons on the N atom in pyridine and piperidine.

Pyridine: **sp^2**

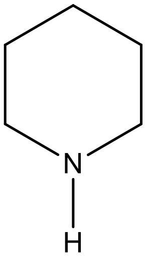
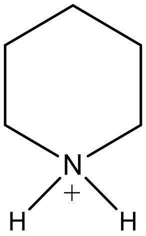
Piperidine: **sp^3**

[1]

(ii) Hence, suggest how the basicity of pyridine might compare to that of piperidine. Give reasons for your answers.

Pyridine is a weaker base than piperidine. Lone pair electrons in sp^2 orbitals is closer to the nucleus / more strongly attracted by the nucleus due to greater s character. Hence, lone pair electrons is less available for donation to acid in pyridine. [2]

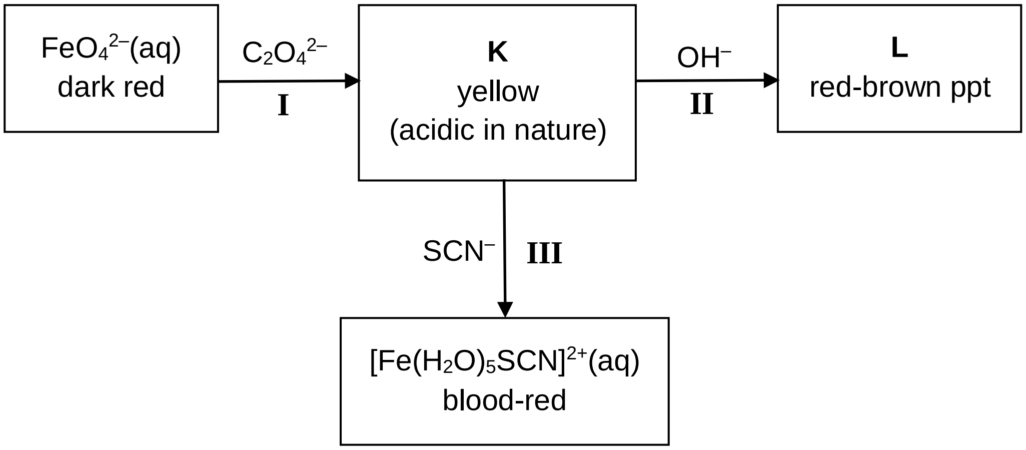
(iii) In an attempt to form a quaternary amine salt, a student treated piperidine with excess iodomethane under acidic condition. Explain why this synthesis will not be successful.

Under acidic conditions,  **is neutralised to form**  **. Hence, the protonated piperidine will not be able to act as a nucleophile since the lone pair on the N is not available for the nucleophilic substitution to form the quaternary amine salt.** [2]

[Total: 17]

6 **(a)** In most of its compounds, iron has the oxidation state +2 or +3. However, other oxidation states of iron are possible. For example, potassium ferrate(VI), K_2FeO_4, contains iron in the +6 oxidation state. Reflecting its high oxidation state, FeO_4^{2-} is a powerful oxidising agent.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Iron is considered to be a transition metal. Justify the statement.

Iron is a d-block element that forms one or more stable ions [Fe^{2+}, Fe^{3+} or Fe(VI)] with partially filled d subshell and therefore considered to be a transition element. [1]

(ii) Explain why FeO_4^{2-}(aq) is coloured.

In the presence of ligands, the degenerate 3d orbitals are split into 2 different energy levels (d-d splitting).
A 3d e from the lower energy level is promoted to the upper energy level by absorbing energy from the visible region of the electromagnetic spectrum, known as d-d transition (which is possible only with partially-filled d subshell configuration).
The complement of the colour absorbed is seen. [2]

(iii) State the type of reaction that occurred in reactions **I** to **III**.

I – Redox reaction
II – Precipitation
III – Ligand exchange [3]

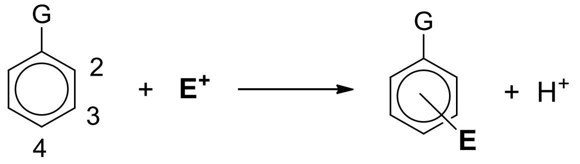
(iv) Write an equation to illustrate the acidic nature of **K**.

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+$$ [1]

(v) Using relevant data from the *Data Booklet,* predict whether a reaction will occur when iodide ions are mixed with **K** and **L** separately. Write an equation for any reaction that occurs.

K – $[Fe(H_2O)_6]^{3+}$
L – $Fe(OH)_3$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^⦵ = +0.77$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^⦵ = +0.54$ V
c $= E^⦵_{red} - E^⦵_{ox}$
$= +0.77 - (+0.54)$
$= +0.23$ V
$E^⦵_{cell} > 0$ V, spontaneous
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
The reaction is likely to occur because the reactants are oppositely charged and can attract each other.
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $E^⦵ = -0.56$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^⦵ = +0.54$ V
$E^⦵_{cell} = E^⦵_{red} - E^⦵_{ox}$
$= -0.56 - (+0.54)$
$= -1.10$ V
$E^⦵_{cell} < 0$ V, not spontaneous
Reaction is unlikely to occur. [2]

(b) In an aromatic substitution reaction, 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**.



(i) Name the type of reaction mechanism between phenol and the incoming group, **E**.

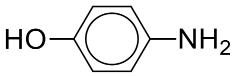
Electrophilic (aromatic) substitution [1]

(ii) Both phenylamine, $C_6H_5NH_2$, and phenol, activate the benzene ring in a similar manner so that the ring becomes highly susceptible to the incoming group, **E**. Comparing the difference in electronegativity between oxygen in phenol and nitrogen in phenylamine, explain the relative rate of phenol and phenylamine with the incoming group, **E**.

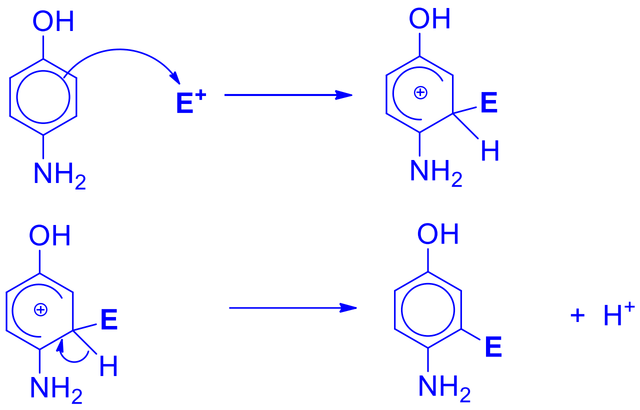
Oxygen is <u>more electronegative</u> than nitrogen. Oxygen in phenol therefore has <u>less tendency to donate the lone pair of electrons to benzene ring</u> compared to nitrogen in phenylamine. This results in <u>lower electron density</u> in benzene and <u>less electron rich</u> to attract electrophile E. Hence

phenol is less reactive towards electrophilic substitution compared to phenylamine. [2]

(iii) From your answers in **(b)(ii)**, write the mechanism for the mono-substitution of 4-aminophenol with the incoming group, **E**$^+$.



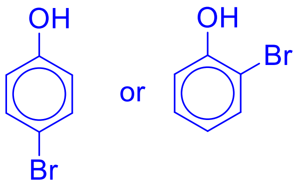
4-aminophenol



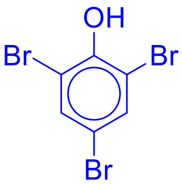
[3]

(c) The choice of solvent used in the bromination of phenol can greatly affect the type of product formed.

(i) Draw the structure of the product formed when phenol undergoes reaction with Br_2 in water and with Br_2 in a non-polar organic solvent like CS_2 separately.



with Br_2 in CS_2



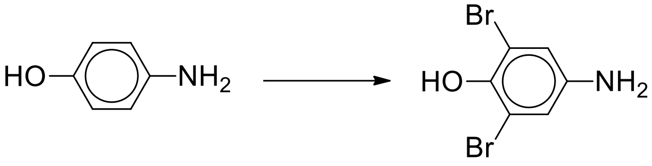
with Br_2 (aq) [1]

(ii) By considering the nature of the incoming group, **E**, suggest an explanation for the difference in the reaction between phenol and bromine dissolved in the two different types of solvent mentioned in **(c)(i)**.

Polar solvent like water can interact and stabilise the partial charge in $Br^{\delta+}$–$Br^{\delta-}$ molecule and therefore results in a higher concentration of polarised Br_2 molecule for multiple substitution in the benzene ring.
OR
Non-polar solvent like CS_2 is unable to interact and stabilise the partial charge in $Br^{\delta+}$–$Br^{\delta-}$ molecule and results in a lower concentration of polarised Br_2 molecule. Hence only mono-substitution can take place.
OR

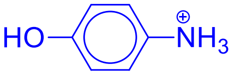
Phenol dissociates in water to form phenoxide carrying negatively charged O which is more electron-donating than –OH group, hence, ring is more activated for multiple substitution. [1]

(d) Suggest the reagents and conditions required to carry out the following transformation and explain the rationale for the choice.



Reagents: Add aqueous bromine with dilute HC*l*

Conditions: room temperature

Rationale: Addition of acid is to form  **that makes $-NH_3^+$ a deactivating group. Being deactivating in nature, the –OH group will now determine the electrophilic substitution at 2- & 6- position with respect to phenol group.** [2]

[Total: 19]

Victoria Junior College
2019 H2 Chemistry Prelim Exam 9729/3
Suggested Answers

Section A

Answer **all** the questions in this section.

1 **(a)** Account for the reactions that occur when $MgCl_2$ and PCl_5 are separately dissolved in water. Predict the pH of the resulting solutions formed and write equations for the reactions that occur. [4]

Mg^{2+} has high charge density due to small ionic radius (and high charge). Mg^{2+} has high polarising power and hence $MgCl_2$ undergoes hydration and partial hydrolysis, producing a slightly acidic solution.

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$ hydration
$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5OH]^+ + H_3O^+$ hydrolysis
pH of resulting solution = 6.5

PCl_5 undergoes complete hydrolysis due to the presence of energetically accessible vacant 3d orbitals on phosphorus which can accommodate lone pair from water molecules. The solution produced is strongly acidic.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
pH of resulting solution = 2

(b) A sample consists of a solid mixture of MgO and Al_2O_3. Describe briefly an experimental procedure that will enable you to separate the mixture and recover each of the oxides in its pure form. [3]

1. Add excess NaOH(aq) to the sample.
2. Filter the resulting mixture. The residue collected is mainly MgO.
3. Wash the residue with distilled water and press between pieces of filter paper to obtain dry solid MgO.
4. To the filtrate, add HCl(aq) dropwise till the maximum mass of precipitate is formed.
5. Filter the resulting mixture. The residue collected is mainly $Al(OH)_3$.
6. Wash the residue with distilled water and press between pieces of filter paper to obtain dry solid $Al(OH)_3$.
7. Heat the residue till constant mass to obtain dry solid Al_2O_3.
[Note: $Al(OH)_3$ is expected to decompose on heating to form Al_2O_3, similar to Group 2 hydroxides.]

(c) The highest fluoride of xenon, XeF_6, can be obtained by heating the octafluoroxenates of the Group 1 metals, M_2XeF_8, where M represents the Group 1 metal.

$$M_2XeF_8 \rightarrow 2MF + XeF_6$$

Suggest reasons why the sodium salt (M = Na) decomposes below 100 °C, whereas the caesium salt (M = Cs) requires a temperature of 400 °C. Hence explain why $MgXeF_8$ is not known to exist. [3]

Down group 1, as ionic radius increases, charge density of cations decreases, polarising power of cations decreases, which polarises the XeF_8^{2-} anion to a lesser extent. The anion becomes more thermally stable and hence higher temperature is required to decompose caesium salt compared to sodium salt.

Mg^{2+} has higher charge density than Na^+, making $MgXeF_8$ very unstable and hence does not exist.

(d) Suggest identities for the following substances **A** to **D**, writing equations where appropriate.

When magnesium is heated with nitrogen under inert conditions, an ionic compound, **A** is produced. When water is added to **A**, a colourless gas **B** which turns damp red litmus paper blue is produced. **B** reacts with chlorate(I) ion, ClO^- in a 2 : 1 mole ratio to form a colourless liquid **C** with empirical formula NH_2. The reaction of **C** with sulfuric acid in a 1 : 1 mole ratio produces a salt **D**, $N_2H_6SO_4$, which contains one cation and one anion per formula unit. [4]

A: Mg_3N_2
B: NH_3
C: N_2H_4
D: $[N_2H_5^+][HSO_4^-]$ (accept $[N_2H_6^{2+}][SO_4^{2-}]$)

$3Mg + N_2 \rightarrow Mg_3N_2$
$Mg_3N_2 + 3H_2O \rightarrow 3MgO + 2NH_3$ (Accept $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$)
$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$
$N_2H_4 + H_2SO_4 \rightarrow [N_2H_5^+][HSO_4^-]$ (accept $[N_2H_6^{2+}][SO_4^{2-}]$)

(e) Real gases do not obey the ideal gas equation exactly. Many chemists have tried to come up with gas equations that describe the behaviour of real gases. In 1873 J D van der Waals introduced an approximate gas equation that is applicable for all real gases. The van der Waals equation is

$$P = \frac{nRT}{V - n\mathbf{b}} - \mathbf{a}\frac{n^2}{V^2}$$

where **a** and **b** are constants which are characteristic of each gas. The other symbols carry their usual meaning and units as in the ideal gas equation.

(i) Using what you have learnt about the differences between ideal and real gases, suggest what the constants **a** and **b** represent. [2]

The constant a takes into account real gas particles have intermolecular forces of attraction, hence the pressure would be lower than expected if assuming ideal gas behaviour (the equation involves subtracting an^2/V^2)

The constant b takes into account real gas particles are of finite size and occupy a significant volume compared to the volume of the container, hence the volume in which the gas particles can freely move about would be lower than expected if assuming ideal gas behaviour (the equation involves subtracting nb from V)

(ii) The values of the constants **a** and **b** for CO_2 are **a** = 0.3658 Pa m^6 mol^{-2} and **b** = 4.29×10^{-5} m^3 mol^{-1}.

Use your answer in **(e)(i)** to suggest how the value of the constant **a** for xenon (Xe) will compare with CO_2. Explain your answer briefly. [1]

Xe will have larger value of a, since it will have stronger instantaneous dipole-induced dipole interactions and have larger particle size than CO_2.

(iii) Use the

- ideal gas equation and
- van der Waals equation

to calculate the pressure exerted by 1 mol of CO_2 at a temperature of 30 °C and volume of 1 dm^3.

[3]

Using ideal gas equation,
pressure = $1 \times 8.31 \times (30 + 273) / (1 \times 10^{-3}) = 2.52 \times 10^6$ Pa

Using van der Waals equation,
pressure
$= [1 \times 8.31 \times (30 + 273)] / (1 \times 10^{-3} - 1 \times 4.29 \times 10^{-5}) - 0.3658\,[1^2 / (1 \times 10^{-3})^2]$
$= 2.26 \times 10^6$ Pa

[Total: 20]

2 **(a)** Malonic acid, $CH_2(CO_2H)_2$ is an organic *weak dibasic acid*. It is a building block chemical to produce numerous valuable compounds, including the flavour and fragrance compound, cinnamic acid, and the pharmaceutical compound, valproate. The two pK_a values of $CH_2(CO_2H)_2$ are 2.83 and 5.69.

(i) Define the term *weak acid*. [1]

Weak acid **<u>partially dissociates</u>** in water to give **<u>H^+ ions</u>**.

(ii) Calculate the pH of 25.0 cm^3 solution of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. [1]

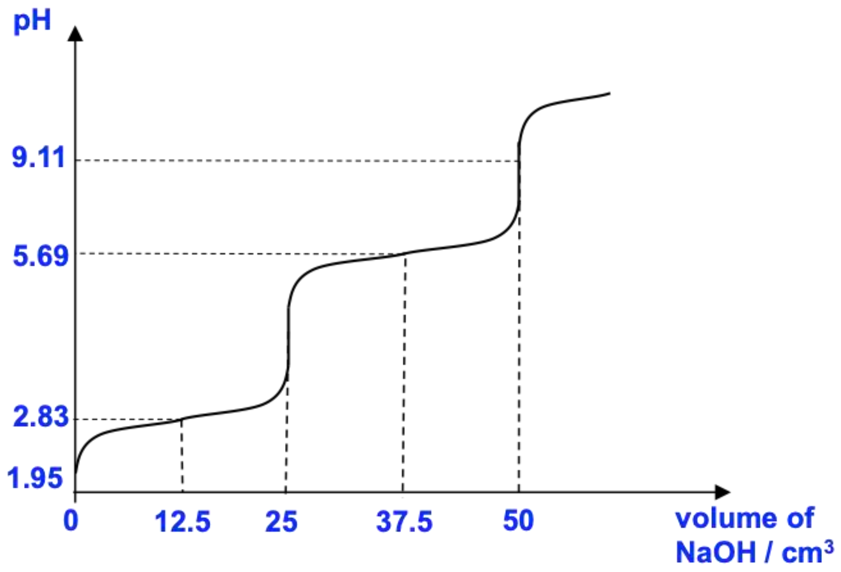
$$K_a = \frac{[H^+][CH_2(COOH)(COO^-)]}{[CH_2(COOH)_2]}$$

$$pH = -lg\sqrt{K_a \times [CH_2(COOH)_2]} = -lg\sqrt{10^{-2.83} \times 0.100} = \underline{\mathbf{1.92}}$$

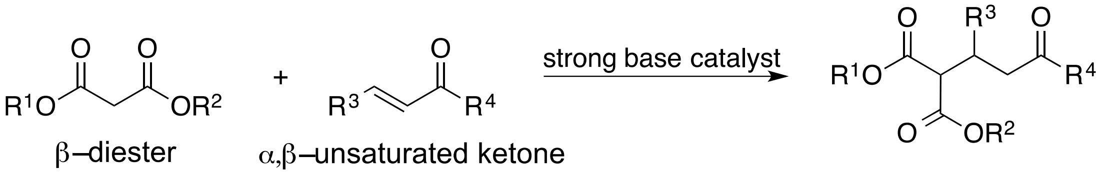
(iii) Calculate pH of the resulting solution when 50 cm^3 of 0.100 mol dm^{-3} NaOH was added to the solution in **(a)(ii)**. [2]

When 50 cm^3 of NaOH added, complete neutralisation has taken place, product is $CH_2(COO^-)_2$.
$[CH_2(COO^-)_2] = 25 \div 75 \times 0.100 = 0.0333$ mol dm^{-3}
pK_b of $(CH_2COO^-)_2 = 14 - 5.69 = 8.31$
$pOH = -lg\sqrt{K_b \times [CH_2(COO^-)_2]} = -lg\sqrt{10^{-8.31} \times 0.0333} = 4.89$
$pH = 14 - pOH = \underline{\mathbf{9.11}}$

(iv) Using your answers in **(a)(ii)** and **(a)(iii)**, as well as the pK_a values provided, sketch a graph to show how the pH of the solution changes as 50 cm^3 of 0.100 mol dm^{-3} NaOH is gradually added to 25.0 cm^3 of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. Clearly indicate the corresponding volumes of NaOH in your graph. [2]



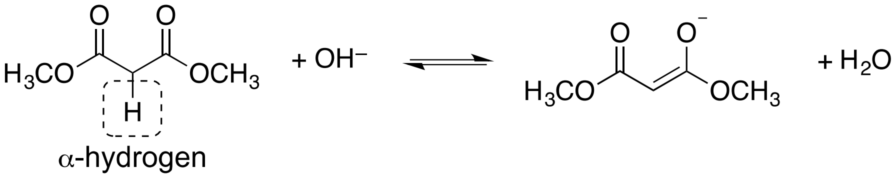
(b) Malonic acid can be converted to its corresponding β–diester. β–diesters are commonly used as starting compounds in the Michael addition reaction, where they react with α,β-unsaturated ketones. It is one of the most useful methods for the formation of C–C bonds.



(i) Suggest reagents and conditions to convert malonic acid to dimethyl malonate, $CH_2(COOCH_3)_2$. State the type of reaction. [2]

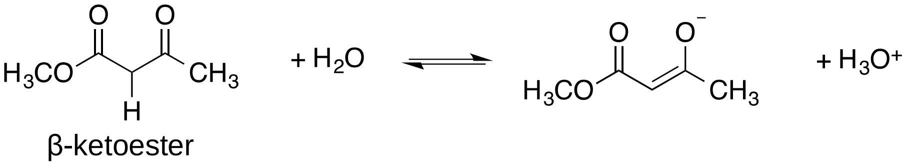
CH_3OH, conc H_2SO_4, heat
condensation

(ii) The first step in the mechanism of Michael addition involves an acid–base reaction where the strong base catalyst extracts an α-hydrogen from the β–diester.

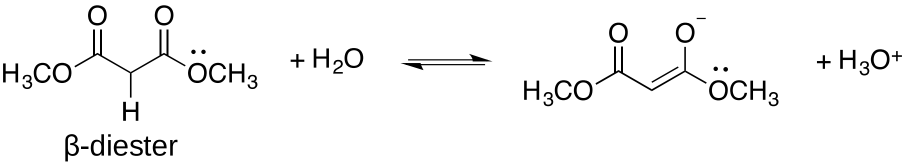


Reagents similar to the malonate ester can undergo the same type of reaction. The pK_a values of malonate ester and another similar reagent are as follows:

pKa



11



13

Explain the difference in pK_a values between the two compounds. [2]

β-ketoester has a **lower pKa** than β-diester, suggesting that it is a **stronger acid** than β-diester.

Strength of acid is dependent on the **stability of anion** formed.

The anion of β-diester is attached to an **$-OCH_3$ group**. **Lone pair in oxygen atom overlaps with p orbitals** of the adjacent unsaturated carbon, and is **delocalized** into the system, increasing the electron density. The negative charge is **intensified to a larger extent**, cause it be less stable and thus a weaker acid.

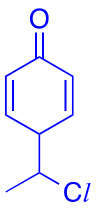
(iii) Compound **A**, C_8H_9ClO, contains a non-aromatic six-membered ring. **A** reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with

Tollen’s reagent. 1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum. When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed. **B** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. When **B** is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed. **D** also gives a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.

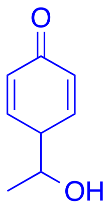
Deduce the structural formulae of compounds **A**, **B**, **C**, **D** and **E**, explaining clearly your reasoning for all reactions described. [10]

Observations	**Deductions**
A, C_8H_9ClO reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.	**A** undergoes **condensation**. **A** contains a **carbonyl**.
A, C_8H_9ClO does not react with Tollen’s reagent.	**A** does not contain aldehyde. **A** is a **ketone**.
1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum.	**A** undergoes **reduction**. **3 degrees of unsaturation**. Ketone reduced A contains **alkene.**
When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed.	**A** undergoes **nucleophilic substitution**. **aliphatic –Cl** substituted to form **–OH** in **B**.
B gives a pale yellow precipitate when warmed with alkaline aqueous iodine.	**B** undergoes **oxidative cleavage** to give **CHI_3.** **B** contains either **$–CH(CH_3)(OH)$ or $–COCH_3$ structural unit**.
B is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed.	**B** undergoes **oxidative cleavage** of **C=C**
D also gives a pale yellow precipitate when warmed with alkaline aqueous iodine.	**D** undergoes oxidative cleavage. **D** contains either **$–COCH_3$ structural unit**.
A is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.	**A** contains **α,β-unsaturated ketones**.

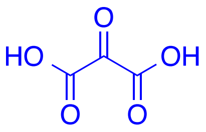
A



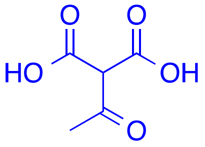
B



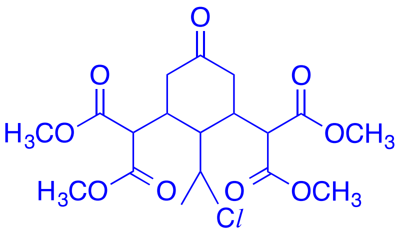
C



D



E



3 **(a)** A Latimer diagram provides a concise way of representing large amount of information about the different oxidation states of an element. In a Latimer diagram, the most highly oxidised form of an element is written on the left, with successively lower oxidation states to the right. The different species are connected by arrows, and the standard electrode potential in volts is written above each arrow.

The Latimer diagrams for chlorine in acidic and alkaline medium are shown below.

In acidic medium:

$$ClO_4^- \xrightarrow{+1.19\text{ V}} ClO_3^- \xrightarrow{+1.21\text{ V}} ClO_2^- \xrightarrow{+1.66\text{ V}} ClO^- \xrightarrow{+1.64\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

In alkaline medium:

$$ClO_4^- \xrightarrow{+0.36\text{ V}} ClO_3^- \xrightarrow{+0.35\text{ V}} ClO_2^- \xrightarrow{+0.65\text{ V}} ClO^- \xrightarrow{+0.40\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

(i) Define the term *standard electrode potential*. [1]

The term standard electrode potential refers to the potential of a half–cell relative to that of a standard hydrogen electrode, measured at 298 K, 1 bar for each gas and 1 mol dm^{-3} for each aqueous ion .

(ii) The standard electrode potentials in a Latimer diagram are not additive. For example, the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is **not** the sum of +1.19 V and +1.21 V and +1.66 V. However, their respective standard Gibbs' free energy changes are additive.

Using relevant data given below, show that the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is 1.34 V. [2]

electrode reaction	$E^\ominus$ / V	$\Delta G^\ominus$ / kJ mol^{-1}
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–220.7
$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$	+1.21	–233.5
$ClO_2^- + 2H^+ + 2e^- \rightleftharpoons ClO^- + H_2O$	+1.66	–320.4
$ClO^- + 2H^+ + e^- \rightleftharpoons \tfrac{1}{2}Cl_2 + H_2O$	+1.64	–158.3
$\tfrac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36	–131.2

$\Delta G^\ominus$ for ClO_4^- to ClO^- = (–220.7) + (–233.5) + (–320.4)
= –774.6 kJ mol^{-1}

Since $\Delta G^\ominus = -nFE^\ominus$

$$E^\ominus \text{ for } ClO_4^- \text{ to } ClO^- = -\frac{(\Delta G^\ominus \text{ for } ClO_4^- \text{ to } ClO^-)}{n \times F}$$

$$= -\frac{(-774.6 \times 1000)}{6 \times 96500}$$

$$= +1.34 \text{ V (shown)}$$

(iii) With the exception of the conversion of Cl_2 to Cl^-, the standard electrode potentials in alkaline medium are less positive than their corresponding conversions in the acidic medium.

Suggest why this is so. [2]

Other than the conversion of Cl_2 to Cl^-, all other conversions have H^+ on the left hand side of the electrode equations. The addition of OH^- will cause $[H^+]$ to decrease . By Le Chatelier's Principle, the equilibrium position will shift to the left to counteract the decrease in $[H^+]$. Hence reduction of each electrode reaction becomes less favoured .

(iv) A disproportionation reaction is a redox reaction in which a chemical species undergo reduction and oxidation simultaneously.

In hot alkaline medium, Cl_2 undergoes disproportionation to form two chlorine-containing species according to the following equation.

$$3Cl_2(g) + xOH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_y^-(aq) + zH_2O(l)$$

By considering the number of moles of electrons transferred and using the Latimer diagram for chlorine in alkaline medium, first solve for y. Then, use it to solve for x and z. [2]

Total electrons gained (Cl_2 to Cl^-) = 5 x 1
= 5 mol

Total electrons lost (Cl_2 to ClO_y^-) = 5 mol

Based on the Latimer diagram, the oxidation state of Cl in ClO_y^- has to be +5 . Thus the other chlorine-containing specie is ClO_3^- i.e. $y = 3$.

[R]: $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
[O]: $Cl_2(g) + 12OH^-(aq) \longrightarrow 2ClO_3^-(aq) + 6H_2O(l) + 10e^-$

Balancing redox equation, 5[R] +1[O]:
$6Cl_2(g) + 12OH^-(aq) \longrightarrow 10Cl^-(aq) + 2ClO_3^-(aq) + 6H_2O(l)$
$3Cl_2(g) + 6OH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

$x = 6$, $z = 3$

(b) Besides the standard hydrogen electrode, other reference electrodes have also been employed in electrochemistry. An example is the silver chloride electrode, which involves dipping silver metal coated with solid silver chloride into a solution of sodium chloride. The solubility product for $AgCl$ is 2.0×10^{-10} $mol^2\ dm^{-6}$.

(i) The standard electrode potential of a silver chloride electrode is +0.230 V. However, when 1.0 mol dm^{-3} sodium chloride is used to set up the silver chloride electrode, this value cannot be achieved.

Explain why this is so. [1]

The sparingly soluble $AgCl$ can also contribute Cl^- to the electrolyte. Hence, $[Cl^-]$ will be more than 1 mol dm^{-3}, which means that the electrode potential value achieved will be non–standard.

At 298 K, the electrode potential of the silver chloride electrode, *E*, can be estimated from the concentration of silver ions present using formula (1):

$$E = 0.80 - 0.0591 \log \frac{1}{[\mathrm{Ag^+}]} \text{ .....formula (1)}$$

(ii) Calculate the value of *E* in each of the following cases:

- in pure water and
- when the addition of sodium chloride results in a chloride ion concentration of 2.5 mol dm^{-3}. [3]

In pure water

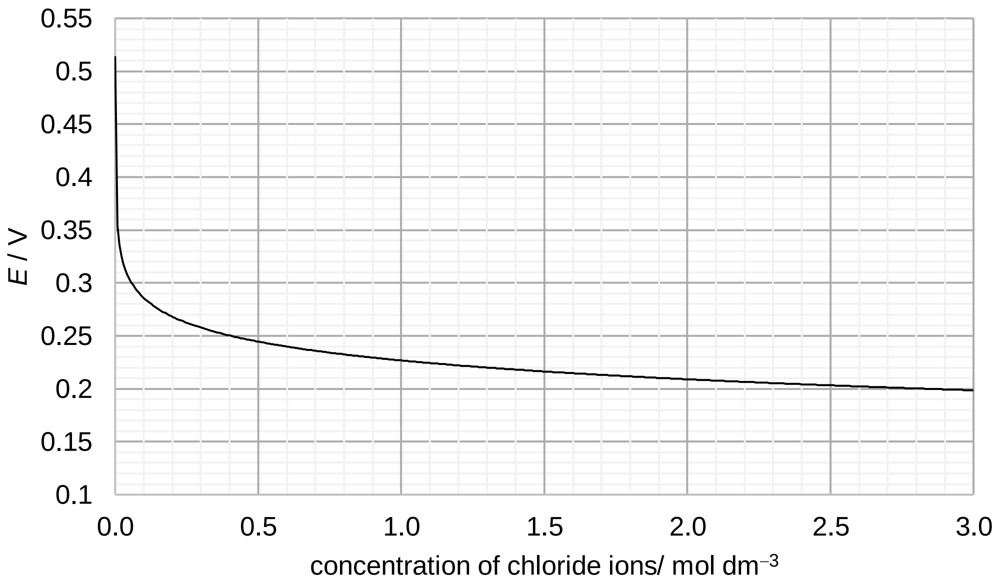
K_{sp} of AgC*l* = $[Ag^+].[Cl^-]$
$2.0 \times 10^{-10} = x^2$
$[Ag^+] = x$
$= 1.41 \times 10^{-5}$ mol dm^{-3}

$E = 0.80 - 0.0591 \log \frac{1}{(1.41 \times 10^{-5})}$
$= +0.513$ V

When $[Cl^-] = 2.5$ mol dm^{-3}
K_{sp} of AgC*l* = $[Ag^+].[Cl^-]$
$2.0 \times 10^{-10} = [Ag^+].[2.5]$
$[Ag^+] = 8.00 \times 10^{-11}$ mol dm^{-3}

$E = 0.80 - 0.0591 \log \frac{1}{(8.00 \times 10^{-11})}$
$= +0.203$ V

(iii) Using the graph given below, suggest why sodium chloride solution ranging from 1.0 mol dm^{-3} to 3.0 mol dm^{-3} is typically used in the setting up of a silver chloride electrode rather than pure water. [1]



The value of *E* when using 1.0 mol dm^{-3} to 3.0 mol dm^{-3} sodium chloride solution is less affected by change in concentration compared to using pure water. This makes the silver chloride electrode more suitable for use as a reference electrode.

(iv) A student attempted to study the validity of formula (1) by adding aqueous ammonia to vary the concentration of silver ions in solution. This is due to the ability of ammonia to form a complex with the silver ions, thus decreasing its concentration in solution.

Explain a potential problem that may arise with this method of analysis. [1]

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$
$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$ .....(I)

By Le Chatelier's Principle, equilibrium position of (I) will shift to the left to counteract the decrease in $[Ag^+]$, causing AgC*l*(s), which is needed for the silver chloride reference electrode, to dissolve.

OR

The decrease in $[Ag^+]$ will cause ionic product of AgC*l* to fall below its K_{sp} value, thus causing AgC*l*(s), which is needed for the silver chloride reference electrode, to dissolve.

(vi) The silver chloride electrode is used in many medical equipment. In a particular device used for electrocardiography, a layer of silver metal is plated with a thickness of 1 mm onto an electrode with a surface area of 0.12 cm^2 before coating it with solid silver chloride.

If a current of 15.0 mA is used for the electroplating process, calculate the time required to completely plate the silver metal onto the electrode from a solution containing $Ag^+(aq)$.

[The density of silver metal is 10.5 g cm^{-3}] [2]

Volume of Ag needed = 0.12 x 0.1
= 0.012 cm^3

Mass of Ag needed = 10.5 x 0.012
= 0.126 g

Amount of Ag needed = 0.126 / 107.9
= 1.17×10^{-3} mol

Amount of e^- needed, n_e = 1.17×10^{-3} mol

Q = n_e F
= (1.17×10^{-3}) (96500)
= 112.9 C

t = Q / I
= (112.9) / (15.0×10^{-3})
= 7.53×10^3 s

(c) When sodium halides react with concentrated sulfuric acid, an acid-base reaction takes place resulting in the formation of 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

Subsequently, depending on the reducing strength of the hydrogen halides, a further reaction might take place with concentrated sulfuric acid, resulting in the formation of halogens, a sulfur-containing product and water.

The observations for the reaction of the different sodium halides with concentrated sulfuric acid are shown below:

sodium halide	observations
NaC*l*	white fumes of HC*l*
NaBr	white fumes of HBr red-brown Br_2 gas which condenses to form a red-brown liquid colourless and pungent SO_2 gas
NaI	white fumes of HI violet I_2 gas which condenses to form a black solid colourless and pungent H_2S gas

(i) Write a balanced molecular equation for each of the following reactions:

- between gaseous HBr and concentrated H_2SO_4

- between gaseous HI and concentrated H_2SO_4

[2]

$2HBr(g) + H_2SO_4(l) \longrightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$
$8HI(g) + H_2SO_4(l) \longrightarrow 4I_2(s) + H_2S(g) + 4H_2O(l)$
[state symbols not required]

(ii) Arrange the hydrogen halides in order of increasing reducing strength. Explain your answer, using relevant information from the *Data Booklet* to support the difference in observations. [3]

In order of increasing reducing strength: HC*l* < HBr < HI

From *Data Booklet*, – for quoting $E^\ominus$ values
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

From C*l* to I, $E^\ominus(X_2/X^-)$ becomes less positive . Thus oxidation of half-equation is more favoured and reducing strength of halides increases.

HC*l*, the weakest reducing agent, cannot reduce S.
HBr, a stronger reducing agent, can reduce S from +6 (H_2SO_4) to +4 (SO_2).
HI, the strongest reducing agent, can reduce S from +6 (H_2SO_4) to –2 (H_2S).

[Total: 20]

Section B

Answer **one** question from this section.

4 Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When a 1.00 g sample of sulfur was dissolved in 1 dm^3 of an organic solvent, the following equilibrium was established:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

The percentages by mass of S_7 and S_8 at equilibrium are:

ring size	S_7	S_8
percentage by mass	0.76	98.92

(a) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium. [2]

No. of moles of S_7 $= \dfrac{\frac{0.76}{100} \times 1.00}{7 \times 32.1}$

$= \dfrac{0.0076}{224.7}$

= 3.38×10^{-5} mol

No. of moles of S_8 $= \dfrac{\frac{98.92}{100} \times 1.00}{8 \times 32.1}$

$= \dfrac{0.9892}{256.8}$

= 3.85×10^{-3} mol

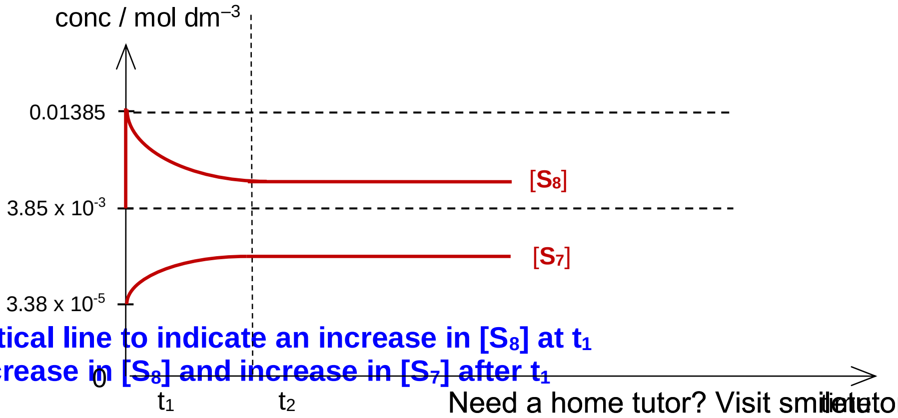
(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

$$K_c = \frac{[S_8]^7}{[S_7]^8}$$

$$= \frac{\left[\frac{3.85 \times 10^{-3}}{1}\right]^7}{\left[\frac{3.38 \times 10^{-5}}{1}\right]^8}$$

$= 7.36 \times 10^{18}$ mol^{-1} dm^3 (ecf from (b)(i))

(iii) The amount of S_8 is increased by 0.01 mol at time t_1. Sketch, on the same axes, two graphs to show how $[S_7]$ and $[S_8]$ vary from t_1 to t_2, the time when equilibrium is re-established at the same temperature.
[You are only required to label the concentrations at t_1.] [2]



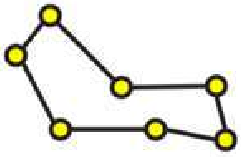
Vertical line to indicate an increase in $[S_8]$ at t_1
Decrease in $[S_8]$ and increase in $[S_7]$ after t_1

Horizontal line to indicate equilibrium re-established at t_2, new equilibrium $[S_8]$ still higher than previous equilibrium

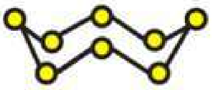
(iv) An inert gas is then added at constant pressure. State and explain how the position of equilibrium would change. [2]

To keep total pressure constant when the inert gas is added, the volume of the system must increase. Hence, the partial pressures of S_7 and S_8 decrease. By Le Chatelier's Principle, the equilibrium will shift left where there are more gas particles, so as to increase the pressure of the system.

The shape of the S_7 and S_8 molecules are as follows.



S_7



S_8

(b) **(i)** Define the term bond energy with reference to the S–S bonds in S_8. [1]

The energy required to break 1 mole of covalent bonds between 2 sulfur atoms in a gaseous S_8 molecule.

(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction between S_7 and S_8. [1]

Enthalpy change of reaction = (8 x 7 x 260.0) – (7 x 8 x 263.3)
= 14560 – 14744.8
= –185 kJ mol^{-1}

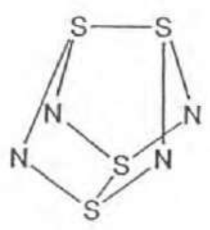
(iii) Using your answers in **(a)(ii)** and **(b)(ii)**, and given that:

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

where T is in Kelvins and ΔG is in J mol^{-1}, calculate the standard entropy change of the reaction. [2]

$$\Delta G^{\ominus} = -RT \ln K_c$$
$$= -8.31 \times 298 \times \ln(7.36 \times 10^{18})$$
$$= -1.08 \times 10^{5} \text{ J mol}^{-1}$$
$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$
$$\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus})/T$$
$$= \frac{-185 \times 10^{3} - (-1.08 \times 10^{5})}{298}$$
$$= -258 \text{ J mol}^{-1} \text{ K}^{-1}$$

(c) Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4. In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The four nitrogen atoms are arranged in a plane, with two sulfur atoms above the plane, and two sulfur atoms below the plane. The shape of a molecule of S_4N_4 is as shown.



S_4N_4

Using the data provided below, construct an energy cycle to calculate the average S–N bond energy in S_4N_4. [3]

enthalpy change of formation of S_4N_4	+460 kJ mol^{-1}
enthalpy change of atomisation of sulfur	+297 kJ mol^{-1}
enthalpy change of atomisation of nitrogen	+497 kJ mol^{-1}
S–S bond energy in S_4N_4	+204 kJ mol^{-1}

By

$$\begin{tikzcd}
\frac{1}{2}S_8(s) + 2N_2(g) \arrow[r, "+460"] \arrow[d, "4(+297)"', "4(+497)"] & S_4N_4(g) \arrow[dl, "2(+204) + 8BE(S\text{-}N)"] \\
4S(g) + 4N(g) &
\end{tikzcd}$$

Hess' law,

$+460 + 8BE(S–N) + 2(+204) = 4(+297) + 4(+497)$

$Be(S–N) = +289$ kJ mol^{-1}

(d) Sulfur and tungsten has certain similarities since both atoms have a total of six valence electrons, even though sulfur is a main group element and tungsten is a transition metal. Both elements reach their maximum +6 oxidation state when combined with electronegative elements such as fluorine and oxygen.

(i) Sulfur trioxide, SO_3 and tungsten(VI) oxide, WO_3 differ markedly in their physical properties. While SO_3 is a gaseous pollutant used in industrial preparation of sulfuric acid, WO_3 is used in electrochromic windows, allowing the windows to change colour when an electrical voltage is applied. Their boiling points are 44.9 ^{o}C and 1700 ^{o}C respectively.

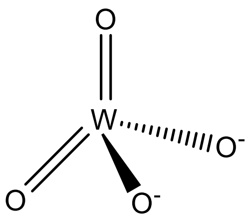
With reference to the structure and type of bonding, account for the difference in boiling points. [3]

SO_3 has a simple molecular structure. Weak instantaneous dipole-induced dipole interactions exist between SO_3 molecules. A small amount of energy is required to overcome the weak intermolecular forces, hence the boiling point of SO_3 is low.

WO_3 has a giant ionic structure. Strong electrostatic forces of attraction exist between the W^{6+} and O^{2-} ions. A large amount of energy is required to overcome the strong ionic bonds, hence the boiling point of WO_3 is very high.

(ii) Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}.

Draw the structure of WO_4^{2-}. State the shape and bond angle of the O–W–O bond. [2]



Dotted and wedge bonds shown
Overall –2 charge shown
Tetrahedral
Bond angle 109.5°

[Total: 20]

5 **(a)** The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

N_2H_4 has a boiling point of 114 °C and decomposes to its elements when passed over a suitable catalyst. The rapid production of hot gaseous products is what provides the thrust.

(i) With the aid of a balanced equation, define the term standard enthalpy change of formation for hydrazine. [2]

$N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)$
The enthalpy change when one mole of N_2H_2 is formed from its constituent elements N_2 and H_2 under standard conditions of 298 K and 1 bar.

(ii) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_r^\ominus = -241.0 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change for the decomposition of 1 mol of hydrazine to its elements using data below. [2]

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
NH_3	–46.1
H_2O_2	–187.8
H_2O	–285.8

$\Delta H_r^\ominus = \sum \Delta H_f^\ominus{}_{(products)} - \sum \Delta H_f^\ominus{}_{(reactants)}$
$-241.0 = [\Delta H_f^\ominus{}_{(N2H4)} + 2(-285.8)] - [2(-46.1) + (-187.8)]$
$\Delta H_f^\ominus{}_{(N2H4)} = 50.6 \text{ kJ mol}^{-1}$

Hence, decomposition enthalpy = $-$ 50.6 kJ mol^{-1}

(b) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as 'C-Stoff', and hydrogen peroxide ('T-Stoff'). The standard enthalpy change of combustion of hydrazine and methanol are −622.2 kJ mol^{-1} and −726.0 kJ mol^{-1}.

The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol. The densities of hydrazine and methanol are 1.021 g cm^{-3} and 0.7918 g cm^{-3} respectively.

Calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel, assuming that all the hydrazine and methanol are fully combusted. [2]

Amount of hydrazine = $\frac{225000 \times 1.021}{32.0}$

$= 7.18 \times 10^2$ **mol**

Amount of methanol = $\frac{862000 \times 0.7918}{32.0}$

$= 2.13 \times 10^4$ **mol**

Total heat energy evolved $= 7.18 \times 10^2 \times 622.2 + 2.13 \times 10^4 \times 726.0$

$= 4.46 \times 10^6 + 1.55 \times 10^7$

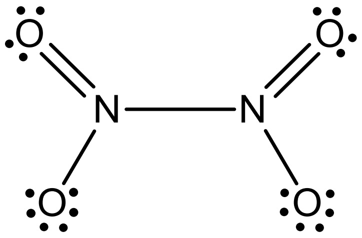
$= 2.0 \times 10^7$ **kJ**

(c) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, that is, the reactants ignite spontaneously on contact.

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4. Briefly explain why. [2]

N_2 and H_2O.
The products formed should be chemically stable with strong bonds, e.g. N≡N and O−H bonds, making the reaction exothermic. They should also be formed as gases which provide thrust.

(ii) Draw the structure of N_2O_4, indicating clearly the shape and bond angle around each nitrogen atom. [2]



Trigonal planar wrt each N
Bond angle 120° indicated

(iii) At room temperature, N_2O_4 exists as a gas while N_2H_4 is a liquid. With reference to their structure and bonding, account for this difference. [3]

Both N_2O_4 and N_2H_4 have a simple molecular structure. Weak permanent dipole-permanent dipole interactions exist between N_2O_4 molecules while stronger hydrogen bonding exist between N_2H_4 molecules. A larger amount of energy is required to overcome these stronger intermolecular forces in N_2H_4, hence the boiling point of N_2O_4 is lower than that of N_2H_4.

(d) At 46 °C, N_2O_4 (colourless gas) exists in equilibrium with nitrogen dioxide, NO_2 (brown gas) with an equilibrium constant, K_p of 0.66 atm. The equation for the equilibrium is

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

(i) Write an expression for the equilibrium constant, K_p. [1]

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

(ii) A certain amount of N_2O_4 is allowed to dissociate in a vessel. At equilibrium, the partial pressure of NO_2 is found to be 0.332 atm.

Calculate the partial pressure of N_2O_4 and total pressure at equilibrium. [2]

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Equilibrium partial pressure / atm	**p**		**0.332**

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

$$= \frac{0.332^2}{p} = 0.66$$

Solving,

$P_{N_2O_4} = 0.167$ **atm**

Total $P_{eqm} = 0.332 + 0.167$

$= 0.499$ **atm**

(iii) Hence, determine the percent dissociation of N_2O_4 at 46 °C. [2]

Since each mole of N_2O_4 dissociates to give 2 moles of NO_2,

Percent dissociation = $\frac{\frac{0.332}{2}}{\frac{0.332}{2}+0.167}\times 100$

= 49.9%

(iv) State and explain what may be observed when the vessel containing the gases is expanded. [2]

The mixture is seen to darken in colour / become more brown in colour. By expansion (i.e. increasing volume), the partial pressures of both gases will decrease. By Le Chatelier's Principle, the system will counteract the decrease in pressure by favouring the forward reaction that will increase the number of gas particles. Position of equilibrium shifts to the right where there is more brown NO_2 gas.

[Total: 20]

H2 CHEMISTRY PAPER 1 ANSWERS

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

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

1 Determination of the dependence of the rate of reaction between glucose and acidified potassium manganate(VII) on temperature

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Glucose, $C_6H_{12}O_6$, is a sugar that can act as a reducing agent. You will investigate how an increase in temperature affects the rate of the redox reaction between glucose and acidified potassium manganate(VII).

FA 1 is 0.020 mol dm^{-3} acidified potassium manganate(VII), $KMnO_4$.
FA 2 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is an aqueous solution containing 32.8 g dm^{-3} glucose, $C_6H_{12}O_6$.
FA 4 is a solid mixture containing an unknown percentage of glucose.

You will measure the time it takes for the purple colour to disappear. Your table of results on the following page should include the rate of reaction for each experiment.

(a) Method

Experiment 1

1. Fill the burette with **FA 1**.
2. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
3. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
4. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
5. Place the beaker on the tripod and heat its contents to between 75 °C and 80 °C.
6. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
7. When the temperature of the contents of the beaker has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with either a cloth or paper towel and place it onto the white tile.
8. Record the temperature of the solution in the beaker.
9. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
10. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
11. Record the temperature of the solution as soon as it is colourless.
12. Calculate and record the average temperature of the reaction mixture to one decimal place.
13. Empty, rinse and dry the beaker so it is ready for use in **Experiment 2**.

Experiment 2

1. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
2. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
3. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
4. Place the beaker on the tripod and heat its contents to between 35 °C and 40 °C.
5. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
6. When the temperature of the contents of the beaker has reached between 35 °C and 40 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with either a cloth or paper towel and place it onto the white tile.
7. Record the temperature of the solution in the beaker.
8. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
9. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
10. Record the temperature of the solution as soon as it is colourless.
11. Calculate and record the average temperature of the reaction mixture to one decimal place.
12. Empty, rinse and dry the beaker so it is ready for use in **Experiment 3**.

Experiments 3, 4 and 5

1. Repeat the method for **Experiment 2** at three different temperatures.
2. Keep the temperature of the contents of the beaker between room temperature and 80 °C.
3. Record all your results in your table.

Results:

The rate of reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

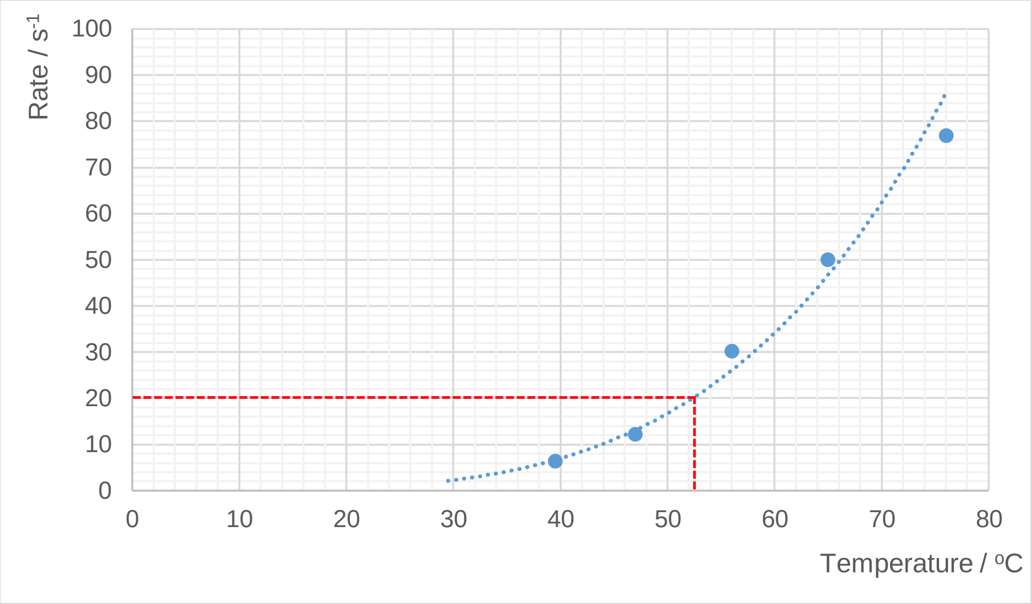
Calculate the rate of reaction for each experiment and include this in your table.

Experiment	T_{initial} / °C	T_{final} / °C	T_{average} / °C	time / s	rate / s^{-1}
1	80.0	72.0	76.0	12	76.9
2	40.0	39.0	39.5	155	6.45
3	49.0	45.0	47.0	82	12.2
4	59.0	53.0	56.0	33	30.3
5	69.0	61.0	65.0	20	50.0

[5]

(b) Plot a graph of rate (*y*-axis) against average temperature (*x*-axis) on the grid below. Select a scale on the *x*-axis to include an average temperature of 30.0 °C. Label any points you consider anomalous.

Draw the most appropriate best-fit curve taking into account all of your plotted points and extrapolate it to 30.0 °C.



[3]

(c) **Use your graph** to calculate the **time** to the nearest second that the reaction would have taken if the average temperature had been 52.5°C.
Show **on the grid** how you obtained your answer.

From the graph, at 52.5 °C,

$$\text{rate} = \frac{1000}{\text{reaction time}} = 20\ \text{s}^{-1}$$

Hence, reaction time = $\frac{1000}{20}$ **= 50 s**

time = **50 s** [2]

(d) Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in temperature.

The rate of reaction increases with increase in temperature. The gradient increases with temperature / graph is exponential / acceleration of rate with temperature increase.

[1]

(e) **(i)** Calculate the maximum percentage error in the reaction time recorded for **Experiment 1**. Assume the error of the timer is ±1 s.

Maximum percentage error = 1 / 12 x 100
= 8.33%

maximum percentage error in **Experiment 1** = **8.33** % [1]

(ii) You have carried out experiments at five different temperatures.

Identify an experiment, if any, you should have repeated. Give a reason for your answer.

Identifies no anomaly as all points are near line of best fit.

[1]

(iii) Suggest one way to improve the accuracy of the results for this investigation.

Use thermostatically controlled water bath to heat both reagents and keep them at constant temperature.

[1]

(f) **(i)** Calculate the concentration of glucose in **FA 3** in mol dm^{-3}.

$$\textbf{Concentration of glucose} = \frac{32.8}{180.0} = 0.182 \text{ mol dm}^{-3}$$

concentration of glucose in **FA 3** = **0.182** mol dm^{-3} [1]

(ii) Calculate the volume of 0.020 mol dm^{-3} acidified $KMnO_4$ that would react with **all** the glucose present in 25.0 cm^3 of **FA 3**.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Amount of glucose in 25.0 cm^3 = 0.182 x 25.0/1000
= 4.55 x 10^{-3} mol

Amount of $KMnO_4$ reduced = 4.55 x 10^{-3} x $\frac{24}{5}$
= 2.18 x 10^{-2} mol

Volume of $KMnO_4$ reduced = 2.18 x 10^{-2}/0.020
= 1.09 dm^3

Volume of acidified $KMnO_4$ required = **1.09 dm^3** [2]

(iii) Comment on the feasibility of conducting a redox titration between the given concentration of glucose and acidified $KMnO_4$.

It is <u>not feasible</u> as the <u>volume</u> required for acidified $KMnO_4$ is <u>too large</u>.

[1]

(g) **Determination of the percentage of glucose in FA 4 by titration**

1. Weigh accurately 1.5 g of **FA 4** in a weighing bottle. Record your weighing appropriately in the space below. If you use **TARE** facility of the balance, please indicate clearly in your recording.
2. Dissolve the solid in a beaker and quantitatively transfer into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Label this **FA 4 solution**.
3. Pipette 25.0 cm^3 of **FA 4 solution** into a conical flask.
4. Using a measuring cylinder add 50.0 cm^3 of **FA 2** into the conical flask.
5. Place the conical flask on the tripod and heat its contents to between 75 °C and 80 °C.
6. When the temperature of the contents of the conical flask has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the <u>neck of conical flask with either a cloth or paper towel</u>.
7. Titrate with **FA 1** until a permanent colour change is observed.

8. Record the burette readings in the suitable format. Repeat titration to achieve consistent results.

Results:

Weighing of ***FA 4***

Mass of weighing bottle and FA 4 / g	**1.825**
Mass of empty weighing bottle / g	**0.325**
Mass of FA 4 used / g	**1.500**

OR

Mass of weighing bottle only / g	**TARE**
Mass of FA 4 / g	**1.500**

Tabulation with ALL readings recorded, clear headers and units for mass table
3 d.p. correct subtraction and mass of solid within stated range (1.450 – 1.550 g)

Titration

Experiment	**1**	**2**
Final burette reading / cm^3	**22.40**	**42.40**
Initial burette reading / cm^3	**0.00**	**20.00**
Volume of FA 1 used / cm^3	**22.40**	**22.40**

Tabulation with ALL readings recorded, clear headers and units for titration table
2 d.p. for titration reading
At least two consistent readings ±0.10 cm^3

[5]

(h) **(i)** 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 = (22.40 + 22.40) ÷ 2
= 22.40 cm^3

volume of **FA 1** = **22.40 cm^3** [1]

(ii) Calculate the amount of **FA 1** required for titration.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Amount of FA 1 used = 22.40/1000 x 0.020
= 4.48 x 10^{-4} mol

amount of **FA 1** = **4.48 x 10^{-4} mol** [1]

(iii) Hence, calculate the amount of glucose in **FA 4**.

Amount of glucose in 25.0 cm^3 of FA 4 solution = 4.48 x 10^{-4} x $\frac{5}{24}$
= 9.33 x 10^{-5} mol

Amount of glucose in 250 cm^3 of FA 4 solution = 9.33 x 10^{-5} x $\frac{250}{25.0}$
= 9.33 x 10^{-4} mol

amount of glucose in **FA 4** = **9.33 x 10^{-4} mol** [1]

(iv) Use your answer in **(h)(iii)** to determine the percentage of glucose in the mixture.
[A_r: C, 12.0; O, 16.0; H, 1.0]

Mass of glucose in 250 cm^3 of FA 4 solution = 9.33 x 10^{-4} x 180.0
= 0.168 g
Percentage of glucose in FA 4 = 0.168/1.500 x 100 %
= 11.2 %

percentage of glucose in the mixture = **11.2 %** [1]

[Total: 27]

2 Planning

An electroplating process uses an electric current to coat an object with a thin layer of metal. An example is *copper plating*. In this process, copper metal is made the anode and is allowed to undergo oxidation. The copper is then reformed at the cathode, coating the object to the plated. The mass of copper plated at the end of the process can be calculated by taking relevant mass measurements.

In the following, you will use the *copper plating* process to determine the Faraday constant, which is the charge in coulombs, C, carried by 1 mole of electrons.

(a) Show that the mass of copper plated onto an object is related to the duration of the *copper plating* process by the following expression:

$$m_{Cu} = \frac{I \times M_{Cu}}{2F}\, t$$

where

m_{Cu} : mass of copper plated onto an object in grams, g

M_{Cu} : molar mass of copper, g mol^{-1}

I : current in amperes, A

F : Faraday constant

t : duration of the *copper plating* process in seconds, s

$Cu^{2+} + 2e^- \rightarrow Cu$

$Q = I\,t$ ……….(1)

$Q = n_e F$ ……….(2)

From (1) and (2)

$I\,t = n_e F$

$I\,t = (2n_{cu}) F$

$I\,t = (\frac{2m_{Cu}}{M_{Cu}}) F$

$m_{Cu} = (\frac{I \times M_{Cu}}{2F})\, t$ (shown)

[2]

(b) A series of experiments can be carried out, in which the duration of each experiment is varied and the corresponding mass of copper plated onto the object is determined. The data obtained is then to be used for plotting a suitable graph to determine the value of the Faraday constant.

You are required to write a plan, describing how such a series of experiments can be carried out for an appreciable mass of copper to be plated. The duration of each experiment should be at least 5 min but not exceeding 50 min.

You may assume that you are provided with:

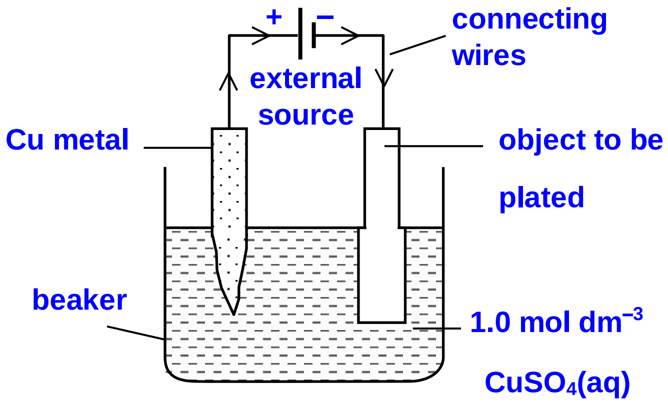
- 1.0 mol dm^{-3} copper(II) sulfate solution;
- five equal pieces of clean, dry copper metals;
- five equal pieces of clean, dry objects to be plated (the object is electrically conductive but is inert during the *copper plating* process);
- an electrical power source that supplies a constant current of 0.50 A (the electrical power source can be switched on and off);

- connecting wires;
- stopwatch;
- the apparatus and chemicals normally found in a school laboratory.

Your plan should include the following:

- a clearly labelled diagram of the *copper plating* setup, including the direction of electron flow;
- the procedure you would follow;
- the measurements you would make and how you would determine the mass of copper plated accurately and reliably to allow a suitable graph to be drawn.

Experimental setup:

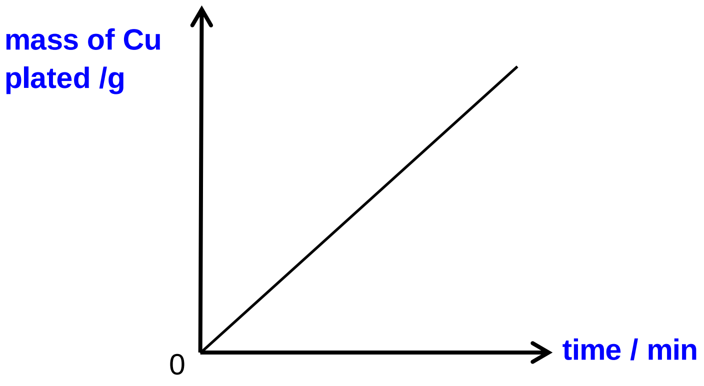


Procedure:

1. **Weigh one of the objects to be plated.**
2. **Set up according to the diagram shown above. Ensure that the electrical power source is switched off.**
3. **Switch on the electrical power source and start the stopwatch simultaneously.**
4. **After 5 min, switch off the electrical power source.**
5. **Remove the plated object, wash the plated object with distilled water and dry it between pieces of filter paper.**
6. **Weigh the plated object. Then calculate the mass of copper plated by taking the difference between the mass of the plated object and the original mass of the object.**
7. **Repeat steps 1 to 6 with durations of 15 min, 25 min, 35 min, 45 min.**

[6]

(c) Sketch, on the axes below, the graph you would expect and describe how it could be used to determine the value of Faraday constant.



Results analysis:

Let the gradient of the graph be k

k $= (\frac{I \times M_{Cu}}{2F})$

F $= (\frac{I \times M_{Cu}}{2k})$

[2]

(d) During the *copper plating* process, the mass lost at the anode should ideally be the same as the mass gained at the cathode. However, the presence of impurities can cause the mass change at one electrode to be numerically larger than the other electrode.

For each of the following, deduce, with explanation, the electrode that will have a numerically larger mass change.

You may find the following information useful:

$Ag^+ + e^- \rightleftharpoons Ag$ $E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $E^\ominus = -0.13$ V

[A_r: Ag, 107.9; Cu, 63.5; Pb, 207.2]

(i) Presence of Pb impurity at the anode.

Electrode with numerically larger mass change: **Anode**

Explanation:

Pb gets preferentially oxidised at the anode but Cu^{2+} gets preferentially reduced at the cathode. For every 1 mol of Pb (1 x 207.2 = 207.2 g) oxidised at the anode, 1 mol of Cu (1 x 63.5 g= 63.5 g) is formed at the cathode. Thus the mass change at the anode will be numerically larger.

[1]

(ii) Presence of Ag^+ impurity in the electrolyte.

Electrode with numerically larger mass change: **Cathode**

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Explanation:

Cu gets oxidised at the anode but Ag^+ gets preferentially reduced at the cathode. For every 1 mol of Cu (1 x 63.5 = 63.5 g) oxidised at the anode, 2 mol of Ag (2 x 107.9 g= 215.8 g) is formed at the cathode. Thus the mass change at the cathode will be numerically larger.

[1]

(e) It is important to ensure that the cathode is dry at the start and at the end of each experiment.

Explain the effect, if any, on the calculated value of the Faraday constant if the cathode is dry at the beginning but wet at the end of each experiment.

Effect on calculated value of the Faraday constant: **Smaller**

Explanation:

If the cathode is dry at the beginning but wet at the end of each experiment, the mass of copper plated calculated for each experiment will be higher than actual. This will lead to a steeper gradient for the graph plotted. Thus calculated Faraday constant will be smaller than actual. [1]

(f) The Faraday constant obtained from the *copper plating* process can be used to provide an estimate for Avogadro's constant.

A student who conducted the *copper plating* process obtained a value of 96480 C mol^{-1} for the Faraday constant. Using this value, calculate Avogadro's constant.

[Note: The charge of an electron has a numerical value of 1.60×10^{-19} C.]

Avogadro's constant = $96480 / 1.60 \times 10^{-19}$

= 6.03×10^{23} electrons mol^{-1}

[1]

[Total: 14]

3 (a) Investigation of some inorganic reactions

FA 5 is an aqueous solution of $CuSO_4$.

FA 6 is a reducing agent.

FA 7 is a solution of ammonium vanadate(V), NH_4VO_3.

You will also need access to the **FA 2** solution you used earlier.

You are to perform the tests described in **Table 3.1** and record your observations in the table.

Test and identify any gases evolved. If there is no observable change, write **no observable change.**

Table 3.1

	tests	observations
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 5** into a boiling tube. Add 4 spatulas of **FA 6**. 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 5 turns colourless** **(OR award below for filtrate colour)** **Red-brown/brown/black/ residue** **colourless filtrate**
(ii)	To 1 cm depth of the filtrate from **(i)**, 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 from **(i)**, add 1 spatula of solid ammonium chloride. Stir to ensure all the solid ammonium chloride dissolves. Then add aqueous ammonia.	No observable change (OR no ppt)

Table 3.1

tests		observations
(iv)	Using a measuring cylinder, transfer 2 cm^3 of **FA 7** and 10 cm^3 of **FA 2** into a boiling tube. Swirl the mixture gently. The resultant yellow solution is **FA 8**, which is an acidified solution of VO_2^+.	
(v)	Transfer about 2 spatulas of **FA 6** into a **dry** weighing bottle. From this sample in the weighing bottle, add a **very small** quantity of **FA 6** to the boiling tube containing **FA 8** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 6** in **small** quantities with swirling, until all the **FA 6** in the weighing bottle is used up. Record all colour changes observed.	**Yellow solution turns green [mixture of yellow VO_2^+ and blue VO^{2+}]** **Green solution turns blue (OR bluish-green OR greenish blue) [more VO^{2+} formed]** **Blue solution turns green (OR dark green) [V^{3+} formed]** **Green solution turns purple (OR violet OR blue) [V^{2+} formed]** **Effervescence of H_2 gas which** **extinguished lighted splint with a 'pop sound**.
	Filter the mixture and retain the filtrate for test **(vi)**.	

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(vi)	To 1 cm depth of the filtrate from test **(v)**, add an equal volume of aqueous hydrogen peroxide.	**Violet solution turns brown (OR orange OR red)** **Effervescence of O_2 gas which** **relighted glowing splint.**

[6]

(b) **(i)** Suggest an identity for **FA 6**. Explain your answer with reference to evidence from relevant tests above.

identity of **FA 6**
Zn

explanation

In test (i), decolourisation of blue $CuSO_4$ suggests reduction of Cu^{2+} to Cu and oxidation of FA 6

In test (ii), formation of white ppt soluble in excess $NH_3(aq)$ suggests presence of Zn^{2+} in filtrate from test (i).

[2]

(ii) Explain the difference in observations between tests **(a)(ii)** and **(a)(iii)**.

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ----(1)

Presence of additional NH_4^+ from NH_4Cl (OR NH_4^+ is a common ion) shifts position of equilibrium (1) to the left.

$[OH^-]$ is lowered and ionic product is lesser than K_{sp}. Hence, no ppt is formed in (a)(iii).

[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 obtained in test **(a)(v)**, a grey precipitate is observed.

Given that the $E^\ominus$ value for **FA 6** is between −1.00 V to –0.50 V, state the identity of the grey precipitate.

$E^\ominus$ values suggest that FA 6 reduces VO_2^+ to V^{2+}. Hence, the grey ppt is $\underline{V(OH)_2}$.

[1]

(c) **Planning**
There are three unlabelled bottles of aqueous solutions. Each bottle contains a different solution from the other two.

The possible identities of the solutions are:

$Na_2CO_3(aq)$ $Al_2(SO_4)_3(aq)$ $Mg(NO_3)_2(aq)$

Plan an investigation, using test–tube reactions, which would allow you to identify each of these three solutions.

Other than the three solutions, the only reagent available is the **FA 5** solution used in **3(a)**, which contains $CuSO_4$.

Your plan should include:

- an outline of the sequence of steps you would follow,
- the expected observations at each step, and
- an explanation of how you would analyse your results in order to identify each solution.

You are **not** required to carry out the plan.

	$Na_2CO_3(aq)$	**$Al_2(SO_4)_3(aq)$**	**$Mg(NO_3)_2(aq)$**
FA 5 (aq $CuSO_4$)	**Blue (OR green) ppt**	**no ppt**	**no ppt**
$Na_2CO_3(aq)$	**---**	**White ppt** **CO_2 effervescence**	**White ppt** **No effervescence**

Add <u>FA 5</u> to each of the three solutions in separate test–tubes. The solution that gives a <u>blue (OR green) ppt</u> can be identified as $\underline{Na_2CO_3}$ while the <u>other two solutions</u> give <u>no ppt</u>.

Add $\underline{Na_2CO_3(aq)}$ to fresh samples of the two remaining unidentified solutions in separate test–tubes.

The solution that gives <u>white ppt</u> and CO_2 <u>effervescence</u> can be identified as $\underline{Al_2(SO_4)_3}$ while the solution that gives <u>white ppt</u> with <u>no effervescence</u> is $\underline{Mg(NO_3)_2}$.

[3]

[Total: 14]